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:

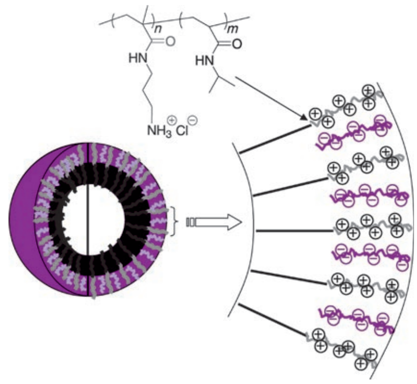
News

Books

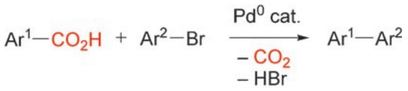
Highlights

Polymer Vesicles

Guilty as charged; lock them up! Recent advances in the field of polymer vesicles are highlighted with particular focus on the temperature-induced, direct formation of vesicles in water from amphiphilic block copolymers and the structural "locking" of the resulting vesicles by formation of polyelectrolyte complexes (see picture).



Cross-Coupling Reactions



$$Ar^1{-}CO_2H + Ar^2{-}Br \xrightarrow[\substack{-CO_2\\ -HBr}]{Pd^0\text{ cat.}} Ar^1{-}Ar^2$$

Closer to nature: Biaryl motifs are common in organic molecules with important biological and physical properties. Carboxylic acids can now be used as aryl donors in palladium-catalyzed cross-coupling reactions to give biaryl compounds of high synthetic value (see scheme).

Contents

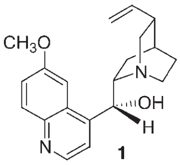
Reviews

History of Chemistry

J. I. Seeman* ____________ **1378 – 1413**

The Woodward–Doering/Rabe–Kindler Total Synthesis of Quinine: Setting the Record Straight

Did they or didn't they? In 1944, R. B. Woodward and W. von E. Doering reported the total synthesis of homomeroquinene and *d*-quinotoxine. On the basis of the conversion of *d*-quinotoxine into quinine reported by P. Rabe and K. Kindler in 1918, Woodward and Doering made the claim of the total synthesis of quinine (**1**). In 2000, G. Stork concluded that this claim was a myth. Previously unpublished archive material and numerous interviews throw new light onto this controversy.



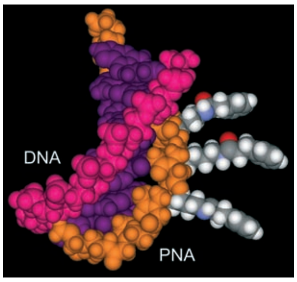
Communications

Peptide Nucleic Acids

E. A. Englund,
D. H. Appella* ____________ **1414 – 1418**

γ-Substituted Peptide Nucleic Acids Constructed from L-Lysine are a Versatile Scaffold for Multifunctional Display

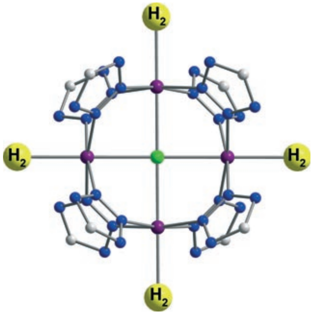
On display: This model shows DNA (pink) annealed to a peptide nucleic acid (PNA; orange) containing several L-lysine γ side chains (ᴸKγ-PNA) in the middle of the PNA oligomer. The ᴸKγ-PNA side chains project away from the nucleobase pairs (purple) and line the periphery of the duplex. This strategy can be used for the multifunctional display of various functional groups from the PNA residues without diminishing the binding affinity or selectivity to DNA.



Hydrogen Storage

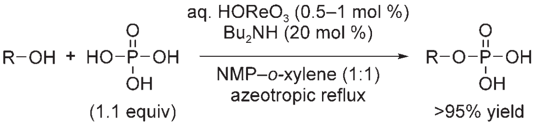
M. Dincă, W. S. Han, Y. Liu, A. Dailly,
C. M. Brown, J. R. Long* ____ **1419 – 1422**

Observation of Cu^{2+}–H_2 Interactions in a Fully Desolvated Sodalite-Type Metal–Organic Framework



Metal–H_2 binding: A new tetrazolate-based metal–organic framework exhibits high H_2 uptake at low temperature and moderate pressure. The evacuation of coordinated solvent molecules from Cu^{2+} ions within the framework provides strong binding sites for H_2 molecules (see picture; Cu purple, C gray, N blue, Cl green).

For the USA and Canada: ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals postage paid at Jamaica, NY 11431. US POSTMASTER: send address changes to *Angewandte Chemie*, Wiley-VCH, 111 River Street, Hoboken, NJ 07030. Annual subscription price for institutions: US$ 5685/5168 (valid for print and electronic / print or electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.

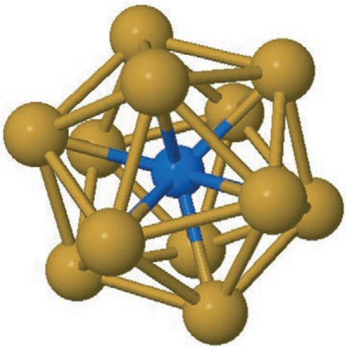


Come together … over Re: Oxorhenium(VII) complexes catalyze the direct condensation of phosphoric acid with an alcohol to selectively give the corresponding phosphoric acid monoester on a 2–100-mmol scale (see scheme). This method should be useful for the industrially important synthesis of phosphoric acid monoesters.

Catalytic Condensation

A. Sakakura, M. Katsukawa,
K. Ishihara* ______ 1423 – 1426

The Oxorhenium(VII)-Catalyzed Direct Condensation of Phosphoric Acid with an Alcohol



The predicted endohedral icosahedral clusters Pu@Pb_{12} (see picture; Pu blue, Pb yellow) and $[Am@Pb_{12}]^+$ have an outermost 32-electron system corresponding to formally occupied 7s, 7p, 6d, and 5f actinide orbitals, each of which interacts with a Pb 6p-based orbital of the $[Pb_{12}]^{2-}$ cage. This study provides the first example of a formal 32-electron principle, and 32 is not a false magic number.

Endohedral Clusters

J.-P. Dognon, C. Clavaguéra,
P. Pyykkö* ______ 1427 – 1430

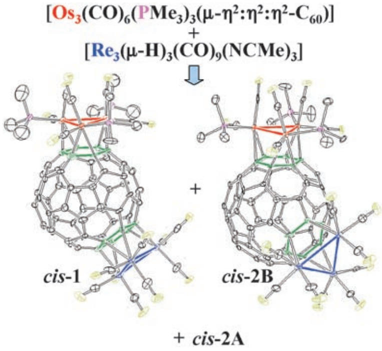
Towards a 32-Electron Principle: Pu@Pb_{12} and Related Systems

It stacks up nicely: Exposure of dihydrogen sulfate salts of appropriately substituted cyclo[8]pyrroles to electron-deficient acceptor molecules gives discotic liquid crystals. The columnar mesophase structures are stabilized by electron-donor/electron-acceptor interactions (see picture; red: trinitrobenzene, green: cyclo[8]pyrrole cores, yellow: sulfate ions, gray: volume occupied by the substituents).

Donor–Acceptor Systems

M. Stępień, B. Donnio,
J. L. Sessler* ______ 1431 – 1435

Supramolecular Liquid Crystals Based on Cyclo[8]pyrrole



A buckyball sandwich: The depicted reaction produces *cis*-**1** and *cis*-**2** (see picture), in which the fullerene is sandwiched between two different clusters. Variable-temperature ^1H NMR spectra reveal that *cis*-**1** and *cis*-**2** are interconvertible and *cis*-**2** exists as two isomers.

Fullerene Complexes

B. K. Park, C. Y. Lee, J. Jung, J. H. Lim,
Y.-K. Han, C. S. Hong,
J. T. Park* ______ 1436 – 1439

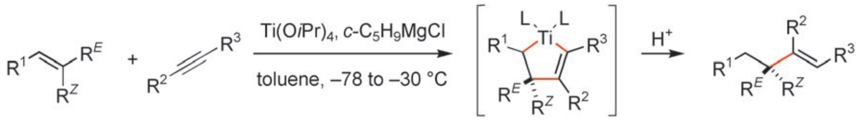
$[Os_3(CO)_6(PMe_3)_3](\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{60})[Re_3(\mu\text{-}H)_3(CO)_9]$: A Fullerene[60] Coordinated to Two Different Trinuclear Clusters

Contents

Synthetic Methods

H. A. Reichard,
G. C. Micalizio* ______ **1440 – 1443**

A Site- and Stereoselective Intermolecular Alkene–Alkyne Coupling Process

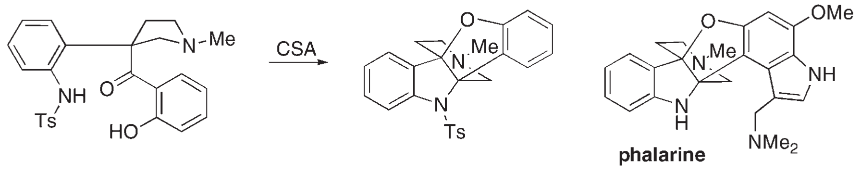


Ti-ght union: A highly regio- and stereoselective bimolecular coupling reaction is described for the union of substituted, unactivated olefins and internal alkynes (see scheme). The titanium-mediated coupling reaction proceeds with C–C bond formation occurring distal to a pendent hydroxy group.

Mechanistic Studies

C. Li, C. Chan, A. C. Heimann,
S. J. Danishefsky* ______ **1444 – 1447**

On the Rearrangement of an Azaspiroindolenine to a Precursor to Phalarine: Mechanistic Insights

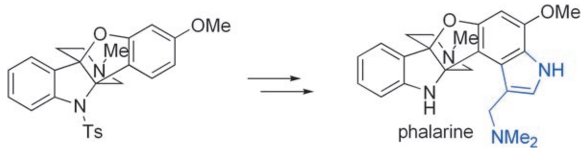


An interesting rearrangement: Management of functional groups in derivatives of indoles enables a rearrangement to take place which provides the pentacyclic ring system found in phalarine (see scheme, CSA = camphorsulfonic acid, Ts = toluene-4-sulfonyl). Studies into the mechanism proved valuable for the total synthesis of phalarine and provided insight into the chemistry of indoles in general.

Natural Products

C. Li, C. Chan, A. C. Heimann,
S. J. Danishefsky* ______ **1448 – 1450**

Total Synthesis of Phalarine

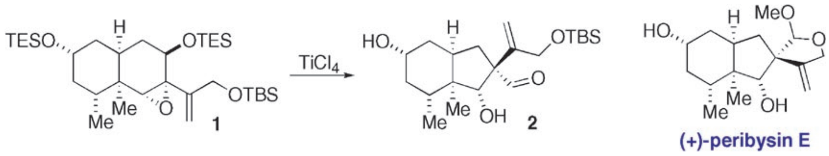


End of the expedition ... for now: Completion of the first total synthesis of phalarine from an advanced rearrangement product brought up interesting obstacles to overcome. Use of the Gassman oxindole synthesis and subsequent manipulations led to the racemic natural product (see scheme, Ts = toluene-4-sulfonyl).

Natural Products

A. R. Angeles, D. C. Dorn, C. A. Kou,
M. A. S. Moore,
S. J. Danishefsky* ______ **1451 – 1454**

Total Synthesis of Peribysin E Necessitates Revision of the Assignment of its Absolute Configuration

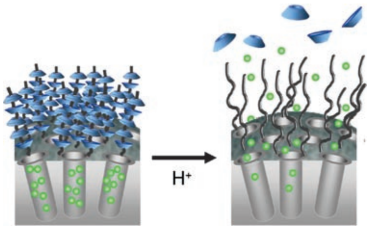


The right way round: Peribysin E, a naturally occurring adhesion inhibitor, has been synthesized and, as a result, its absolute configuration reassigned. The natural and nonnatural enantiomers can be reached starting from (*R*)- or (*S*)-carvone, respectively. A key step is the ring contraction of **1** to **2** (see scheme, TBS = *tert*-butyldimethylsilyl, TES = triethylsilyl).

Supramolecular Chemistry

C. Park, K. Oh, S. C. Lee,
C. Kim* ———— 1455 – 1457

Controlled Release of Guest Molecules from Mesoporous Silica Particles Based on a pH-Responsive Polypseudorotaxane Motif



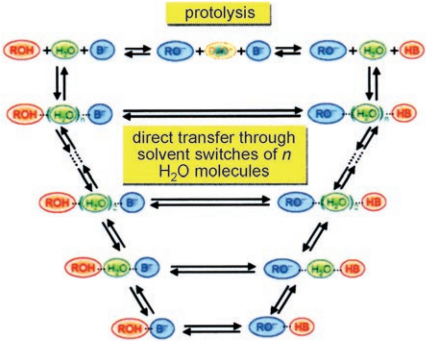
Stringing them along: The pores of a mesoporous silica particle were filled with guest molecules and then blocked by threading cyclodextrin molecules (CDs) onto the surface-grafted polyethylenimine (PEI) chains at pH 11. At pH 5.5, the guest molecules can be released from the pores of the particle by reversible dethreading of the CDs from the PEI chains.

Aqueous Proton Transfer

O. F. Mohammed, D. Pines,
E. T. J. Nibbering,* E. Pines* 1458 – 1461

Base-Induced Solvent Switches in Acid–Base Reactions

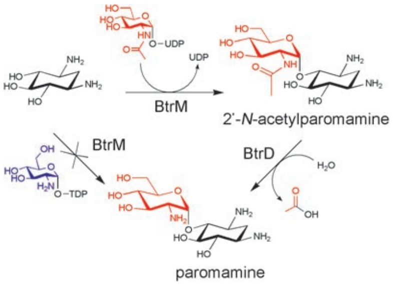
Fast switches: Eigen and Weller's classic diffusion reaction model for aqueous acid–base neutralization reactions is used to interpret the proton-transfer dynamics between pyranine and trichloroacetate. Upon mutual diffusion of the acid and base to form an encounter reaction complex, solvent switches mediate the proton transfer between acid and base and provide a general framework for all observed dynamic features (see picture; ROH = acid, B = base).



Biosynthetic Enzymes

A. W. Truman, F. Huang, N. M. Llewellyn,
J. B. Spencer* ———— 1462 – 1464

Characterization of the Enzyme BtrD from *Bacillus circulans* and Revision of Its Functional Assignment in the Biosynthesis of Butirosin



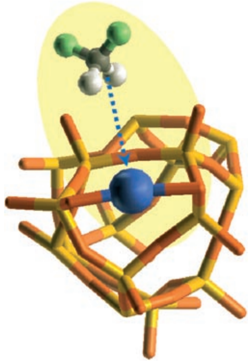
A functional reassignment: BtrD, a protein encoded in the butirosin gene cluster, functions as a deacetylase rather than a nucleotidyltransferase as previously reported. BtrD was found to selectively catalyze the conversion of 2′-*N*-acetylparomamine to paromamine, strongly suggesting that butirosin's neosamine moiety originates from uridine diphospho(UDP)-*N*-acetylglucosamine (see picture).

Heterogeneous Catalysis

C. N. Nenu, E. Groppo, C. Lamberti,
A. M. Beale, T. Visser, A. Zecchina,
B. M. Weckhuysen* ———— 1465 – 1468

Dichloromethane as a Selective Modifying Agent To Create a Family of Highly Reactive Chromium Polymerization Sites

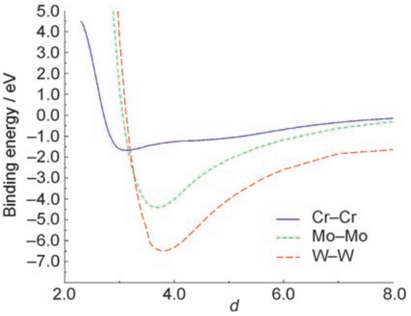
Uniform polymerization sites with high activity can be created by treating a Phillips-type Cr^{II}/SiO_2 catalyst with CH_2Cl_2 (as shown schematically in the picture) under well-defined conditions. A mechanism is proposed in which CH_2Cl_2 increases the catalytic activity of a small fraction of Cr sites while poisoning the remainder.



Metal–Metal Multiple Bonds

B. O. Roos,* A. C. Borin,
L. Gagliardi ______ **1469 – 1472**

Reaching the Maximum Multiplicity of the Covalent Chemical Bond

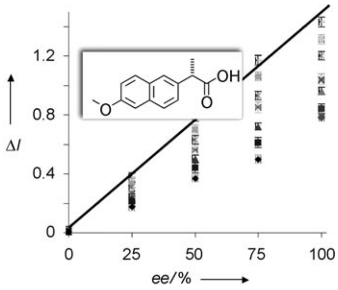


Maxing out at six: The maximum bond order that can be achieved between two equal atoms in the periodic system is six. The picture shows the potential energy curves for the diatoms Cr_2, Mo_2, and W_2, where the latter two are sextuply bonded molecules (d = internuclear distance in atomic units).

Chirality in Liquid Crystals

D. M. Walba,* L. Eshdat, E. Korblova,
R. Shao, N. A. Clark ______ **1473 – 1475**

A General Method for Measurement of Enantiomeric Excess by Using Electrooptics in Ferroelectric Liquid Crystals



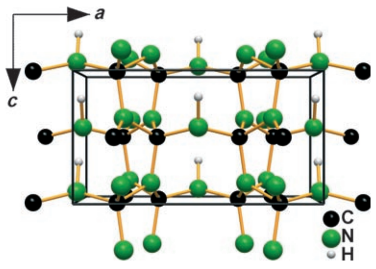
It's *ee*rie: A new method for quantitative measurement of *ee* values is described. The method exploits the unique electro-optic properties of the chiral smectic A liquid-crystal phase and is potentially applicable to the high-throughput ($>10^6$ determinations per day) measurement of *ee* values for any chiral analyte.

Nitrides

E. Horvath-Bordon, R. Riedel,*
P. F. McMillan, P. Kroll, G. Miehe,
P. A. van Aken, A. Zerr, P. Hoppe,
O. Shebanova, I. McLaren, S. Lauterbach,
E. Kroke, R. Boehler ______ **1476 – 1480**

High-Pressure Synthesis of Crystalline Carbon Nitride Imide, $C_2N_2(NH)$

Extreme chemistry: The carbon nitride imide $C_2N_2(NH)$ is synthesized from the single-source precursor 1-cyanoguanidine under high-pressure and high-temperature conditions in a laser-heated diamond-anvil cell. Characterization of single crystals recovered at ambient conditions reveals that the new compound adopts a defect wurtzite structure (see picture).

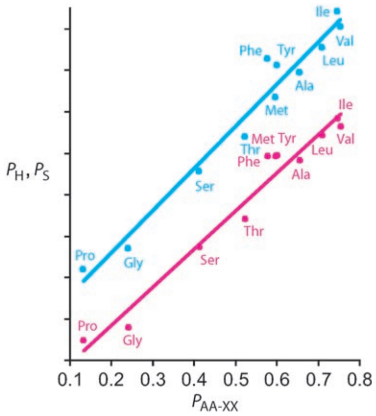


Peptide Fragmentation

M. M. Savitski, F. Kjeldsen, M. L. Nielsen,
S. O. Garbuzynskiy, O. V. Galzitskaya,
A. K. Surin, R. A. Zubarev* _ **1481 – 1484**

Backbone Carbonyl Group Basicities Are Related to Gas-Phase Fragmentation of Peptides and Protein Folding

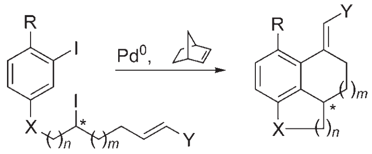
A strong correlation is found between the propensity of individual amino acids to induce peptide-bond cleavage in the gas phase (P_{AA-XX}) and their structure-forming propensity (P_S, red) and H-bond-accepting propensity (P_H, blue). Thus, the same fundamental parameter, carbonyl group basicity, governs the formation of secondary protein structures in solution and directs fragmentation in the gas phase.



C–H Functionalization

A. Rudolph, N. Rackelmann,
M. Lautens* ——— **1485 – 1488**

Stereochemical and Mechanistic Investigations of a Palladium-Catalyzed Annulation of Secondary Alkyl Iodides



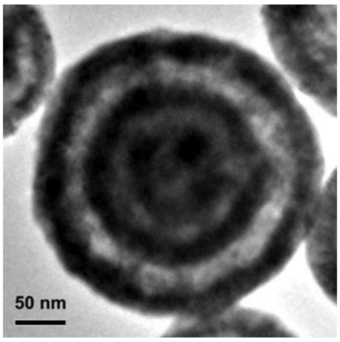
Inversion versus retention: A palladium-catalyzed annulation with enantioenriched secondary alkyl iodides gives mechanistic insight into the stereochemistry of this C–H bond functionalization reaction (see scheme) involving a proposed Pd^{II}/Pd^{IV} catalytic cycle.

Hollow Structures

H. Xu, W. Wang* ——— **1489 – 1492**

Template Synthesis of Multishelled Cu_2O Hollow Spheres with a Single-Crystalline Shell Wall

Shells within shells: Simply varying the concentration of the cetyltrimethylammonium bromide surfactant in a template process leads to single-, double-, triple-, and quadruple-shelled Cu_2O hollow spheres (see TEM image). Thus, the vesicle-directed synthesis of inorganic multishelled hollow spheres is feasible.

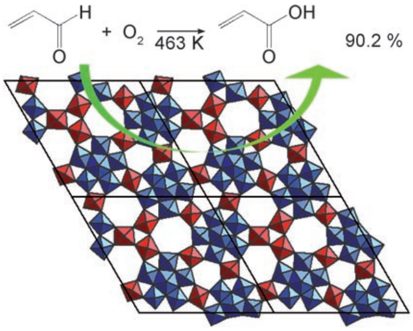


Polyoxometalates

M. Sadakane,* N. Watanabe, T. Katou,
Y. Nodasaka, W. Ueda* ——— **1493 – 1496**

Crystalline Mo_3VO_x Mixed-Metal-Oxide Catalyst with Trigonal Symmetry

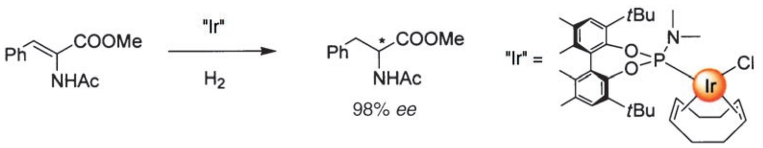
Outstanding catalytic activity for the selective oxidation of acrolein (see picture) is observed with a crystalline metal oxide, Mo_3VO_x ($x \leq 11.1$). The catalyst is synthesized from a solution containing pentagonal units of $\{Mo(Mo_5O_{27})\}$ (blue), which further react with molybdenum and vanadium species (red) to form a 3D metal oxide.



Asymmetric Hydrogenation

F. Giacomina, A. Meetsma, L. Panella,
L. Lefort,* A. H. M. de Vries,
J. G. de Vries* ——— **1497 – 1500**

High Enantioselectivity Is Induced by a Single Monodentate Phosphoramidite Ligand in Iridium-Catalyzed Asymmetric Hydrogenation



The Full Monty? Stripping a catalyst down to its bare essentials gives a neutral iridium complex containing only one monodentate phosphoramidite ligand that is an efficient catalyst for the enantioselective hydrogenation of α-dehydroamino acids (see picture).

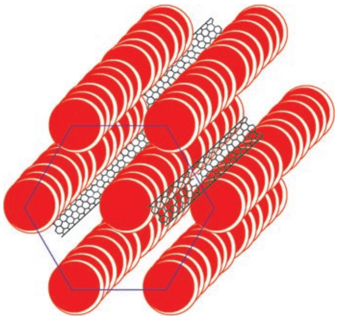
Contents

Carbon Nanotubes

S. Kumar,* H. K. Bisoyi ____ **1501 – 1503**

Aligned Carbon Nanotubes in the Supramolecular Order of Discotic Liquid Crystals

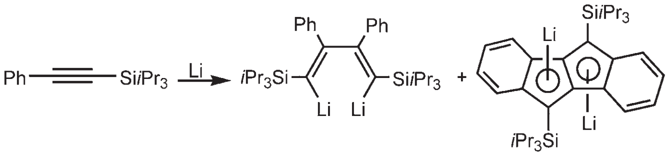
Between the lines: Functionalized single-walled carbon nanotubes (SWNTs) can be aligned in the hexagonal columnar mesophase of discotic liquid crystals (DLCs). The thermophysical properties of SWNT–DLC composites indicate inclusion of SWNTs in the supramolecular order of DLCs (see picture).



Lithiated Compounds

M. Saito,* M. Nakamura, T. Tajima, M. Yoshioka ____ **1504 – 1507**

Reduction of Phenyl Silyl Acetylenes with Lithium: Unexpected Formation of a Dilithium Dibenzopentalenide

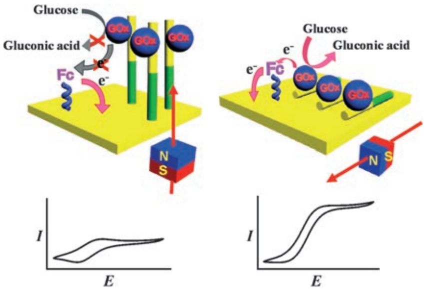


The degree of bulkiness of the silyl substituent strongly affects the reduction mode of phenyl silyl acetylenes. For example, the treatment of phenyl(triisopropylsilyl)acetylene with lithium led to the unprecedented formation of a dilithium dibenzopentalenide together with the expected 1,4-dilithio-1,3-butadiene (see scheme), whereas the reduction of phenyl(*tert*-butyldimethylsilyl)acetylene gave only the corresponding 1,4-dilithio-1,3-butadiene.

Bioelectrocatalysis

Ó. A. Loaiza, R. Laocharoensuk, J. Burdick, M. C. Rodríguez, J. M. Pingarron, M. Pedrero, J. Wang* ____ **1508 – 1511**

Adaptive Orientation of Multifunctional Nanowires for Magnetic Control of Bioelectrocatalytic Processes

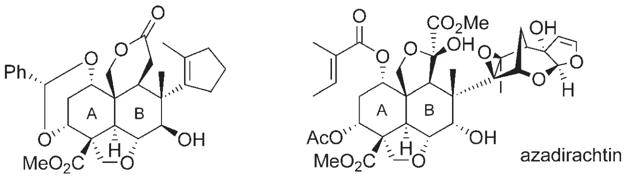


Charging ahead: Adaptive functional nanowires can be used for magneto-switchable bioelectrocatalysis. This control is accomplished by changing the surface orientation of two-segment gold/nickel nanowires, which are functionalized with glucose oxidase (GOx), in connection to a surface-bound ferrocene (Fc) electron-transfer mediator (see picture).

Natural Products

H. Watanabe,* N. Mori, D. Itoh, T. Kitahara, K. Mori ____ **1512 – 1516**

Synthetic Study Towards Azadirachtin: An Efficient and Stereoselective Construction of the AB Rings with Full Functionality

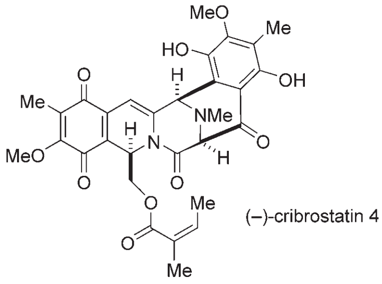


From A to B: The decalin moiety of azadirachtin, which includes the fully functionalized AB ring system (see picture), was synthesized stereoselectively in only 23 steps. Key steps include an intramolecular Diels–Alder reaction, a decarboxylation, a Claisen rearrangement, and finally a tandem radical cyclization.

Tetrahydroisoquinoline Alkaloids

G. Vincent, R. M. Williams* **1517 – 1520**

Asymmetric Total Synthesis of (−)-Cribrostatin 4 (Renieramycin H)



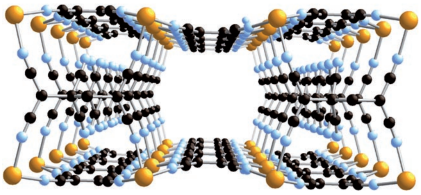
(−)-cribrostatin 4

Out of the blue: The convergent asymmetric total synthesis of the antitumor antibiotic (−)-cribrostatin 4 from the blue sponge *Cribrochalina* features asymmetric Staudinger and Pictet–Spengler reactions to form the tetrahydroisoquinoline moiety. These reactions were followed by a reductive opening/elimination of a tricyclic β-lactam and a Pictet–Spengler cyclization to access the unsaturated pentacyclic core.

Magnetic Materials

J.-H. Her, P. W. Stephens,*
K. I. Pokhodnya, M. Bonner,
J. S. Miller* **1521 – 1524**

Cross-Linked Layered Structure of Magnetically Ordered $[Fe(TCNE)_2]\cdot zCH_2Cl_2$ Determined by Rietveld Refinement of Synchrotron Powder Diffraction Data



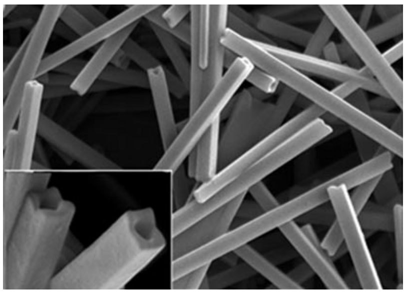
The wages of spin: Insight into the elusive structure of $[V(TCNE)_x]$-based magnets is provided by the structural analysis of the title compound ($T_c \approx 100$ K; TCNE = tetracyanoethylene; $z \approx 0.3$), in which $\{Fe^{II}\text{-}(\mu_4\text{-}[TCNE])^{\bullet -}\}$ layers are bridged by diamagnetic TCNE dimers $\mu_4\text{-}[C_4(CN)_8]^{2-}$ (see picture; Fe gold; C black; N blue). Strong intralayer spin coupling between the Fe^{II} centers leads to the observed magnetic ordering.

Organic Microstructures

X. Zhang, X. Zhang,* W. Shi, X. Meng,
C. Lee, S. Lee* **1525 – 1528**

Single-Crystal Organic Microtubes with a Rectangular Cross Section

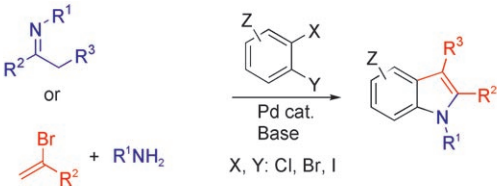
A simple solution process without the assistance of surfactant, catalyst, or template under ambient conditions in air has been used to prepare single-crystal hollow microtubes with a rectangular cross section from [2-(*p*-dimethylaminophenyl)-ethenyl]phenylmethylenepropanedinitrile (DAPMP). The DAPMP microtubes (see picture for SEM images) show remarkably strong frequency-doubling nonlinear optical properties.



Multicomponent Catalysis

J. Barluenga,* A. Jiménez-Aquino,
C. Valdés, F. Aznar **1529 – 1532**

The Azaallylic Anion as a Synthon for Pd-Catalyzed Synthesis of Heterocycles: Domino Two- and Three-Component Synthesis of Indoles

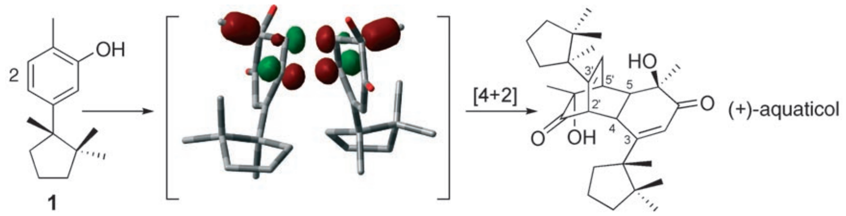


Piecing it all together with palladium: Two- and three-component cascade processes that are promoted by a multifunctional Pd catalyst lead to indoles in a highly efficient manner (see scheme). The key step is the Pd-catalyzed α-arylation of imines with *o*-dihalobenzene derivatives.

Diels–Alder Cycloaddition

J. Gagnepain, F. Castet,
S. Quideau* ______ 1533 – 1535

Total Synthesis of (+)-Aquaticol by Biomimetic Phenol Dearomatization: Double Diastereofacial Differentiation in the Diels–Alder Dimerization of Orthoquinols with a C_2-Symmetric Transition State

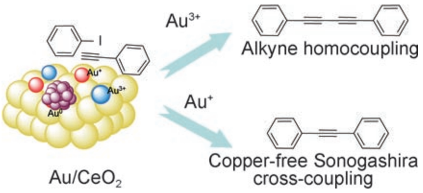


Double or nothing: The bissesquiterpene (+)-aquaticol was synthesized by biomimetic oxidative dearomatization of **1** via an orthoquinol intermediate that undergoes spontaneous and selective dimerization; only like diastereomers react. The remarkable double diastereofacial differentiation observed is explained in terms of a double hyperconjugative "Cieplak–Fallis" effect expressed in a C_2-symmetric bispericyclic transition state.

Gold Catalysis

C. González-Arellano, A. Abad, A. Corma,*
H. García, M. Iglesias,
F. Sánchez ______ 1536 – 1538

Catalysis by Gold(I) and Gold(III): A Parallelism between Homo- and Heterogeneous Catalysts for Copper-Free Sonogashira Cross-Coupling Reactions



Zero, one, or three? The role of Au^0, Au^I, and Au^{III} cations in the heterogeneous gold catalyst Au/CeO_2 was investigated with the copper-free Sonogashira cross-coupling reaction of iodobenzene and phenyl acetylene (see picture). Reactions carried out under both heterogeneous and homogeneous conditions using distinct Au^0, Au^I, and Au^{III} species reveal that Au^I is the active species for the cross-coupling reaction.

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).

The issues for February 2007 appeared online on the following dates
Issue 5: January 12. · Issue 6: January 22. · Issue 7: January 29. · Issue 8: February 5

Service