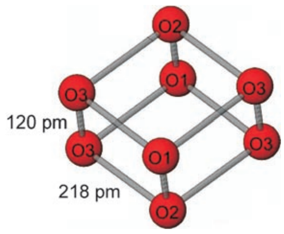
VIP *The following Communications have been judged by at least two referees to be "very important papers" and will be published online at www.angewandte.org soon:*

Obituary

Books

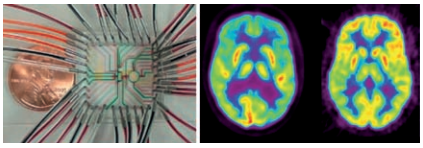
Highlights



Under pressure and full of surprises: At very high pressure, oxygen molecules O_2 combine to give—rather than the well-known crown-shaped ring form of elemental sulfur—the novel molecular unit O_8, or $(O_2)_4$, which exhibits strong bonds in the diatomic units but with much weaker π^*–π^* bonds between them (see picture).

Solid Oxygen

The best of both worlds: Can something tangible come from the merging of two different microworlds? An application of lab-on-a-chip technology in the nuclear medical field for the synthesis of positron emission tomography radiopharmaceuticals demonstrates this possibility.



Microfluidic Systems

Contents

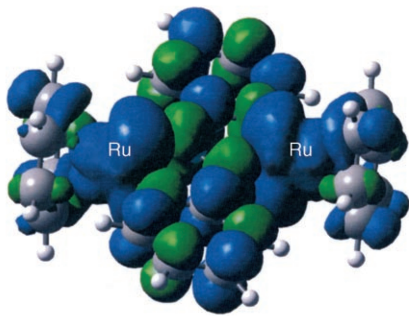
Reviews

Mixed Valence

W. Kaim,* G. K. Lahiri* ____ 1778–1796

Unconventional Mixed-Valent Complexes of Ruthenium and Osmium

Diversity: There are many different forms for dinuclear and oligonuclear complexes containing the heavier homologues of iron in neighboring oxidation states. A combination of methods is available to establish the criteria to characterize the metal–metal interaction in these complexes (see picture: spin density of $[(\mu\text{-abpy})\{Ru(C_6H_6)\}_2]^+$, abpy = 2,2′-azobispyridine). The potential for such interactions to function in molecular devices is discussed.

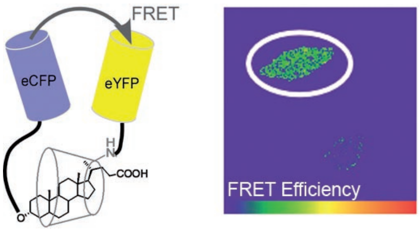


Communications

Protein Assembly

L. Zhang, Y. Wu,
L. Brunsveld* ____ 1798–1802

A Synthetic Supramolecular Construct Modulating Protein Assembly in Cells

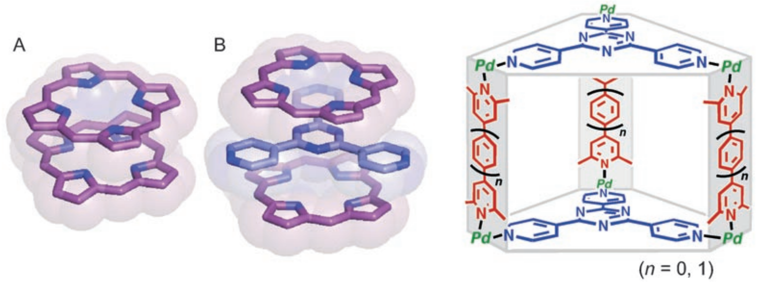


Supramolecular chemistry in the cell: Synthetic supramolecular constructs ligated to proteins modulate protein assembly (see picture). The interaction between the supramolecular elements is operative both in vitro and in cells, and drives the proteins to assemble, as revealed by a strong FRET effect between the engineered proteins.

Host–Guest Systems

K. Ono, M. Yoshizawa, T. Kato,
K. Watanabe, M. Fujita* ____ 1803–1806

Porphine Dimeric Assemblies in Organic-Pillared Coordination Cages



A box of porphine pi: Two types of porphine dimeric assemblies (A and B) are formed in the box-shaped cavity of organic-pillared Pd coordination cages. Depending on the cavity size (see picture, right), the two porphine molecules are π-stacked directly (A) or layered with an aromatic spacer (B).

For the USA and Canada:
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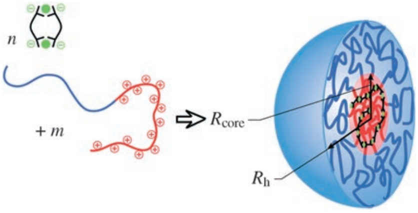
Nanostructures

Y. Yan,* N. A. M. Besseling, A. de Keizer,
A. T. M. Marcelis, M. Drechsler,
M. A. Cohen Stuart* ——— **1807 – 1809**

Hierarchical Self-Assembly in Solutions Containing Metal Ions, Ligand, and Diblock Copolymer

Cores for thought: The combination of reversible self-assembly (polymerization through weak coordination) and micellization driven by electrostatic interactions has resulted in hierarchical self-assembly of a mixture of metal ions (green circles), bisligands, and a cationic–neutral diblock copolymer. This approach results in the formation of well-defined, stable, and equilibrated core–shell nanostructures (see picture, R_h = hydrodynamic radius).

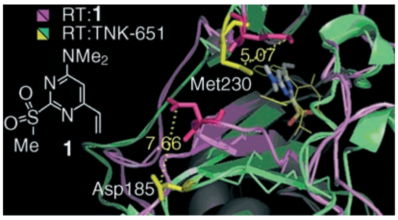


Competitive Inhibitors

G. Maga, M. Radi, S. Zanoli, F. Manetti,
R. Cancio, U. Hübscher, S. Spadari,
C. Falciani, M. Terrazas, J. Vilarrasa,
M. Botta* ——— **1810 – 1813**

Discovery of Non-Nucleoside Inhibitors of HIV-1 Reverse Transcriptase Competing with the Nucleotide Substrate

How odd! A new class of non-nucleoside reverse transcriptase inhibitors with a 6-vinylpyrimidine scaffold (**1**) has been found to inhibit HIV-1 reverse transcriptase (RT) by competition with the nucleotide substrate after binding to the non-nucleoside inhibitor binding pocket of the enzyme. Molecular modeling studies have been performed to elucidate their peculiar behavior.

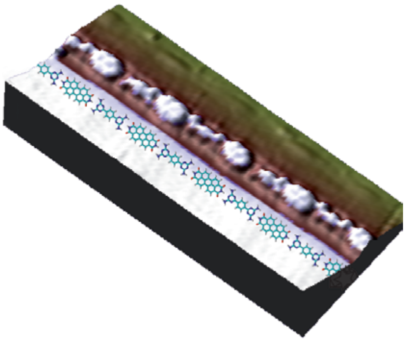


Supramolecular Chemistry

M. E. Cañas-Ventura, W. Xiao,
D. Wasserfallen, K. Müllen, H. Brune,
J. V. Barth, R. Fasel* ——— **1814 – 1818**

Self-Assembly of Periodic Bicomponent Wires and Ribbons

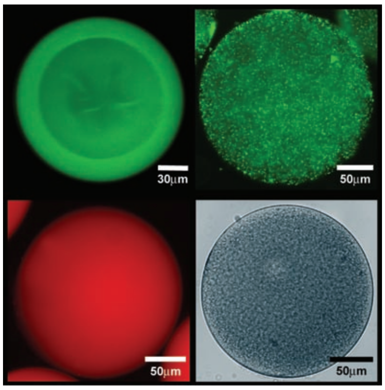
Extended order: Co-deposition of two molecular species with complementary hydrogen-bonding motifs on a naturally patterned template surface has been shown by STM studies to promote the formation of the anticipated three hydrogen bonds per heteromolecular pair to give 1D heteromolecular "wires" (see picture) and supramolecular ribbons. The superlattice of the template surface guides the supramolecular organization over extended surface areas.



Microfabrication

J. W. Kim, A. S. Utada,
A. Fernández-Nieves, Z. Hu,
D. A. Weitz* ——— **1819 – 1822**

Fabrication of Monodisperse Gel Shells and Functional Microgels in Microfluidic Devices



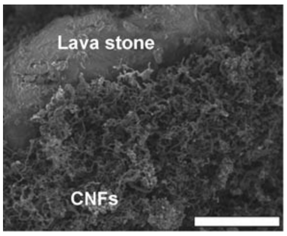
Microgel structures such as spherical microgel shells (picture on the upper left) and spherical microgel particles that incorporate quantum dots, magnetic nanoparticles, and polymer microparticles (other images) have been prepared by a capillary microfluidic technique. Because these particles change their volume with changes in temperature, they may find application in, for example, drug delivery.

Nanomaterials Synthesis

D. S. Su,* X.-W. Chen —— **1823 – 1824**

Natural Lavas as Catalysts for Efficient Production of Carbon Nanotubes and Nanofibers

Mount Etna provided the lava rocks used for the direct synthesis of carbon nanotubes and nanofibers by chemical vapor deposition (see image; scale bar: 15 μm). Since the iron oxide particles abundantly present serve as a natural catalyst, this could be an effective approach for the efficient production of nanocarbons.

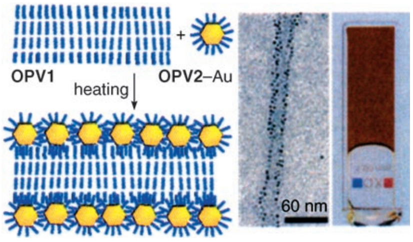


Organic–Inorganic Hybrid Composites

J. van Herrikhuyzen, S. J. George,
M. R. J. Vos, N. A. J. M. Sommerdijk,
A. Ajayaghosh, S. C. J. Meskers,*
A. P. H. J. Schenning* —— **1825 – 1828**

Self-Assembled Hybrid Oligo(*p*-phenylenevinylene)–Gold Nanoparticle Tapes

Taped energy transfer: A hybrid gel consisting of π-conjugated oligo(*p*-phenylenevinylene) tapes (**OPV1** and **OPV2**) and gold nanoparticles has been constructed in toluene through noncovalent interactions (see picture). The proximity of the metal particles to the π-conjugated molecules results in transfer of electronic excitation energy from the molecules to the metal in the gel state.

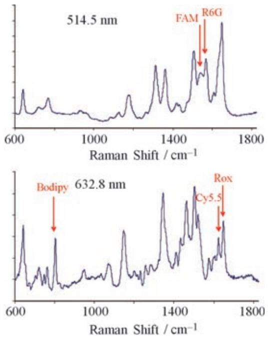


DNA Detection

K. Faulds,* F. McKenzie, W. E. Smith,
D. Graham* —— **1829 – 1831**

Quantitative Simultaneous Multianalyte Detection of DNA by Dual-Wavelength Surface-Enhanced Resonance Raman Scattering

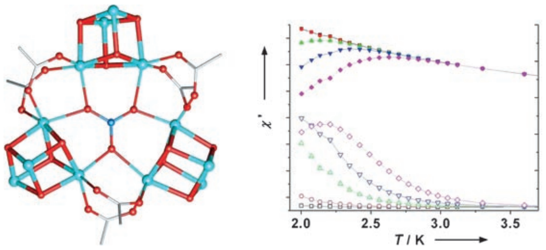
Dear SERRS: The quantitative detection of five labeled oligonucleotides by the title method (SERRS) without any separation is reported. The sensitivity of the multiplex analysis is the same as that for the individual dyes and indicates there is no compromise in the multiplexed format.



Single-Molecule Magnets

M.-H. Zeng,* M.-X. Yao, H. Liang,*
W.-X. Zhang, X.-M. Chen —— **1832 – 1835**

A Single-Molecule-Magnetic, Cubane-Based, Triangular Co_{12} Supercluster

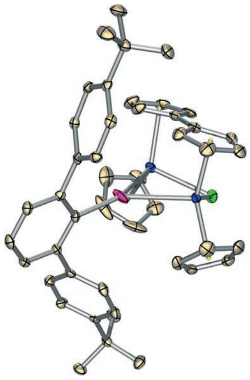


Extraordinary structure: An unprecedented Co_{12} supercluster in which three Co_4O_4 cubes surround a central μ_6-nitrate ligand exhibits single-molecule magnet behavior. The picture shows the structure of the Co_{12} core and the temperature dependence of the in-phase (χ′, full symbols) and out-of-phase (χ″, open symbols) components of the magnetic susceptibility at various ac frequencies.

Gallium-Bridged Dizirconocene

B. Quillian, Y. Wang, C. S. Wannere, P. Wei, P. v. R. Schleyer, G. H. Robinson* ______ **1836 – 1838**

A Trimetallic Fulvalene-Bridged Dizirconocene–Gallium Complex

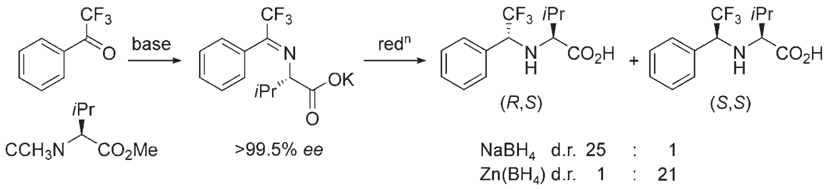


Star GaZr: The X-ray structure of **1** (see picture; Ga pink, Zr blue, Cl green, C gold) illustrates a new metal–metal bonding motif between gallium and zirconium atoms: a gallium atom bonded to two zirconium atoms. Spectroscopic and computational data support the presence of a bridging Zr-H-Zr hydride in **1** that was undetected by single-crystal X-ray analysis.

Diastereoselective Reductions

G. Hughes,* P. N. Devine,* J. R. Naber, P. D. O'Shea, B. S. Foster, D. J. McKay, R. P. Volante ______ **1839 – 1842**

Diastereoselective Reductive Amination of Aryl Trifluoromethyl Ketones and α-Amino Esters

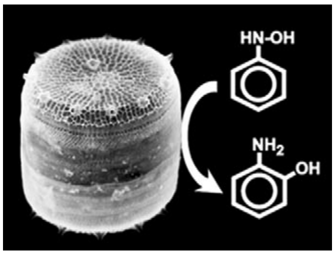


Reductionist art: Careful choice of the reducing agent in the reductive amination of trifluoromethyl ketones with α-amino esters allows stereoselective access, from the imine formed, to either the *R*,*S* or *S*,*S* diastereomers of the resulting amino acids. Whereas $NaBH_4$ affords the *R*,*S* diastereomers, $Zn(BH_4)_2$ affords the *S*,*S* diastereomers (see scheme), which can be easily converted into potent cathepsin K inhibitors.

Silica Biotechnology

N. Poulsen, C. Berne, J. Spain, N. Kröger* ______ **1843 – 1846**

Silica Immobilization of an Enzyme through Genetic Engineering of the Diatom *Thalassiosira pseudonana*

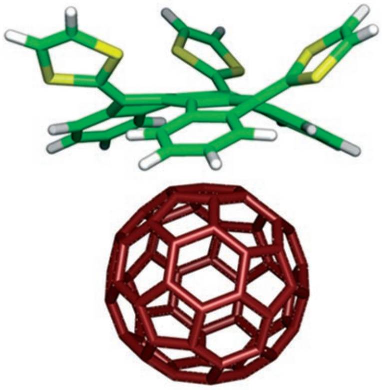


Biosilica structures containing foreign proteins with desired functionalities can be generated by a molecular genetic method. An enzyme immobilized in diatom silica was found to display better activity than purified hydroxylaminobenzene mutase in solution. Such immobilized active biomolecules may find application for the fabrication of sensor materials and reusable catalysts.

Fullerene Complexes

E. M. Pérez, M. Sierra, L. Sánchez, M. R. Torres, R. Viruela, P. M. Viruela, E. Ortí,* N. Martín* ______ **1847 – 1851**

Concave Tetrathiafulvalene-Type Donors as Supramolecular Partners for Fullerenes



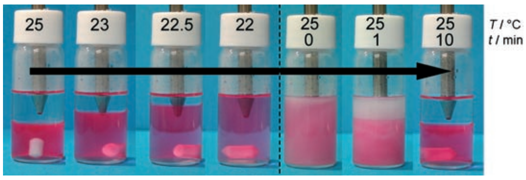
The cap fits! A new class of concave π-extended tetrathiafulvalene (TTF) derivatives, truxene-TTFs, were prepared and characterized, and their self-assembly with fullerenes was investigated (see picture). Truxene-TTFs represent the first example of TTF-related electron donors that serve, without chemical modification, as monotopic receptors for fullerenes in solution.

Contents

Ionic Liquids

K. Fukumoto, H. Ohno* —— **1852 – 1855**

LCST-Type Phase Changes of a Mixture of Water and Ionic Liquids Derived from Amino Acids



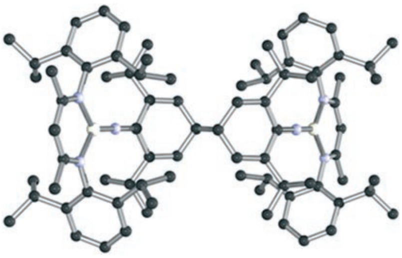
Out of phase: Ionic liquids (ILs) derived from amino acids exhibit phase separation with a lower critical solution temperature after mixing with water (see picture; upper phase water; lower phase IL). The phase-separation temperature of these mixtures depends on the ion structure and water content, and is lowered by an increase in the hydrophobicity of the ionic liquid.

Ketimide Complexes

G. Bai, D. W. Stephan* —— **1856 – 1859**

Formation of C–C and C–N Bonds in Ni^{II} Ketimide Complexes via Transient Ni^{III} Aryl Imides

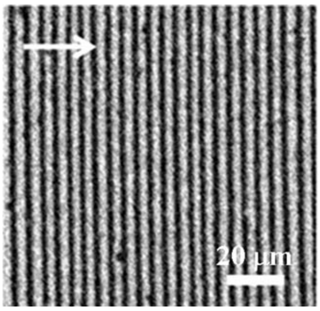
Has a real nacnac for coupling: Ligand-to-metal electron transfer results from the reactions of the Ni^I synthon $[\{(nacnac)Ni\}_2(\mu\text{-}\eta^3\!:\!\eta^3\text{-}C_6H_5Me)]$ (nacnac = CH-$\{CMeN(2,6\text{-}iPr_2C_6H_3)\}_2$) with the azides $2,6\text{-}iPr_2C_6H_3N_3$ or $2,6\text{-}Me_2C_6H_3N_3$ to give Ni^{II} ketimides (see picture for example; C black, N light blue, Ni white). The reactions proceed via transient Ni^{III} imides, and the differing pathways are directed by the steric demands of the azide substituents.



Nanotechnology

J. Xu, J. Xia, Z. Lin* —— **1860 – 1863**

Evaporation-Induced Self-Assembly of Nanoparticles from a Sphere-on-Flat Geometry



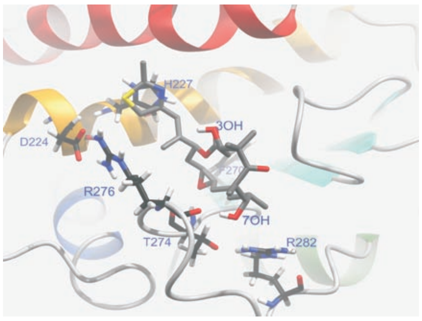
Nanoscience in coffee rings: Nanoparticles with easily tailored optical and electronic properties can be dynamically self-assembled into spatially ordered, 2D patterns (see SEM picture) simply by allowing a drop of a nanoparticle solution to evaporate in a confined, axially symmetric geometry. Utilizing the "coffee-ring" phenomenon, this approach, which dispenses with the need for lithography and external fields, is fast, cheap, and robust.

Drug Binding Modes

M. Reese, V. M. Sánchez-Pedregal, K. Kubicek, J. Meiler, M. J. J. Blommers, C. Griesinger, T. Carlomagno* —— **1864 – 1868**

Structural Basis of the Activity of the Microtubule-Stabilizing Agent Epothilone A Studied by NMR Spectroscopy in Solution

Fits in a pocket: The binding mode of epothilone A (EpoA) to tubulin (see picture; rods: C gray, H white, N blue, O red, S yellow) is determined by NMR spectroscopy in aqueous solution. The results explain the existing structure–activity relationship data for epothilones with both native and mutant tubulins, and support the existence of a common pharmacophore for EpoA and paclitaxel.



Fused-Ring Systems

J. A. Bull, M. G. Hutchings,
P. Quayle* ______ **1869 – 1872**

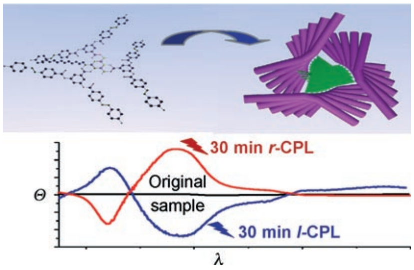
A Remarkably Simple and Efficient Benzannulation Reaction

On a short fuse: Although fused aromatic rings are common structural motifs in natural products, there are relatively few direct methods for the preparation of such systems from acyclic precursors. An atom-transfer radical cyclization carried out under microwave (MW) irradiation has now been developed which gives rapid access to functionalized aromatic compounds from readily available starting materials (see scheme).

Chiral Photoinduction

F. Vera, R. M. Tejedor, P. Romero,
J. Barberá, M. B. Ros, J. L. Serrano,*
T. Sierra* ______ **1873 – 1877**

Light-Driven Supramolecular Chirality in Propeller-Like Hydrogen-Bonded Complexes That Show Columnar Mesomorphism

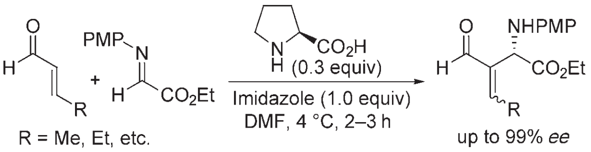


Shine a light! Columnar mesomorphic assembles of propeller-like hydrogen-bonded complexes show a chiral photoresponse upon irradiation with circularly polarized light (CPL) of a given handedness (see picture). The materials can behave as a supramolecular switch that undergoes helix inversion when irradiated with the oppositely polarized light.

Asymmetric Synthesis

N. Utsumi, H. Zhang, F. Tanaka,*
C. F. Barbas III* ______ **1878 – 1880**

A Way to Highly Enantiomerically Enriched aza-Morita–Baylis–Hillman-Type Products

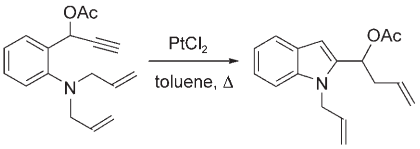


Going Mannich: Difficult to synthesize β-amino carbonyl compounds bearing α-alkylidene groups have been prepared enantioselectively (up to 99 % *ee*) by reaction of β-substituted α,β-unsaturated aldehydes and α-imino esters in the presence of (*S*)-proline and imidazole under mild conditions (see scheme, PMP = *p*-methoxyphenyl). Studies suggest that the reaction mechanism involves a Mannich-type reaction/isomerization sequence.

Synthetic Methods

K. Cariou, B. Ronan, S. Mignani,
L. Fensterbank,*
M. Malacria* ______ **1881 – 1884**

From $PtCl_2$- and Acid-Catalyzed to Uncatalyzed Cycloisomerization of 2-Propargyl Anilines: Access to Functionalized Indoles

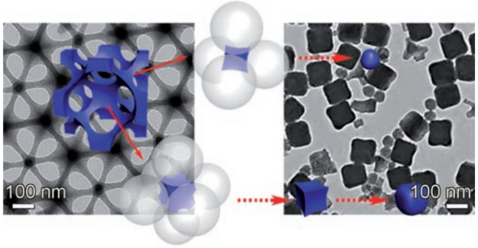


On the move: $PtCl_2$-catalyzed electrophilic activation of an alkyne moiety triggers a heterocyclization accompanied by migrations of both an allyl group and an acetate group to produce an indole (see scheme). Variation of the reaction conditions (particularly the temperature) as well as substituents at the propargylic position and on the nitrogen atom allows easy and versatile access to a myriad of indole substrates.

Nanoparticle Shaping

F. Li, Z. Wang, A. Stein* 1885 – 1888

Shaping Mesoporous Silica Nanoparticles by Disassembly of Hierarchically Porous Structures



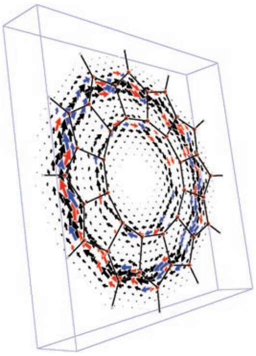
Shipshape: Mesoporous silica nanocubes and spheroids with controllable bimodal size distributions were synthesized within a colloidal crystal template by using a weak acid catalyst to effect the disassembly of an inverse opal silica skeleton. The shaped nanoparticles could be replicated by nanocasting to obtain carbon or polymer nanoparticles with similar morphologies.

Coronenes

G. Monaco, P. W. Fowler, M. Lillington, R. Zanasi* 1889 – 1892

Designing Paramagnetic Circulenes

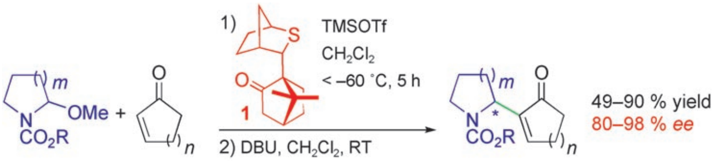
Paramagnetic closed-shell neutral molecules were devised by using the ipsocentric approach to calculation and interpretation of ring current. In [4*n*,5]coronenes, two antiaromatic cycles of C atoms are weakly coupled. Confirmation of concentric, conrotating paratropic ring currents (see picture for current-density map) leading to overall paramagnetism was obtained by ab initio calculations on [8,5]- and [12,5]coronenes.



Asymmetric Synthesis

E. L. Myers, J. G. de Vries, V. K. Aggarwal* 1893 – 1896

Reactions of Iminium Ions with Michael Acceptors through a Morita–Baylis–Hillman-Type Reaction: Enantiocontrol and Applications in Synthesis

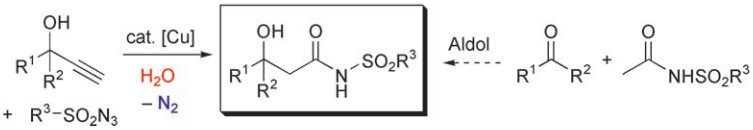


All adducts one way: Iminium ions, generated in situ from the corresponding N,O-acetals, can be used as electrophiles in a Morita–Baylis–Hillman-type reaction with a wide range of Michael acceptors (enones, enals, *S*- and *O*-acrylates). The reaction has been rendered asymmetric using sulfide **1** (see scheme; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, TMSOTf = trimethylsilyl trifluoromethanesulfonate).

Hydrative Amide Synthesis

S. H. Cho, S. Chang* 1897 – 1900

Rate-Accelerated Nonconventional Amide Synthesis in Water: A Practical Catalytic Aldol-Surrogate Reaction

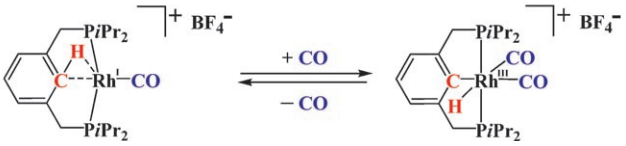


An aldol alternative: Cu-catalyzed hydrative amide synthesis is significantly accelerated in aqueous cosolvent systems. Under environmentally friendly conditions and with N_2 released as the single side product, a wide range of propargyl alcohols and sulfonyl azides react to provide β-hydroxy *N*-sulfonamides in good to excellent yields. Polyhydroxy amides could be synthesized stereoselectively, proving this as a new practical aldol-surrogate strategy.

C–H Bond Activation

M. Montag, L. Schwartsburd, R. Cohen, G. Leitus, Y. Ben-David, J. M. L. Martin,* D. Milstein* ——— **1901 – 1904**

The Unexpected Role of CO in C–H Oxidative Addition by a Cationic Rhodium(I) Complex

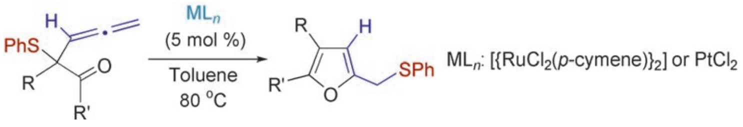


CO(mpletely) unexpected: The oxidative addition of C–H bonds to transition-metal ions usually requires high electron density at the metal center, and therefore strong π-acceptor ligands, such as carbon monoxide, are normally expected to inhibit such reactions. Hence surprisingly, an electron-poor cationic Rh^I system is observed in which addition of a CO ligand can actually promote oxidative addition of a strong C–H bond (see scheme).

Synthetic Methods

L. Peng, X. Zhang, M. Ma, J. Wang* ——— **1905 – 1908**

Transition-Metal-Catalyzed Rearrangement of Allenyl Sulfides: A Route to Furan Derivatives

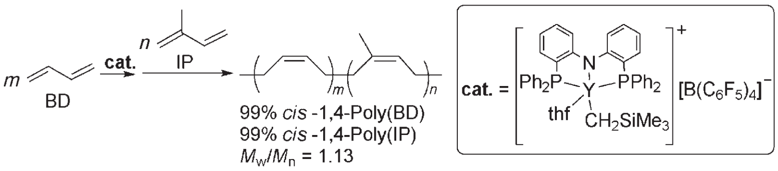


Mass migration: Allenyl sulfides undergo 1,4-migration of the phenylsulfanyl group when catalyzed by a transition-metal complex to give furan derivatives (see scheme). Evidence suggests that the reaction proceeds via a metal carbene intermediate, which is trapped intramolecularly by a carbonyl group. A one-pot sequential catalytic transformation of α-diazocarbonyl compounds to furan derivatives is also developed.

Living Polymerization

L. Zhang, T. Suzuki, Y. Luo, M. Nishiura, Z. Hou* ——— **1909 – 1913**

Cationic Alkyl Rare-Earth Metal Complexes Bearing an Ancillary Bis(phosphinophenyl)amido Ligand: A Catalytic System for Living *cis*-1,4-Polymerization and Copolymerization of Isoprene and Butadiene

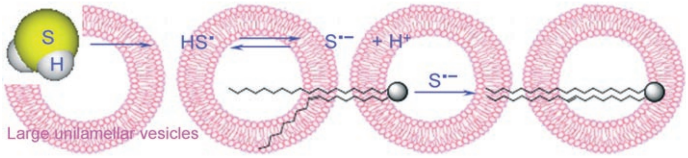


Excellent activator: Living *cis*-1,4-polymerization and copolymerization of isoprene (IP) and butadiene (BD) are achieved for the first time in the presence of an in situ formed cationic alkyl yttrium species (see scheme). A related cationic alkyl lutetium complex, which provides a well-defined structural model for the true catalytically active species, is isolated and structurally characterized by X-ray crystallography.

Biomimetic Chemistry

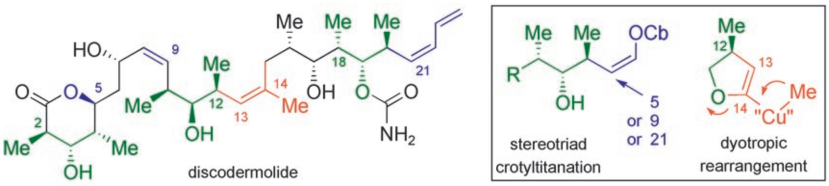
I. N. Lykakis, C. Ferreri, C. Chatgilialoglu* ——— **1914 – 1916**

The Sulfhydryl Radical ($HS^{\bullet}/S^{\bullet -}$): A Contender for the Isomerization of Double Bonds in Membrane Lipids



The biologically relevant gas hydrogen sulfide is a source of radicals that have been found to catalyze the *cis*–*trans* isomerization of unsaturated lipids in a vesicle suspension (see picture). This biomimetic model highlights the importance of double-bond geometry in membrane lipids and has significance for the investigation of H_2S activity (damaging and signaling) in a biological milieu.

Natural Product Synthesis



A complete strategy: The total synthesis of discodermolide relies on the elaboration of *syn–anti* stereotriads linked to a *Z*-*O*-enecarbamate group, its direct transformation into the terminal *Z* diene, and stereocontrolled generation of the trisubstituted *Z* double bond by a dyotropic rearrangement (see scheme; OCb = *N*,*N*-diisopropylcarbamoyloxy). The synthesis was achieved in 21 steps with 1.6% overall yield.

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).

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Service

The Guy Ourrisson Colloqium
In Commemoration of the 50 year career of the late Guy Ourisson in Strasbourg

Grande Amphitheatre, Campus Esplanade, Université Louis Pasteur
March 26 – 27, 2007 ● Strasbourg

Programme

March 26, 2007, 10.00:
Speeches by personalities from research, education & politics commemorating the career of the late Guy Ourisson:
● University Louis Pasteur de Strasbourg ● Academy of Sciences ● Ministry of Research
● CNRS ● French Society of Chemistry ● Mayor of Strasbourg ● Japanese Consulate

14.00 : Scientific seminars
- **Metal-Mediated Activation of Methane: In Search of a Holy Grail** - Helmut Schwarz (Berlin, Germany)
- **From Chemistry to Life: Chance or Necessity?** - André Brack (Orléans, France)
- **To be announced** - Jacques Reisse (Brussels, Belgium)
- **ABC Transporters: Structural Studies, Tackling the Functions and Genetic Diseases** - Jean-Yves Lallemand (Paris)

March 27, 2007, 9.00:
- **To be announced** - Duilio Arigoni (ETH, Zürich)
- **Chemoselective Reactions and Synthesis of Biologically Active Compounds** - Janine Cossy (Paris, France)
- **Bio-Organic Studies on Natural Products** - Koji Nakanishi (Columbia, USA)