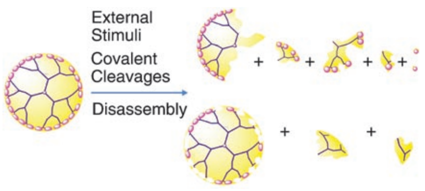
The following Communications have been judged by at least two referees to be “very important papers” and will be published online at www.angewandte.org soon:

News

Books

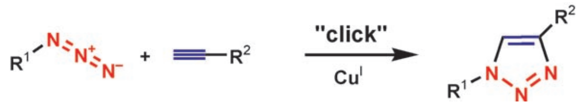
Highlights



Breaking up is not hard to do: There has been great interest in the synthesis of dendrimers, but their degradability or disassembly has been less-well studied. A summary of the most recent developments in the disassemby of cleavable dendrimers by dissociation of covalent bonds (see picture) is given in this Highlight. This emerging field has already made a fundamental impact on drug delivery, nanomedecine (oncology), and materials science.

Supramolecular Chemistry

Minireviews



Clicking into place: Within the last two years, the synthetic concept of “click” chemistry proposed by Sharpless has become tremendously popular in material science. In particular, the copper-catalyzed click 1,3-dipolar cycloaddition of azides and alkynes has been extensively explored in the fields of polymer chemistry, biotechnology, and nanoscience.

Click Chemistry

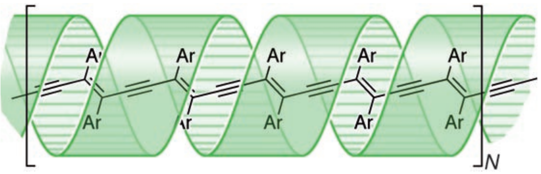
Contents

Reviews

Nanoelectronics

M. J. Frampton,
H. L. Anderson* ________ 1028 – 1064

Insulated Molecular Wires



Plastic nanoelectronics! Threading a molecular organic semiconductor inside an insulating sheath (see example) provides control of properties such as luminescence, electrical transport, and chemical stability. Applications in electroluminescent displays, sensors, and hydrogen generators are now within reach.

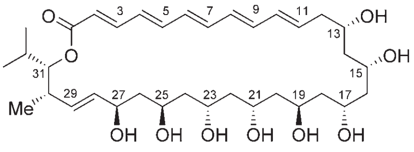
Communications

Natural Products

M. J. Mitton-Fry, A. J. Cullen,
T. Sammakia* ________ 1066 – 1070

The Total Synthesis of the Oxopolyene Macrolide RK-397

It works both ways: The convergent total synthesis of the oxopolyene macrolide RK-397 utilizes remote asymmetric induction and a two-directional chain synthesis to prepare the polyol portion of the molecule, as well as a cross-metathesis reaction of a trienal with a terminal alkene to append the polyene to the polyol.



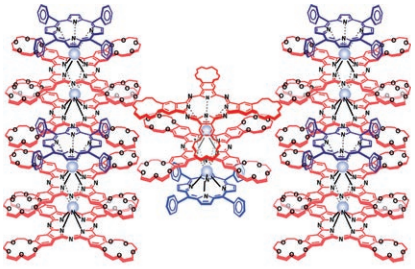
RK-397

Sandwich Complexes

S. Yoshimoto,* T. Sawaguchi, W. Su,
J. Jiang,* N. Kobayashi* ________ 1071 – 1074

Superstructure Formation and Rearrangement in the Adlayer of a Rare-Earth-Metal Triple-Decker Sandwich Complex at the Electrochemical Interface

Sense of direction: A characteristic well-ordered domain of a 2:1 sandwich complex consisting of phthalocyanines and tetraphenylporphyrin was observed on an Au(111) surface by STM in situ, indicating that a highly ordered array was formed by alternately arranging the molecules in two different orientations.

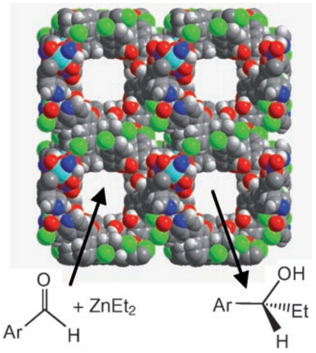


Heterogeneous Asymmetric Catalysis

C.-D. Wu, W. Lin* ________ 1075 – 1078

Heterogeneous Asymmetric Catalysis with Homochiral Metal–Organic Frameworks: Network-Structure-Dependent Catalytic Activity

It's all in the preparation: Heterogeneous asymmetric catalysts based on two homochiral highly porous metal–organic frameworks formed from the same building blocks show remarkably different activity. Although both catalysts are based on twofold interpenetrated structures, one catalyzes the addition of diethylzinc to aromatic aldehydes with high enantioselectivity (up to 90% *ee*), while the other is inactive.



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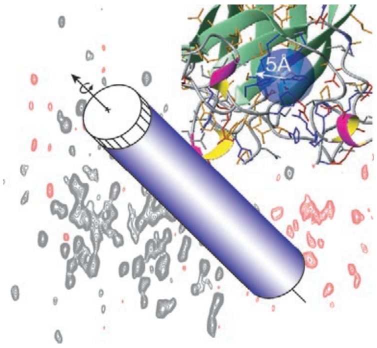
Biomolecular Solid-State NMR

G. Pintacuda, N. Giraud, R. Pierattelli, A. Böckmann, I. Bertini, L. Emsley* ———— **1079 – 1082**

Solid-State NMR Spectroscopy of a Paramagnetic Protein: Assignment and Study of Human Dimeric Oxidized $\mathrm{Cu^{II}}$–$\mathrm{Zn^{II}}$ Superoxide Dismutase (SOD)

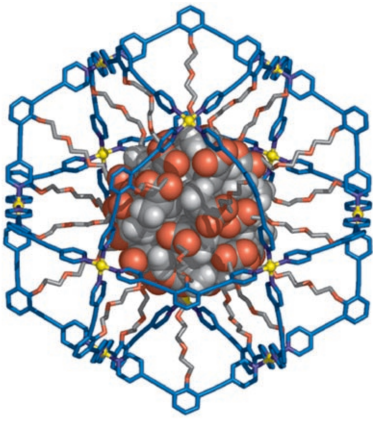


A solid story: The paramagnetic form of the protein superoxide dismutase (SOD; see portion of structure in upper right corner of picture with detectability sphere in blue) is shown to be accessible to high-resolution solid-state magic angle spinning NMR studies when in microcrystalline form. A nearly complete assignment of the signals of this 32-kDa dimer has been achieved (^{13}C–^{15}N NMR correlation spectrum shown in background).

Molecular Nanoparticles

T. Murase, S. Sato, M. Fujita* ———— **1083 – 1085**

Nanometer-Sized Shell Molecules That Confine Endohedral Polymerizing Units



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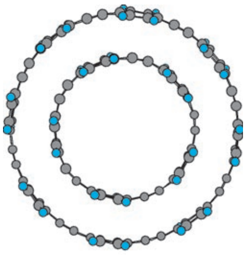
Polymerization in a nutshell: A discrete spherical $Pd_{12}L_{24}$ complex was prepared that confines 24 tethered methyl methacrylate (MMA) units internally (see picture; shell blue, Pd yellow, O red, C gray; MMA shown as space-filling representation). Endohedral radical polymerization of the monomer proceeds efficiently as a result of the high concentration of MMA units within the restricted space of the core (inner diameter: 3.7 nm).

Noncovalent Interactions

T. Kawase,* Y. Nishiyama, T. Nakamura, T. Ebi, K. Matsumoto, H. Kurata, M. Oda ———— **1086 – 1088**

Cyclic [5]Paraphenyleneacetylene: Synthesis, Properties, and Formation of a Ring-in-Ring Complex Showing a Considerably Large Association Constant and Entropy Effect



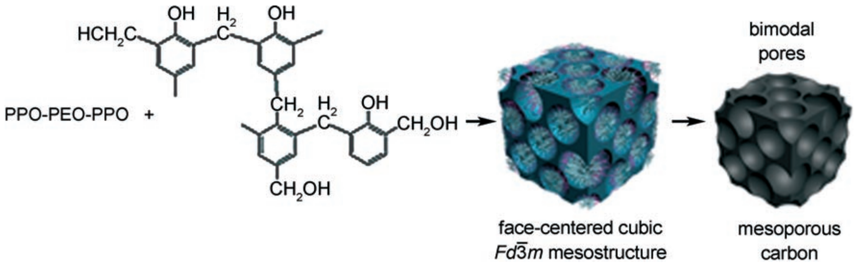
[8]CPPA⊃[5]CPPA

In the ring: The title compound ([5]CPPA), the smallest belt-shaped conjugated system known to date, forms a considerably stable ring-in-ring complex with [8]CPPA (see picture). [8]CPPA⊃[5]CPPA has a smaller contact area than [9]CPPA⊃[6]CPPA but its large K_a and ΔH values reveal that the interaction results from the electrostatic attractive force rather than the dispersion force.

Mesoporous Materials

Y. Huang, H. Q. Cai, T. Yu, F. Q. Zhang, F. Zhang, Y. Meng, D. Gu, Y. Wan, X. Sun, B. Tu, D. Y. Zhao* ———— **1089 – 1093**

Formation of Mesoporous Carbon With a Face-Centered-Cubic $Fd\bar{3}m$ Structure and Bimodal Architectural Pores From the Reverse Amphiphilic Triblock Copolymer PPO-PEO-PPO

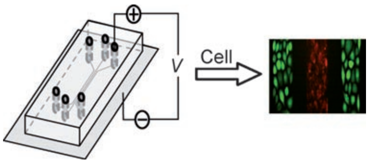


From polymer templates to mesoporous materials: With the reverse amphiphilic triblock copolymer PPO-PEO-PPO and a resol resin precursor an organic–organic self-assembly process leads to the formation of an ordered polymer and a carbon mesostructure with a face-centered-cubic $Fd\bar{3}m$ symmetry and bimodal pores (see scheme). PPO = polypropylenoxide, PEO = polyethylenoxide.

Cell Adhesion

Y. Li, B. Yuan, H. Ji, D. Han, S. Chen, F. Tian, X. Jiang* ———— **1094 – 1096**

A Method for Patterning Multiple Types of Cells by Using Electrochemical Desorption of Self-Assembled Monolayers within Microfluidic Channels

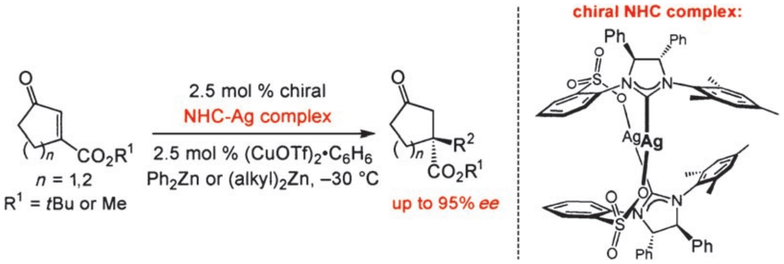


Fenced in: Selective electrochemical desorption of self-assembled monolayers of $HS(CH_2)_{11}(OCH_2CH_2)_6OH$ was carried out on parts of a gold substrate restricted to microfluidic channels. This chemical transformation activates parts of the surface for adhesion of multiple types of cells with well-controlled geometry.

Chiral Carbenes

M. K. Brown, T. L. May, C. A. Baxter, A. H. Hoveyda* ———— **1097 – 1100**

All-Carbon Quaternary Stereogenic Centers by Enantioselective Cu-Catalyzed Conjugate Additions Promoted by a Chiral N-Heterocyclic Carbene



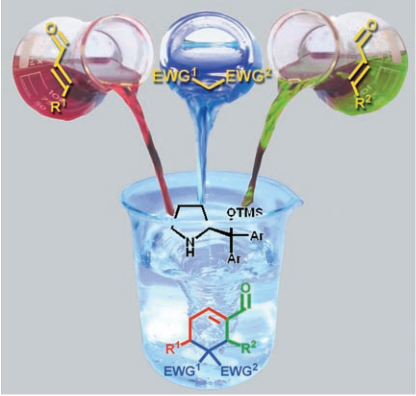
Necessity is the mother of invention: When the available catalysts do not cut it, a new one has to be developed. A chiral N-heterocyclic carbene (NHC) is used in the first catalytic asymmetric conjugate addition of alkyl- and arylzinc reagents to γ-keto esters (see scheme).

Multicomponent Reactions

A. Carlone, S. Cabrera, M. Marigo, K. A. Jørgensen* ———— **1101 – 1104**

A New Approach for an Organocatalytic Multicomponent Domino Asymmetric Reaction

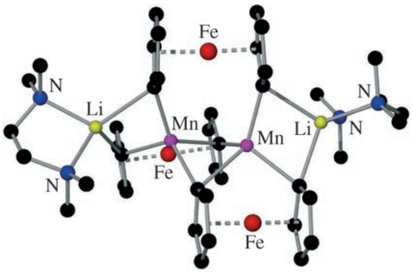
As easy as pouring! Three C–C bonds, up to three stereocenters, and *ee* values greater than 97% are created in a new organocatalyzed multicomponent domino reaction (see picture; TMS = trimethylsilyl; EWG = electron-withdrawing group). Very high enantioselectivity, control of the substituents, easy handling, and user-friendly reaction conditions are key features of this transformation.



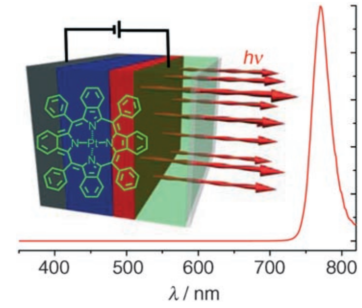
Direct Manganation

J. Garcia-Álvarez, A. R. Kennedy, J. Klett, R. E. Mulvey* ———— **1105 – 1108**

Alkali-Metal-Mediated Manganation: A Method for Directly Attaching Manganese(II) Centers to Aromatic Frameworks



Magic Metalation: Inert towards conventional organomanganese reagents, ferrocene can now be directly manganated by using a specially designed mixed lithium/manganese(II) mixed dialkyl/amido reagent. The picture shows the structure of a dimanganese compound with three manganated 1,1′-ferrocenediyl fragments.



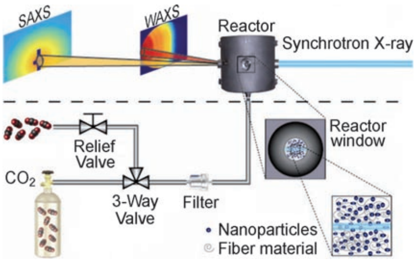
Red-shifting beyond red: The nonplanar porphyrin complex [Pt(tpbp)] (tpbp = tetraphenyltetrabenzoporphyrin) has been used as a phosphorescent dopant in highly efficient electrophosphorescent devices that emit in the near-infrared region (see normalized emission spectrum). The high efficiencies of these NIR devices make them amenable to many night-vision display and sensing applications.

Light-Emitting Diodes

VIP

C. Borek, K. Hanson, P. I. Djurovich, M. E. Thompson,* K. Aznavour, R. Bau, Y. Sun, S. R. Forrest, J. Brooks, L. Michalski, J. Brown ——— **1109 – 1112**

Highly Efficient, Near-Infrared Electrophosphorescence from a Pt–Metalloporphyrin Complex

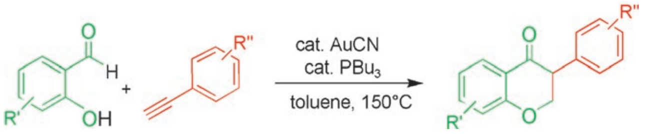


Sol–gel chemistry can be performed in minutes instead of hours in a supercritical fluid, a process that has now been monitored in situ by a combination of small- and wide-angle X-ray scattering (SAXS and WAXS) with high-energy synchrotron radiation. The setup used to monitor the growth of TiO_2 nanoparticles, seeded by polypropylene fibers, in supercritical CO_2 is shown schematically in the picture.

Nanoparticles

H. Jensen, M. Bremholm, R. P. Nielsen, K. D. Joensen, J. S. Pedersen, H. Birkedal, Y. Chen, J. Almer, E. G. Søgaard, S. B. Iversen, B. B. Iversen* **1113 – 1116**

In Situ High-Energy Synchrotron Radiation Study of Sol–Gel Nanoparticle Formation in Supercritical Fluids

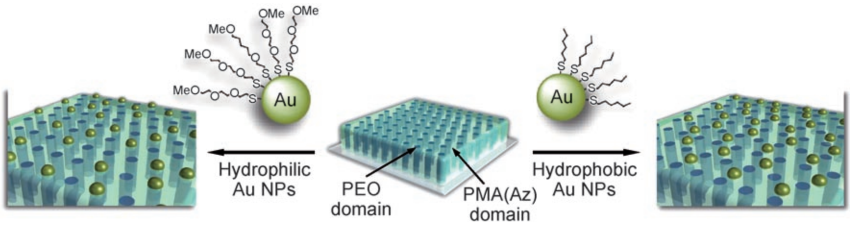


The value of gold ‘n’ rings: An isoflavanone moiety is the key structural feature of many complex natural products. It is now shown that such structures can be generated efficiently and atom economically by the annulation of simple *o*-hydroxybenzaldehydes with alkynes in the presence of a gold(I) catalyst (see scheme).

Transition-Metal Catalysis

R. Skouta, C.-J. Li* ——— **1117 – 1119**

Gold(I)-Catalyzed Annulation of Salicylaldehydes and Aryl Acetylenes as an Expedient Route to Isoflavanones



Likes attract: Site-specific recognition of the nanophase-separated surface of a PEO_m-*b*-$PMA(Az)_n$ film (PEO = polyethylene oxide, PMA(Az) = polymethacrylate with azobenzene-based liquid-crystalline side-chain) by hydrophilic and hydrophobic gold nanoparticles (Au NPs) was studied. The hydrophilic and hydrophobic Au NPs were found to selectively assemble on the hydrophilic PEO and hydrophobic PMA(Az) domains, respectively.

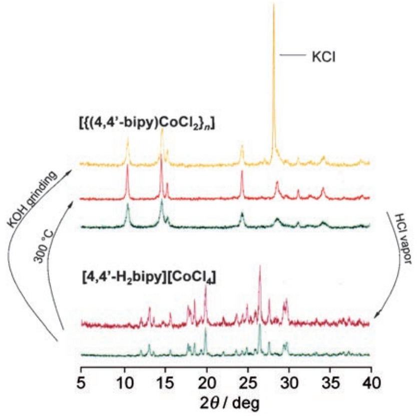
Gold Nanoparticles

S. Watanabe,* R. Fujiwara, M. Hada, Y. Okazaki, T. Iyoda ——— **1120 – 1123**

Site-Specific Recognition of Nanophase-Separated Surfaces of Amphiphilic Block Copolymers by Hydrophilic and Hydrophobic Gold Nanoparticles

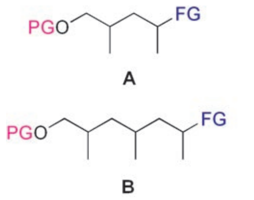
Crystal Synthesis

Thermal or chemical treatment of crystalline 4,4′-bipyridinium salts of $[MCl_4]^{2-}$ (M = Co, Zn, Fe, or Pt) leads to HCl loss and formation of coordination network solids $[\{MCl_2(4,4'\text{-bipy})\}_n]$. For M = Co, Zn, and Fe, these solids can also be prepared by mechanochemical means. Their exposure to HCl vapor or the mechanochemical reaction of metal dichlorides with $[4,4'\text{-}H_2bipy]Cl_2$ gives $[4,4'\text{-}H_2bipy]^{2+}$ salts of $[CoCl_4]^{2-}$, $[ZnCl_4]^{2-}$, and, for the first time, $[FeCl_4]^{2-}$.



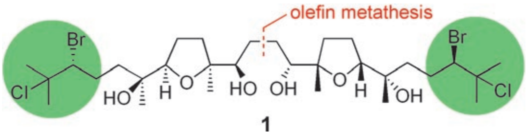
Asymmetric Catalysis

A match made in heaven: All the possible stereoisomers of α,ω-functionalized 2,4-dimethylpentane dyad and 2,4,6-trimethylheptane triad chirons (see picture; **A** and **B**, respectively; FG = functional group, PG = protecting group) can be reached by using a combination of a chiral catalyst and substrate effects in the hydrogenation of mainly nonfunctionalized alkenes. Excellent diastereo- and enantioselectivities were achieved.



>99 % *ee*
11:1 to 34:1 d.r. (unpurified)
40:1 to >120:1 d.r. (purified)

Natural Products Synthesis



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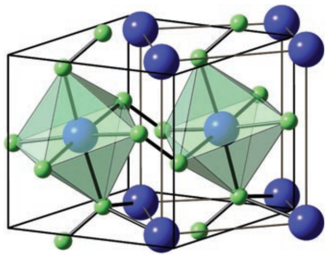
A victory for synthesis: The total synthesis of the marine triterpene polyether (+)-intricatetraol (**1**) has revealed its absolute configuration, which could not be determined even by spectroscopic methods. The approach features the enantioselective construction of the unique vicinal bromochloro functionality and an efficient olefin-metathesis strategy that takes the C_2 symmetry of the target into consideration.

Solid-State Chemistry

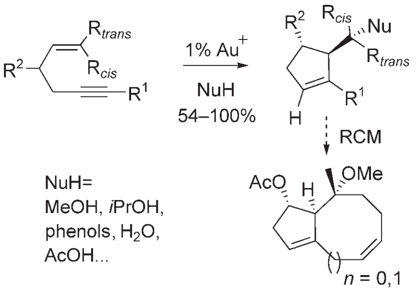
Unexpected crystal structures: The noble-metal pernitrides OsN_2 and IrN_2 are found to adopt structure types never before observed in nitrides (see picture; Os/Ir blue, N green). Furthermore, the crystal structures of RuN_2 and RhN_2, which have yet to be synthesized, are predicted. A pressure-induced displacive phase transition and a semiconductor–metal transition are predicted for IrN_2.



Homogeneous Catalysis

A. K. Buzas, F. M. Istrate,
F. Gagosz* ______________ 1141 – 1144

Gold(I)-Catalyzed 5-*endo* Hydroxy- and Alkoxycyclization of 1,5-Enynes: Efficient Access to Functionalized Cyclopentenes



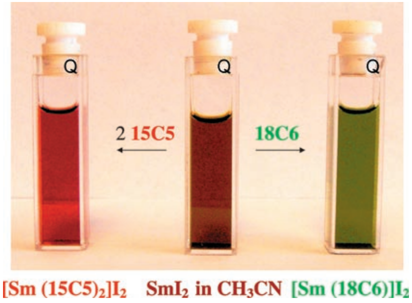
The rapid and stereoselective construction of highly functionalized cyclopentenes is possible through gold(I)-catalyzed 5-*endo* hydroxy- and methoxycyclizations of 1,5-enynes. More complex 5,7- and 5,8-fused bicyclic structures of a type found in many terpene natural products can be formed by combining the cyclization reaction with ring-closing metathesis (RCM; see scheme).

Lanthanide Luminescence

VIP

J. A. Teprovich, Jr., E. Prasad,*
R. A. Flowers, II* ______________ 1145 – 1148

Solvation-Controlled Luminescence of Sm^{II} Complexes

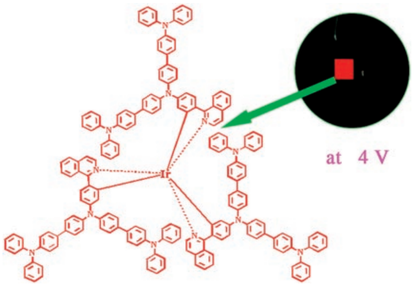


The jewel in the crown: Addition of a crown ether to SmI_2 in acetonitrile produces a complex that insulates the Sm^{II} ion from interaction with solvent and substrates. Consequently, solvent-induced luminescence quenching is decreased, leading to a significantly increased excited-state lifetime. Thus, it is possible to generate highly stable and luminescent Ln^{II} complexes in solution through proper choice of ligand and solvent.

Red-Emitting OLEDs

G.-J. Zhou, W.-Y. Wong,* B. Yao, Z.-Y. Xie,*
L.-X. Wang ______________ 1149 – 1151

Triphenylamine-Dendronized Pure Red Iridium Phosphors with Superior OLED Efficiency/Color Purity Trade-Offs



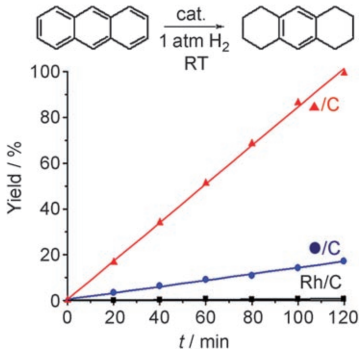
As good as red: Highly efficient pure red OLEDs based on iridium electrophosphors functionalized with hole-transporting triphenylamine dendrons are prepared (see picture). These bifunctional dendrimers give a peak efficiency of 11.7% with an excellent color quality and offer an attractive avenue for the development of metal phosphors with the optimized efficiency/color purity trade-offs required for pure red-emitting devices. OLED = organic light-emitting diode.

Shape-Dependent Catalysis

K. H. Park, K. Jang, H. J. Kim,
S. U. Son* ______________ 1152 – 1155

Near-Monodisperse Tetrahedral Rhodium Nanoparticles on Charcoal: The Shape-Dependent Catalytic Hydrogenation of Arenes

The shape of things to come? Monodisperse (4.9 ± 0.4)-nm tetrahedral rhodium nanoparticles on charcoal (▲/C) are compared to (4.8 ± 0.4)-nm spherical rhodium nanoparticles on charcoal (●/C) and commercial Rh/C as a catalyst for the hydrogenation of anthracene (see picture). The former is 5.8- and 109-times more active than the latter two, respectively. It also shows a higher selectivity and excellent activity in the hydrogenation of several other arenes.

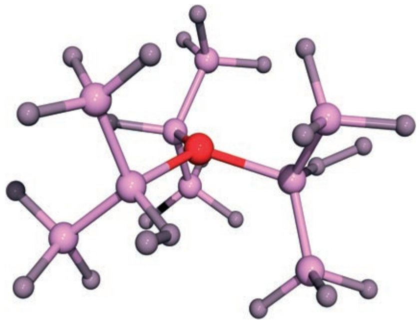


Lead-Centered Radical

C. Förster, K. W. Klinkhammer,* B. Tumanskii, H.-J. Krüger, H. Kelm ———— **1156–1159**

Stable Mononuclear Lead(III) Compound: A Lead-Centered Radical

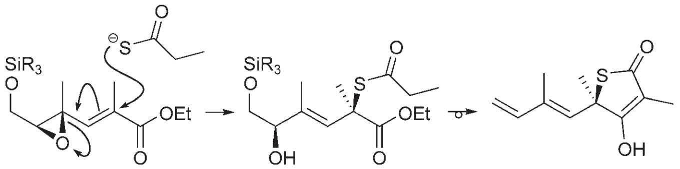
Plumb radical: The kinetically stable plumbyl radical $Pb[SiEt(SiMe_3)_2]_3$ (see molecular structure; red Pb, light purple Si, dark purple C) was obtained through oxidation of $Pb[SiEt(SiMe_3)_2]_3^-$ ions. With a half-life of about 8.5 hours at room temperature, it cleanly decomposes to elementary lead and $Pb[SiEt(SiMe_3)_2]_4$.



Natural Product Synthesis

K. L. Dormann, R. Brückner* ———— **1160–1163**

Variable Synthesis of the Optically Active Thiotetronic Acid Antibiotics Thiolactomycin, Thiotetromycin, and 834-B1



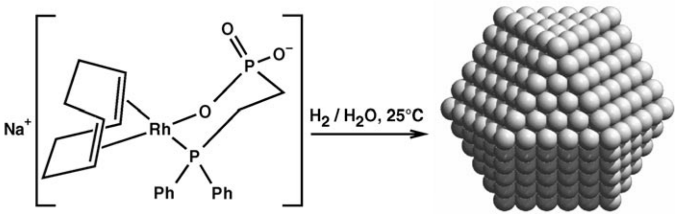
(+)-thiolactomycin

In seven steps: The antibiotic (+)-thiolactomycin was synthesized in seven steps and with 16 % overall yield from 4-acetoxy-2-methyl-2-buten-1-al, an intermediate of the industrial synthesis of vitamin A. Key transformations were the catalytic asymmetric Sharpless epoxidation of an ethoxycarbonyl-substituted pentadienol (93 % *ee*) and a regio- and stereoselective thiolysis of the resulting epoxide (see scheme).

Cluster Catalysis

J. Glöckler, S. Klützke, W. Meyer-Zaika, A. Reller, F. J. García-García, H.-H. Strehblow, P. Keller, E. Rentschler, W. Kläui* ———— **1164–1167**

With Phosphinophosphonic Acids to Nanostructured, Water-Soluble, and Catalytically Active Rhodium Clusters

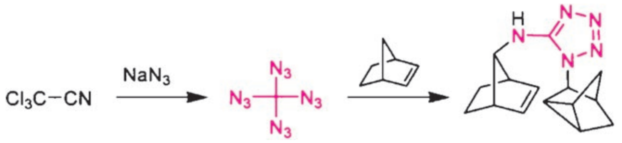


Pressure-sized clusters: Aqueous solutions of rhodium complexes stabilized by phosphinophosphonic acid ligands turn ink-black under a hydrogen atmosphere. Depending on the hydrogen pressure applied, rhodium clusters of 2–6 nm can be isolated (see scheme). These clusters are catalysts for the biphasic hydrogenation of olefins, arenes, and nitro compounds.

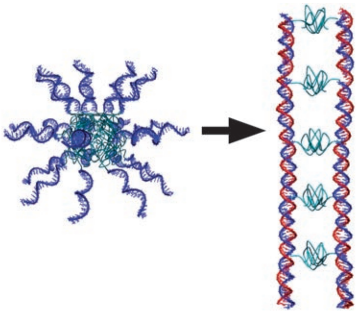
Nitrogen-Rich Compounds

K. Banert,* Y.-H. Joo, T. Rüffer, B. Walfort, H. Lang ———— **1168–1171**

The Exciting Chemistry of Tetraazidomethane



With a nitrogen content of 93.3 %, "perazidomethane" (CN_{12}) is highly explosive but nevertheless isolable. The title compound, which is accessible from commercially available trichloroacetonitrile in one step, undergoes simple dissociation and trapping reactions as well as more-complex transformations (for example, in the presence of norbornene; see scheme).

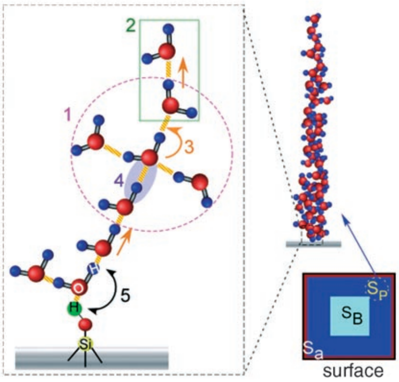


Transforming micelle structure: Amphiphilic DNA block copolymers form spherical micelles in solution. They can be transformed into rodlike micelles by hybridization with long DNA sequences, which consist of parallel aligned double-stranded DNA molecules "glued" together by hydrophobic interactions of the organic polymer (see picture). The template determines the length of the rodlike aggregates.

DNA Block Copolymers

The major bottleneck of rapid NMR-based structure determination is data analysis. The solution to this problem is a method that enables automatic high-resolution protein-structure determination from unassigned, experimental NMR data without manual intervention in less than 24 h.

NMR Spectroscopic Methods



Does water suffer from claustrophobia? The local structural and dynamic properties of water in confined (300–4000 nm) spaces were characterized by an NMR study of the size-dependent relaxation phenomena, which in turn reflect changes in water mobility and proton transfer. The results are important for understanding fluidics in extended nanospaces and in implementing micro-/nanofluidic devices.

Micro-/Nanofluidics

VIP

Supporting information is available on the WWW (see article for access details).

A video clip is available as Supporting Information on the WWW (see article for access details).

Service

Corrigendum

Synthesis of the Southern FGHI Ring System of Azaspiracid-1 and Investigation into the Controlling Elements of C28- and C36-Ketalization

X.-T. Zhou, L. Lu, D. P. Furkert, C. E. Wells, R. G. Carter* ______ **7622–7626**

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The incorrect Cambridge Crystallographic Data Center (CCDC) deposition number was listed for the X-ray crystal data of compound **22** in this Communication. The correct deposition number should be CCDC-617059. We thank Dr. Stephen Holgate (CCDC) for pointing out this error.