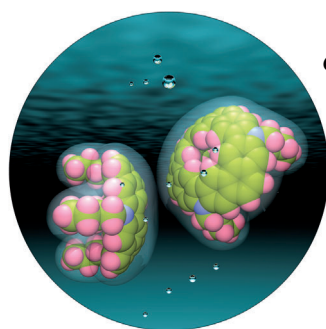
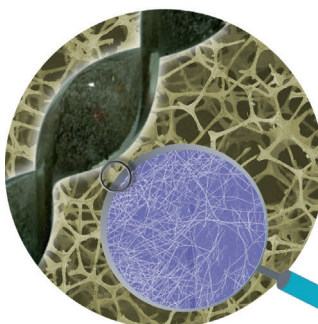


... based on a polyynes framework are well documented, while properties of the cumulenenic form of these allotropes remain mysterious. In their Communication on page 1817 ff., R. R. Tykwinski and co-workers shed new light on the properties of cumulenes (such as bond length alternation) through the synthesis, spectroscopic study, and crystallographic analysis of cumulenes that contain up to nine consecutive double bonds (i.e., a [9]cumulene). Cover art: Annie Tykwinski; based on a concept from D. Wendinger.

## Conducting Materials

In their Communication on page 1654 ff., S. H. Yu and co-workers detail a new type of stretchable conductor based on a binary structure design, which enhances the electronic performance and electromechanical stability of the material.

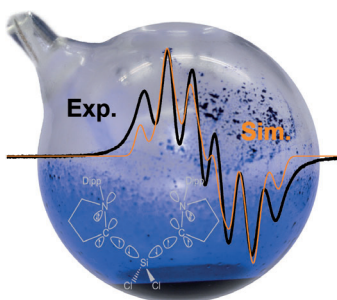


## Geodesic Polyarenes

In their Communication on page 1713 ff. D. Myśliwiec and M. Stępień describe the synthesis of chrysaorole. This strained system was obtained from a carbazole-based macrocyclic precursor by using a new “fold-in” strategy.

## Main Group Chemistry

An air-stable silicon biradical was synthesized from a silicon(II) precursor. In their Communication on page 1801 ff., H. W. Roesky, I. Tkach, D. Stalke et al. observed a C–C bond formation during the reaction at room temperature.



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1618 – 1621

## Service



*"Chemistry is fun because it creates its own object (Berthelot).  
My favorite way to spend a holiday is with a rental car, lots of time, and no itinerary ..."*  
This and more about Mathias Christmann can be found on page 1624.

## Author Profile

Mathias Christmann — 1624

## News

Académie des Sciences Prizes — 1625 – 1626

New Members of the Deutsche Akademie der Naturforscher Leopoldina — 1625 – 1626



L. Emsley



M. Ephritikhine



L. Jullien



C. Bruneau



F. Babonneau



M. Suhm



M. Driess



A.G. Beck-Sickinger



G. Rimbach

## Books

Applied Homogeneous Catalysis

Arno Behr, Peter Neubert

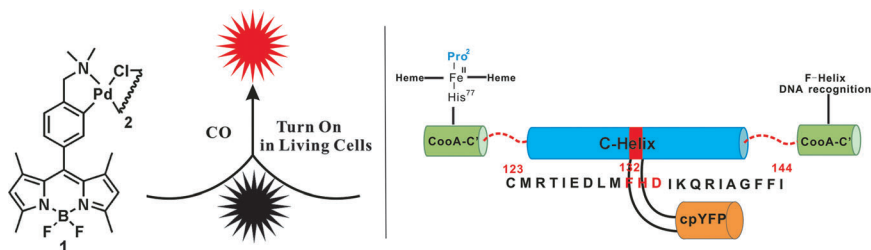
reviewed by P. S. Pregosin — 1627

## Highlights

### Biosensing

L. Yuan, W. Lin,\* L. Tan, K. Zheng,  
W. Huang ————— 1628 – 1630

Lighting up Carbon Monoxide:  
Fluorescent Probes for Monitoring CO in  
Living Cells



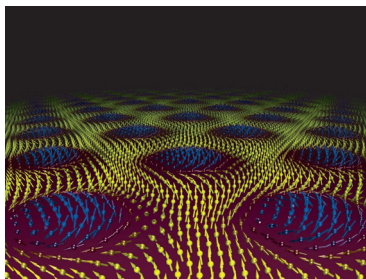
**All aglow:** Both a fluorescent biosensor, composed of a circularly permuted yellow fluorescent protein (cpYFP), and a small-molecule fluorescent probe (**1**) for the detection of CO in living cells have been

recently reported. Though different these novel probes were designed based on the unique binding ability of CO to transition-metal ions.

### Magnetic Properties

C. Felser\* ————— 1631 – 1634

Skyrmions



**Topologically stable** magnetic screw-like nanostructures called skyrmions were designed by using the concept of topology and the guidance of theory. These particles in real space are found in non-centrosymmetric compounds such as MnSi. Skyrmions might have an enormous impact in the context of future spintronics applications.

## Reviews

### Antibacterial Silver

S. Chernousova, M. Epple\* 1636 – 1653

Silver as Antibacterial Agent: Ion,  
Nanoparticle, and Metal

**Silver shield:** Silver is used in different forms as an antibacterial agent. Earlier, sparingly soluble silver salts were predominantly used, but today, silver nanoparticles (see picture for an SEM image of cubic silver nanoparticles) are gaining increasing importance. As silver is also toxic towards mammalian cells, there is the question of the therapeutic window in the cases of consumer products and medical devices.



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ANGEWANDTE CHEMIE International  
Edition (ISSN 1433-7851) is published weekly  
by Wiley-VCH, PO Box 191161, 69451 Wein-  
heim, Germany. Air freight and mailing in the  
USA by Publications Expediting Inc., 200  
Meacham Ave., Elmont, NY 11003. Periodicals

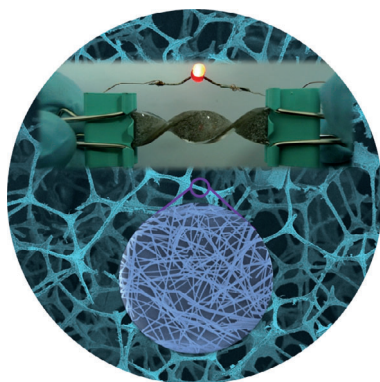
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## Communications

### Conducting Materials

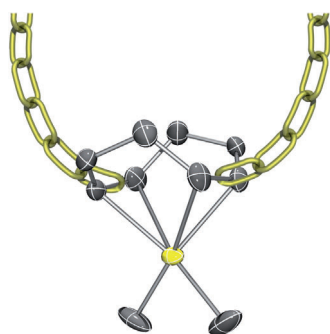


**Stretching the role of a conductor:** A new kind of polyurethane sponge–Ag nano-wire–poly(dimethylsiloxane) (PUS–AgNW–PDMS) stretchable conductors can be easily fabricated based on a novel binary network structure design, which greatly enhances their electronic performance. These PUS–AgNW–PDMS elastomeric conductors show improved electromechanical stability compared to previously reported stretchable conductors.

J. Ge, H. B. Yao, X. Wang, Y. D. Ye, J. L. Wang, Z. Y. Wu, J. W. Liu, F. J. Fan, H. L. Gao, C. L. Zhang, S. H. Yu\* **1654–1659**

Stretchable Conductors Based on Silver Nanowires: Improved Performance through a Binary Network Design

Frontispiece

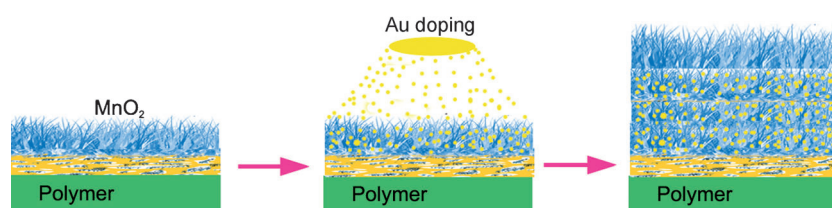


**A Missing Gold Link:** An Au<sup>III</sup> alkene complex has been prepared and characterized by NMR spectroscopy and X-ray crystallography. Its bonding features have been analyzed by DFT calculations and natural bond orbital (NBO) analysis. In [(cod)AuMe<sub>2</sub>]<sup>+</sup>, the unequal Au–C bond lengths result from the domination of the preference of 1,5-cyclooctadiene (cod) for nonparallel double bonds over back donation from the metal which favors parallel double bonds.

### Gold Complexes

E. Langseth, M. L. Scheuermann, D. Balcells, W. Kaminsky, K. I. Goldberg, O. Eisenstein, R. H. Heyn, M. Tilset\* **1660–1663**

Generation and Structural Characterization of a Gold(III) Alkene Complex



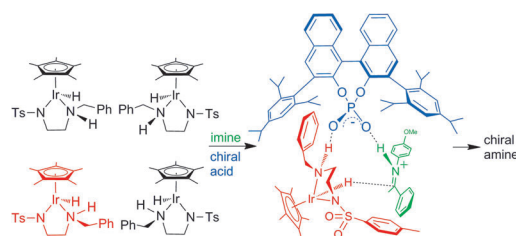
**Electrochemical energy storage:** The performance of MnO<sub>2</sub> as a pseudo-capacitive material was enhanced by doping electrodeposited MnO<sub>2</sub> with physically deposited gold atoms (see picture). The

resulting MnO<sub>2</sub> electrodes showed an enhanced electronic conductivity and a remarkable stability under voltammetric cycling.

### Electrochemistry

J. L. Kang, A. Hirata, L. J. Kang, X. Zhang, Y. Hou, L. Y. Chen, C. Li, T. Fujita, K. Akagi, M. W. Chen\* **1664–1667**

Enhanced Supercapacitor Performance of MnO<sub>2</sub> by Atomic Doping



**One of four:** A chiral phosphoric acid enables asymmetric hydrogenation of imines with an achiral iridium catalyst by virtue of noncovalent interactions. These

interactions lead to the formation of a highly organized ternary complex, and the hydride is transferred highly enantioselectively.

### Asymmetric Hydrogenation

W. Tang, S. Johnston, J. A. Iggo,\* N. G. Berry, M. Phelan, L. Lian, J. Bacsá, J. Xiao\* **1668–1672**

Cooperative Catalysis through Noncovalent Interactions

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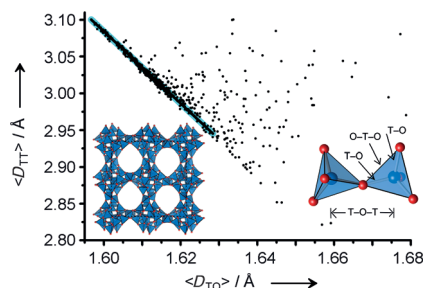
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**The huge pool of hypothetical zeolites** can be screened for likely candidates for successful targeted synthesis on the basis of a set of reliable criteria derived from the observation that the local interatomic distances in all existing zeolites strictly obey several rules. For example, the average T-T and T-O distances ( $\langle D_{TT} \rangle$  and  $\langle D_{TO} \rangle$ ; T is Si, Al, P, or another element) in existing zeolites (graph region highlighted in cyan) have a linear relationship.

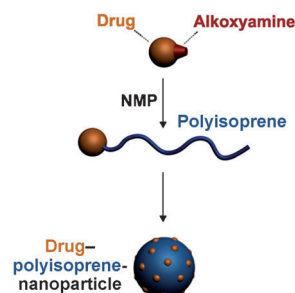
## Zeolite Structures

Y. Li, J. Yu,\* R. Xu — 1673 – 1677

Criteria for Zeolite Frameworks Realizable for Target Synthesis



**Magic rubber bullets:** Novel anticancer nanoparticles made of well-defined polymer–drug conjugate amphiphiles are prepared by the controlled growth of a hydrophobic polyisoprene chain from a drug macroinitiator by using nitroxide-mediated polymerization (NMP; see picture). The resulting conjugates self-assembled into nanoparticles exhibiting high drug payloads and significant anti-cancer activities both in vitro and in vivo.



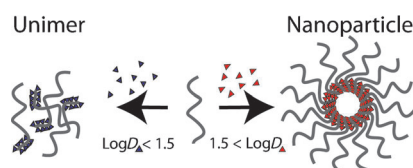
## Polymer Nanoparticles

S. Harrison, J. Nicolas,\* A. Maksimenko, D. T. Bui, J. Mougin, P. Couvreur — 1678 – 1682

Nanoparticles with In Vivo Anticancer Activity from Polymer Prodrug Amphiphiles Prepared by Living Radical Polymerization



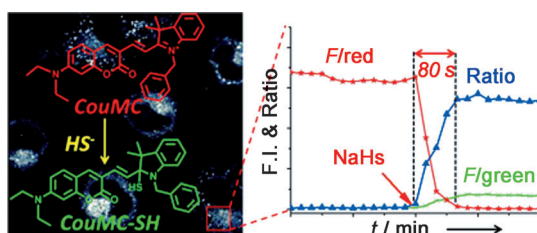
**Nanoparticles on demand:** Upon the site-specific covalent attachment of hydrophobic molecules to one end of the biopolymer backbone, chimeric polypeptides (derived from elastin-like polypeptides) can self-assemble to form thermoresponsive nanoparticles suitable for drug delivery. Molecules with a distribution coefficient greater than 1.5 imparted sufficient amphiphilicity to drive self-assembly into sub-100 nm nanoparticles (see picture).



## Drug-Delivery Systems

J. R. McDaniel, J. Bhattacharyya, K. B. Vargo, W. Hassounah, D. A. Hammer, A. Chilkoti\* — 1683 – 1687

Self-Assembly of Thermally Responsive Nanoparticles of a Genetically Encoded Peptide Polymer by Drug Conjugation



**Quick:** An exogenously induced quick increase of the  $H_2S$  concentration (80 s) in MCF-7 cells can be visualized by ratio-metric imaging using a new probe (CouMC) that can target mitochondria.

CouMC was constructed by combining merocyanine and coumarin fluorophores. The selective nucleophilic addition of  $HS^-$  to the merocyanine derivative at neutral pH is crucial for the rapid  $H_2S$  detection.

## Fluorescence Imaging

Y. Chen, C. Zhu, Z. Yang, J. Chen, Y. He, Y. Jiao, W. He,\* L. Qiu, J. Cen, Z. Guo\* — 1688 – 1691

A Ratiometric Fluorescent Probe for Rapid Detection of Hydrogen Sulfide in Mitochondria



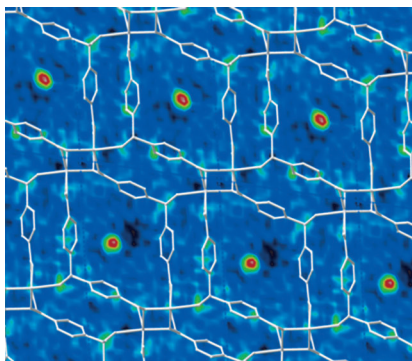


## CO<sub>2</sub> Adsorption

A. M. Plonka, D. Banerjee, W. R. Woerner,  
Z. Zhang, N. Nijem, Y. J. Chabal, J. Li,\*  
J. B. Parise\* ————— 1692–1695



Mechanism of Carbon Dioxide Adsorption  
in a Highly Selective Coordination  
Network Supported by Direct Structural  
Evidence



**Trapped in a porous material:** The position of adsorbed CO<sub>2</sub> in a nanoporous coordination framework was determined using a combination of techniques including single-crystal X-ray diffraction, in situ X-ray powder diffraction coupled with differential scanning calorimetry, and theoretical calculations. The study reveals that the adsorbed CO<sub>2</sub> stays in a “pocket” between two phenyl rings, interacting with the aromatic electron density (see picture).

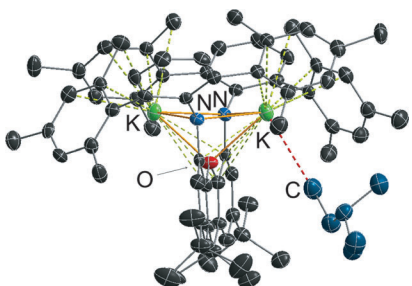
## Inside Cover

## Alkali Metals

N. R. Andreychuk,  
D. J. H. Emslie\* ————— 1696–1699



Potassium–Alkane Interactions within  
a Rigid Hydrophobic Pocket



**A NON-issue:** Potassium complexes of an extremely rigid and sterically encumbered NON-donor ligand have been prepared, and the solid-state structures (see figure) feature remarkably short potassium–alkane distances. DFT calculations highlight the presence of an electrostatic cation-induced dipole potassium–alkane interaction supported by interactions between the alkane and the surrounding ligand framework.

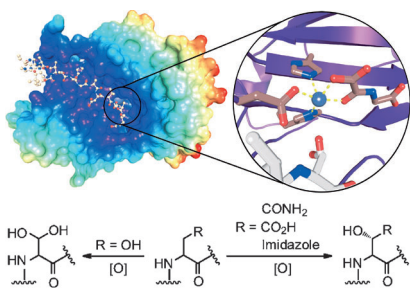


## Bioorganic Chemistry

M. Yang, A. P. Hardy, R. Chowdhury,  
N. D. Loik, J. S. Scotti, J. S. O. McCullagh,  
T. D. W. Claridge, M. A. McDonough,  
W. Ge,\* C. J. Schofield\* — 1700–1704



Substrate Selectivity Analyses of Factor  
Inhibiting Hypoxia-Inducible Factor



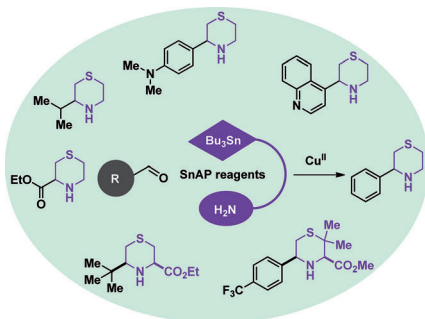
**Substrate specificity:** Biochemical and crystallographic analyses reveal the hypoxia-inducible factor hydroxylase (FIH) as being promiscuous with respect to the residues that it can hydroxylate in  $\beta$ -position, which in addition to Asn, Asp, and His include Leu and Ser residues. The Ser substrate is oxidized to an epimeric  $\beta$ -geminal diol product (see picture).

## Saturated Heterocycles

C.-V. T. Vo, G. Mikutis,  
J. W. Bode\* ————— 1705–1708

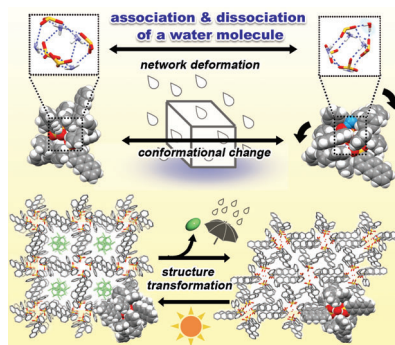


SnAP Reagents for the Transformation of  
Aldehydes into Substituted  
Thiomorpholines—An Alternative to  
Cross-Coupling with Saturated  
Heterocycles



**It's a SnAP!** The transformation of aldehydes into *N*-unsubstituted 3-thiomorpholines provides a convenient alternative to metal-catalyzed cross-coupling reactions, which are generally unsuited to the functionalization of saturated *N*-heterocycles. A copper-mediated radical cyclization is the key to the mild conditions, high functional group tolerance, and broad substrate scope offered by these reagents.

**Just add water:** A cube-like hydrogen-bonding network in a fluorescent supramolecular cluster dynamically deforms upon the specific addition of a water molecule. The deformation is amplified through the conformational change of the cluster to result in the transformation of host frameworks. This transformation provides water-responsive guest-exclusion and fluorescent-modulation behaviors.



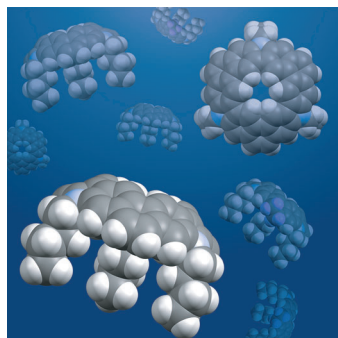
## Supramolecular Chemistry

A. Yamamoto, T. Hamada, I. Hisaki,  
M. Miyata, N. Tohnai\* — 1709–1712

Dynamically Deformable Cube-like  
Hydrogen-Bonding Networks in Water-  
Responsive Diamondoid Porous Organic  
Salts



**Molecular jellyfish:** A new family of bowl-shaped aromatic compounds swims into view (see picture). Quite unlike true jellyfish, chrysaoroles possess a rigid skeleton, which is assembled from fused carbazole units. Their synthesis involves a fold-in step to convert a macrocyclic precursor into the bowl-shaped target molecule.



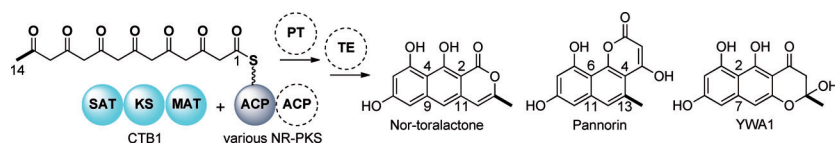
## Geodesic Polyarenes

D. Myśliwiec, M. Stępień\* — 1713–1717

The Fold-In Approach to Bowl-Shaped  
Aromatic Compounds: Synthesis of  
Chrysaoroles



Inside Back Cover



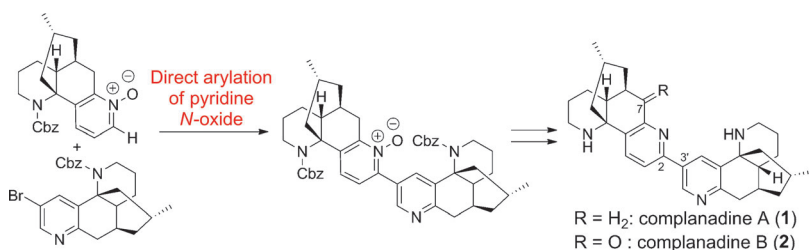
**Playing by the rules:** Combinatorial domain swaps among “deconstructed” non-reducing polyketide synthases (NR-PKSs) revealed the rules behind product assembly (see scheme). The control

exerted by individual catalytic domains was found to be sufficiently great that heterocombinations of domains from different NR-PKSs synthesized products in a predictable manner.

## Combinatorial Biosynthesis

A. L. Vagstad, A. G. Newman, P. A. Storm,  
K. Belecki, J. M. Crawford,  
C. A. Townsend\* — 1718–1721

Combinatorial Domain Swaps Provide  
Insights into the Rules of Fungal  
Polyketide Synthase Programming and  
the Rational Synthesis of Non-Native  
Aromatic Products



**Twice as nice:** Total syntheses of dimeric alkaloids, (–)-complanadines A (1) and B (2), were achieved from (–)-lycodine. The unsymmetrical motif was assembled through direct arylation of the pyridine N-

oxide. The absolute configuration and specific rotations of complanadines A and B were identified. Cbz = Benzyloxycarbonyl.

## Natural Products

L. Zhao, C. Tsukano,\* E. Kwon,  
Y. Takemoto, M. Hiram — 1722–1725

Total Syntheses of Complanadines A  
and B



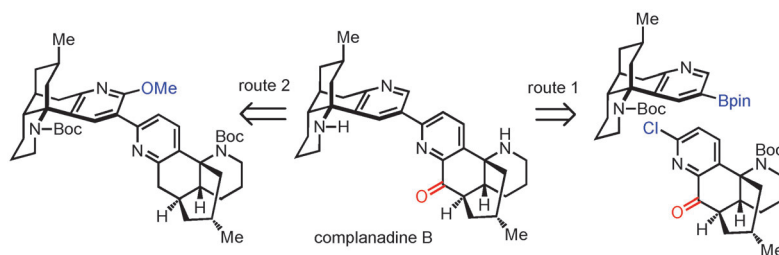


## Natural Products

J. N. Newton, D. F. Fischer,  
R. Sarpong\* 1726–1730



Synthetic Studies on Pseudo-Dimeric  
Lycopodium Alkaloids: Total Synthesis of  
Complanadine B



**Two approaches** to the total synthesis of the dimeric *Lycopodium* alkaloid complanadine B have been achieved. In the first approach (see scheme; route 1), a keto lycopodium unit is coupled to another lyco-

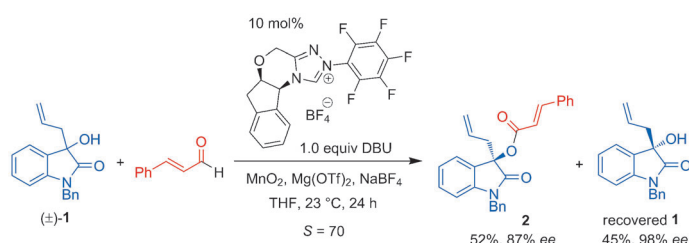
dine unit whereas in the latter approach (route 2), selective oxygenation of one of two pseudo-benzylic positions is achieved.

## Asymmetric Catalysis

S. Lu, S. B. Poh, W.-Y. Siau,  
Y. Zhao\* 1731–1734



Kinetic Resolution of Tertiary Alcohols:  
Highly Enantioselective Access to  
3-Hydroxy-3-Substituted Oxindoles



**Enantioselective:** The first highly enantioselective kinetic resolution of 3-hydroxy-3-substituted oxindoles has been developed through oxidative esterification catalyzed by a N-heterocyclic carbene (see picture).

This method uses a simple procedure and provides 3-hydroxy-oxindoles with various substituents at the 3-position in excellent enantiopurity. *S* = selectivity.

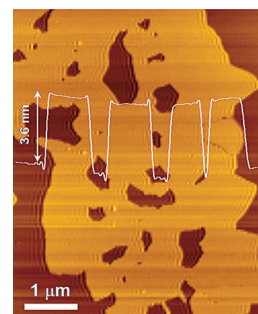
## Conjugated Polymers

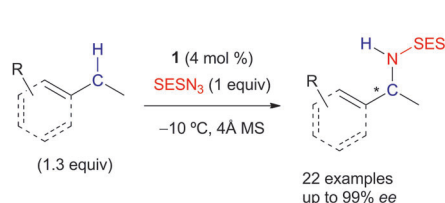
Z. Lin, X. Wang\* 1735–1738



Nanostructure Engineering and Doping of  
Conjugated Carbon Nitride  
Semiconductors for Hydrogen  
Photosynthesis

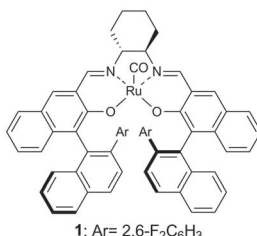
**Going flat out:** Simultaneous modifications of the textural, surface, and electronic structures of a rigid conjugated carbon nitride polymer has been achieved using direct co-condensation of urea and  $\text{Ph}_4\text{BNa}$ . This method gives boron-doped carbon nitride nanosheets (see picture) that optimize the capture of light, improve the charge-separation kinetics, and enhance the surface reactivity for hydrogen photosynthesis.





**Smooth salen:** Ru(CO)–salen complex **1** is an effective catalyst for asymmetric benzylic and allylic C–H bond amination using 2-(trimethylsilyl)ethanesulfonyl azide (SESN<sub>3</sub>) as the nitrene source. The reaction proceeded with high enantio-

selectivity and excellent regioselectivity. An ethyl group can be selectively aminated, even in the presence of an *n*-propyl group. No migration or isomerization of the double bond was observed.

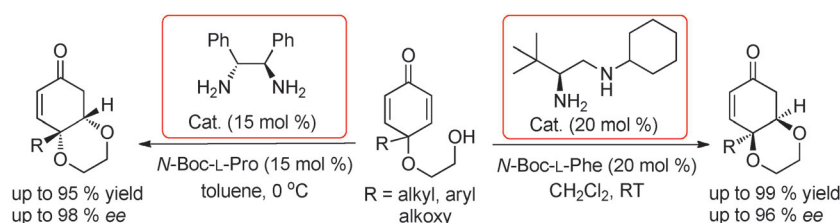


1: Ar = 2,6-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub>

## C–H Amination

Y. Nishioka, T. Uchida,  
T. Katsuki\* 1739–1742

Enantio- and Regioselective  
Intermolecular Benzylic and Allylic C–H  
Bond Amination



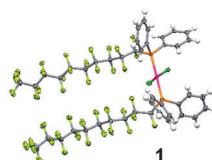
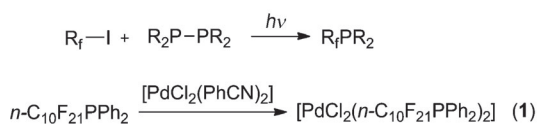
**Michael brings the rings:** An asymmetric intramolecular oxa-Michael reaction involving iminium activation has been developed. This reaction provides enantioenriched 1,4-dioxane derivatives with up to 99% yield and 98% ee. The method

allows for concise and stereoselective access to stereodiverse, complex tetracyclic compounds containing a bicyclo-[2.2.2]octan-2-one backbone with multiple chiral centers.

## Asymmetric Catalysis

W. Wu, X. Li, H. Huang, X. Yuan, J. Lu,  
K. Zhu, J. Ye\* 1743–1747

Asymmetric Intramolecular Oxa-Michael  
Reactions of Cyclohexadienones Catalyzed  
by a Primary Amine Salt



1

**A 'F'lurry of activity:** The title reaction provides a convenient procedure for direct synthesis of perfluoroalkylated phosphines. The synthesized phosphine *n*-C<sub>10</sub>F<sub>21</sub>PPh<sub>2</sub> forms a complex with palla-

dium(II) to give **1** and several runs of coupling reactions are attained with *n*-C<sub>10</sub>F<sub>21</sub>PPh<sub>2</sub> by using a fluororous/organic biphasic system.

## Synthetic Methods

S.-i. Kawaguchi, Y. Minamida, T. Ohe,  
A. Nomoto, M. Sonoda,  
A. Ogawa\* 1748–1752

Synthesis and Properties of Perfluoroalkyl  
Phosphine Ligands: Photoinduced  
Reaction of Diphosphines with  
Perfluoroalkyl Iodides



**A new twist:** A one-pot nitrous acid free, diazonium-free, and transition-metal-free variation of the Fischer indole synthesis has been developed. Condensation of quinone monoketals and aliphatic hydrazine hydrochlorides afforded indoles via intermediate alkylaryldiazenes. This method will complement the classical Fischer indole synthesis by providing indoles in two steps from widely available phenols under mild conditions.



## Indole Synthesis

J. Zhang, Z. Yin, P. Leonard, J. Wu,  
K. Sioson, C. Liu, R. Lapo,  
S. Zheng\* 1753–1757

A Variation of the Fischer Indolization  
Involving Condensation of Quinone  
Monoketals and Aliphatic Hydrazines

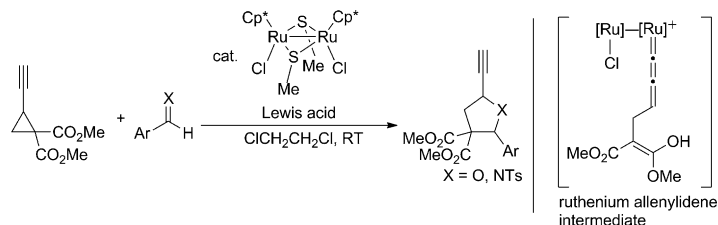


## Synthetic Methods

Y. Miyake, S. Endo, T. Moriyama,  
K. Sakata,\* Y. Nishibayashi\* **1758–1762**



Ruthenium-Triggered Ring Opening of  
Ethylnylcyclopropanes:  
[3+2] Cycloaddition with Aldehydes and  
Aldimines Involving Metal Allenylidene  
Intermediates



**It's complex:** Ruthenium-catalyzed [3+2]  
cycloaddition of ethylnylcyclopropanes  
with aldehydes and aldimines has been  
found to give the corresponding 2-ethy-  
nyltetrahydrofurans or -pyrrolidines in

high to excellent yields. In both cases, the  
formation of a ruthenium allenylidene  
complex as a key reactive intermediate is  
supported by density functional theory  
calculations.  $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ .

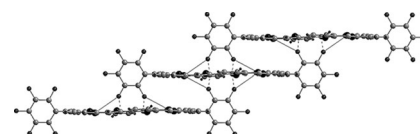
## Antiaromaticity

T. Y. Gopalakrishna, J. S. Reddy,  
V. G. Anand\* **1763–1767**



Antiaromatic Supramolecules:  $\text{F}\cdots\text{S}$ ,  
 $\text{F}\cdots\text{Se}$ , and  $\text{F}\cdots\pi$  Intermolecular  
Interactions in  $32\pi$  Expanded Isophlorins

**Count against:** Stable and planar anti-  
aromatic, expanded vinylous isophlor-  
ins encourage chalcogen–fluorine nonco-  
valent interactions. The wide cavity of the  
macrocycle accommodates covalently  
bound fluorine substituents, thus leading  
to multiple nonbonding interactions

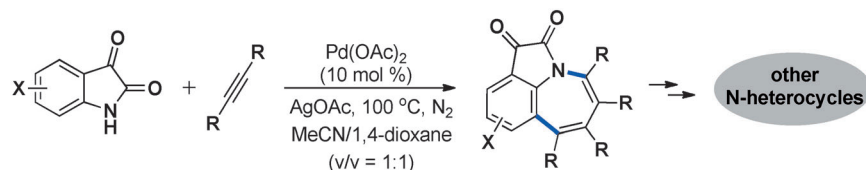


## Benzazepine Synthesis

L. Wang, J. Y. Huang, S. Y. Peng, H. Liu,  
X. f. Jiang,\* J. Wang\* **1768–1772**



Palladium-Catalyzed Oxidative  
Cycloaddition through C–H/N–H  
Activation: Access to Benzazepines



**Rings beget rings:** Benzazepines, well-  
known structural design elements in  
medicinal chemistry, are readily prepared

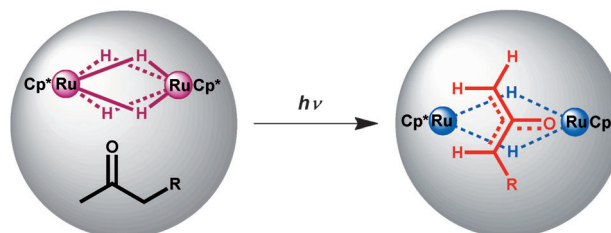
by a one-pot palladium-catalyzed oxida-  
tive cycloaddition of isatins with various  
alkynes.

## Photoexcited Hydride Cluster

H. Suzuki,\* R. Shimogawa, Y. Muroi,  
T. Takao, M. Oshima,  
G. Konishi **1773–1776**



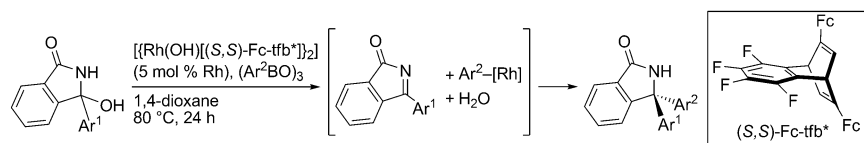
Bimetallic Activation of 2-Alkanones  
through Photo-Induced  $\alpha$ -Hydrogen  
Abstraction Mediated by a Dinuclear  
Ruthenium Tetrahydride Complex



**Hydrogen abstraction in the spotlight:** UV  
irradiation (365 nm) of dinuclear ruth-  
enium tetrahydride,  $[(\text{Cp}^*\text{Ru})(\mu\text{-H})_4(\text{RuCp}^*)]$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ), in a 2-alka-  
none, such as acetone or 2-butanone,  
resulted in the formation of dinuclear

oxatrimethylenemethane complexes,  
 $[(\text{Cp}^*\text{Ru})(\mu\text{-}\eta^3\text{:}\eta^1\text{-CH}_2\text{COCHR})(\mu\text{-H})_2\text{-(RuCp}^*)]$  ( $\text{R} = \text{H}$  and  $\text{CH}_3$ ), through  
hydrogen abstraction from the  $\alpha$  and  
 $\alpha'$  positions of the carbonyl group.





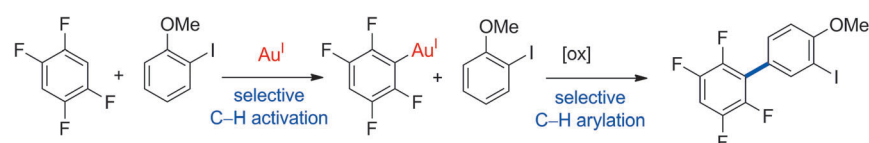
**Water is out, aryl is in!** Asymmetric synthesis of isoindoline-1-ones bearing an  $\alpha$ -triaryl-substituted stereogenic center was realized in the enantioselective addition of arylboronoxines to 3-aryl-3-hydroxyisoindolin-1-ones

in the presence of a hydroxorhodium/chiral diene catalyst, where cyclic *N*-carbonyl ketimines were generated in situ by dehydration.

## Asymmetric Arylation

T. Nishimura,\* A. Noishiki, Y. Ebe, T. Hayashi\* 1777–1780

Hydroxorhodium/Chiral Diene Complexes as Effective Catalysts for the Asymmetric Arylation of 3-Aryl-3-hydroxyisoindolin-1-ones



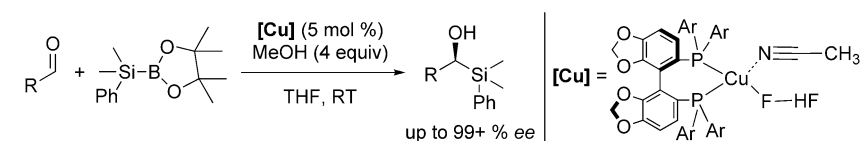
**Gold brings us together:** Taking advantage of the orthogonal reactivities of  $\text{Au}^{\text{I}}$  and  $\text{Au}^{\text{III}}$  towards C–H activation of electron-poor and electron-rich arenes, respectively, a novel approach for the

synthesis of biaryls through double C–H activation is proposed. Stoichiometric studies demonstrate that these oxidative couplings occur with high selectivity at low temperature.

## Oxidative Coupling

X. C. Cambeiro, T. C. Boorman, P. Lu, I. Larrosa\* 1781–1784

Redox-Controlled Selectivity of C–H Activation in the Oxidative Cross-Coupling of Arenes



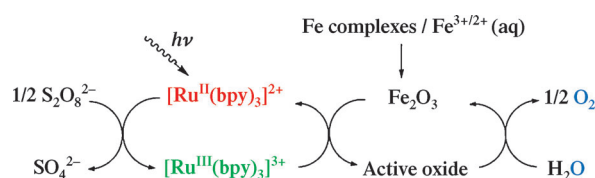
**How to train your silane:** A new family of chiral copper(I) complexes that bear a bifluoride counteranion were prepared and used in the first example of the

enantioselective transfer of a silyl group to an aldehyde. This procedure provides fast access to non-racemic  $\alpha$ -hydroxysilanes in high enantioselectivities.

## Enantioselective Silylation

V. Cirriez, C. Rasson, T. Hermant, J. Petriguet, J. Díaz Álvarez, K. Robeyns, O. Riant\* 1785–1788

Copper-Catalyzed Addition of Nucleophilic Silicon to Aldehydes



**Ironing out a solution:** Chemical and visible-light-driven water oxidation by iron complexes and iron salts at pH 7–9 has been investigated. The iron complexes

and salts act as precatalysts (see scheme) to produce  $\alpha$ - $\text{Fe}_2\text{O}_3$  nanoparticles that are the real catalyst for the water oxidation with a turnover number over 1000.

## Water Oxidation

G. Chen, L. Chen, S. M. Ng, W. L. Man, T. C. Lau\* 1789–1791

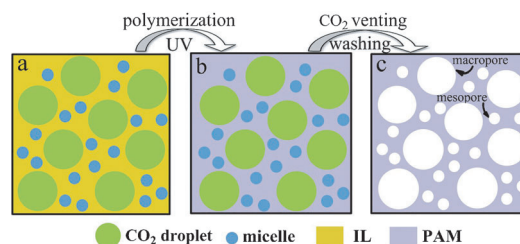
Chemical and Visible-Light-Driven Water Oxidation by Iron Complexes at pH 7–9: Evidence for Dual-Active Intermediates in Iron-Catalyzed Water Oxidation

## Heterogeneous Catalysis

L. Peng, J. Zhang,\* J. Li, B. Han, Z. M. Xue,  
G. Yang ————— 1792 – 1795



Macro- and Mesoporous Polymers  
Synthesized by a CO<sub>2</sub>-in-Ionic Liquid  
Emulsion-Templating Route



**Poring over polymers:** Highly porous polymers with hierarchical macro- and mesoporous structures were synthesized by using the title method and UV radiation. The porosity properties of the poly-

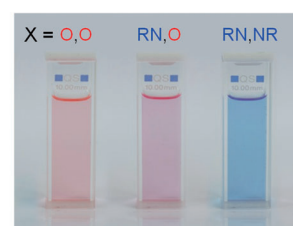
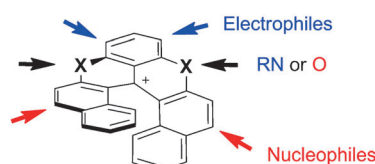
mers can be easily tuned by controlling the CO<sub>2</sub> pressure used, and the polymers have potential applications in catalysis. IL = ionic liquid, PAM = polyacrylamide.

## Helicenes

F. Torricelli, J. Bosson, C. Besnard,  
M. Chekini, T. Bürgi,  
J. Lacour\* ————— 1796 – 1800



Modular Synthesis, Orthogonal Post-  
Functionalization, Absorption, and  
Chiroptical Properties of Cationic  
[6]Helicenes



**Pick and choose:** Novel cationic diaza-, azaoxo-, and dioxo[6]helicenes are readily prepared and functionalized selectively by orthogonal aromatic electrophilic and vicarious nucleophilic substitutions (see scheme). Reductions, cross-coupling, or

condensation reactions introduce additional diversity and allow tuning of the absorption properties up to the near-infrared region. The diaza salts can be resolved into single enantiomers.



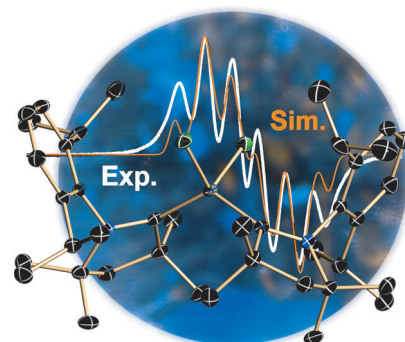
## Biradicals

K. C. Mondal, H. W. Roesky,\*  
M. C. Schwarzer, G. Frenking,\* I. Tkach,\*  
H. Wolf, D. Kratzert, R. Herbst-Irmer,  
B. Niepötter, D. Stalke\* — 1801 – 1805



Conversion of a Singlet Silylene to a stable  
Biradical

**Silicon becomes colored:** Stable biradicals were prepared from an N-heterocyclic carbene stabilized SiCl<sub>2</sub> and a cyclic alkyl-(amino)carbene, and characterized as two polymorphs. The deep-blue crystals of one polymorph are stable upon exposure to air for about a week, while the solution in THF decomposes rapidly when exposed to air. In a side reaction, the different carbene species react with each other under C–H activation and C–C bond formation in the presence of the biradical.



**Back Cover**

## Hydroaminoalkylation

J. Dörfler, S. Döy\* ————— 1806 – 1809



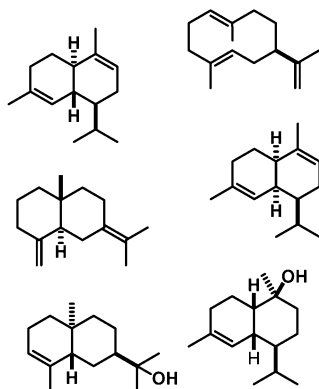
Aminopyridinato Titanium Catalysts for  
the Hydroaminoalkylation of Alkenes and  
Styrenes



**The linear product** is formed as the major product when in situ generated titanium complexes with aminopyridinato ligands are used as catalysts for hydroaminoalkylation reactions of styrenes (see scheme). The reaction is not limited to the use of N-

methylanilines and for the first time can be performed with N-alkylanilines bearing alkyl groups larger than methyl, or even with dialkylamines. The best selectivities in favor of a linear product are better than 90:10.

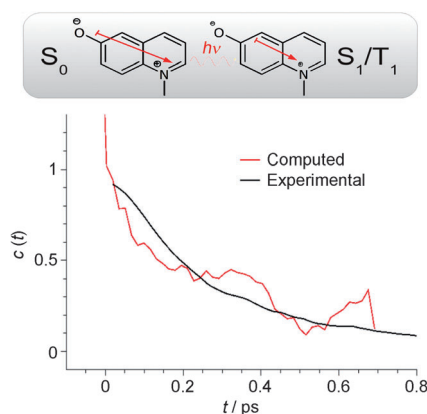
**Modern sequencing techniques** deliver more and more genetic information about bacterial terpene cyclases. Chemical characterization of these enzymes must stay up to date with these developments. For this purpose a rapid and efficient method for the characterization of bacterial terpene cyclases by heterologous expression in *E. coli* and direct headspace analysis was developed. The products of six bacterial terpene cyclases have been identified (see structures).



## Terpene Biosynthesis

P. Rabe, J. S. Dickschat\* — 1810–1812

Rapid Chemical Characterization of Bacterial Terpene Synthases

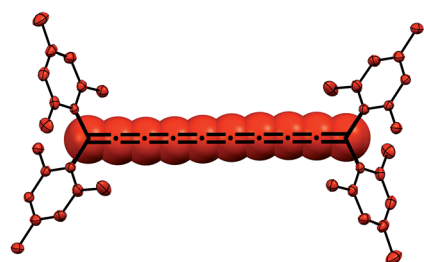


**Beyond bulk dielectric relaxation:** The experimentally observed time-dependent Stokes shift of a molecular probe (MQ) can be explained by molecular dynamics simulations in combination with DFT calculations. Decomposition of the MD trajectories shows that an important contribution to the time-dependent Stokes shift originates from a group of water molecules that strongly interact with the molecular dipole of MQ.

## Molecular Dynamics Simulations

C. Allolio, M. Sajadi, N. P. Ernsting, D. Sebastiani\* — 1813–1816

An Ab Initio Microscope: Molecular Contributions to the Femtosecond Time-Dependent Fluorescence Shift of a Reichardt-Type Dye



**BLA = 0? Not so fast!** A series of tetraarylcumulenes up to the length of a [9]cumulene has been synthesized and analyzed by X-ray crystallography. The structural data show a distinct reduction in bond-length alternation (BLA) as a function of molecule length, but this trend appears to reach a limit before a cumulenic structure with BLA = 0 is achieved.

## Cumulenes

J. A. Januszewski, D. Wendinger, C. D. Methfessel, F. Hampel, R. R. Tykwinski\* — 1817–1821

Synthesis and Structure of Tetraarylcumulenes: Characterization of Bond-Length Alternation versus Molecule Length



Front Cover





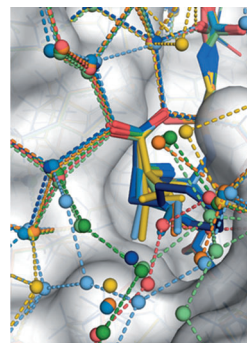
### Protein–Ligand Complexes

A. Biela, N. N. Nasief, M. Betz, A. Heine,  
D. Hangauer,\* G. Klebe\* — 1822 – 1828



Dissecting the Hydrophobic Effect on the Molecular Level: The Role of Water, Enthalpy, and Entropy in Ligand Binding to Thermolysin

**The hydrophobic effect** is associated with the successive replacement of water molecules in the binding site of a protein by hydrophobic groups of the ligand. Although the hydrophobic effect is assumed to be entropy-driven, large changes in enthalpy and entropy are observed with the model system thermolysin. Structural changes in the binding features of the water molecules ultimately determine the thermodynamics of the hydrophobic effect.



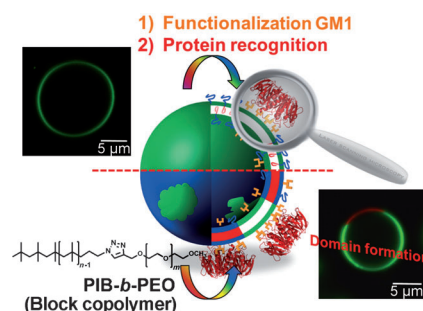
### Hybrid Vesicles

M. Schulz, S. Werner, K. Bacia,\*  
W. H. Binder\* — 1829 – 1833



Controlling Molecular Recognition with Lipid/Polymer Domains in Vesicle Membranes

**The molecular recognition** between cholera toxin B and GM1-functionalized phospholipid/block copolymer hybrid membranes can be controlled by varying the lipid/block copolymer composition. Confocal laser scanning microscopy and fluorescence correlation spectroscopy were used to study the protein–receptor interaction and dynamic processes in the membrane.

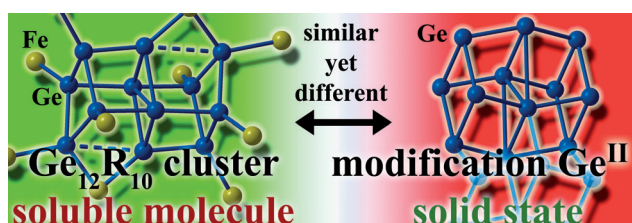


### Main-Group Chemistry

C. Schenk, F. Henke,  
A. Schnepf\* — 1834 – 1838



[Ge<sub>12</sub>{FeCp(CO)<sub>2</sub>}<sub>8</sub>{FeCp(CO)<sub>2</sub>}]<sub>2</sub>: A Ge<sub>12</sub> Core Resembles the Arrangement of the High-Pressure Modification of Germanium (II)



**Similar yet different:** The reaction of a GeBr solution with K[FeCp(CO)<sub>2</sub>] (Cp = η-C<sub>5</sub>H<sub>5</sub>) gives [Ge<sub>12</sub>{FeCp(CO)<sub>2</sub>}<sub>8</sub>{FeCp(CO)<sub>2</sub>}]<sub>2</sub> (**1**), whose oblong, highly cross-linked cluster core reveals a cut-out of the high-pressure solid-state structure

of germanium (II) (see scheme). Mass spectrometric investigations on the gas-phase species [Ge<sub>6</sub>{FeCp(CO)<sub>2</sub>}]<sub>6</sub><sup>−</sup> {FeCp(CO)}<sub>2</sub><sup>−</sup> (**2**) and theoretical calculations on **1** and **2** illuminate the formation of the metalloid cluster **1**.



Supporting information is available on [www.angewandte.org](http://www.angewandte.org) (see article for access details).



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



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