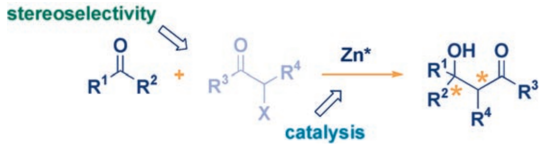
The following Communications have been judged by at least two referees to be "very important papers" and will be published online at www.angewandte.org soon:

News

Books

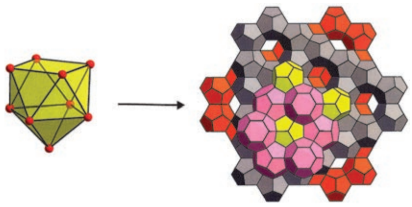
Highlights

Classical Reactions



Classics reformed: The condensation reaction between aldehydes and ketones and α-halocarbonyl compounds, known as the Reformatsky reaction, has undergone enormous development in recent times, including stereoselective and catalytic variants (see scheme, X = halide), The reliable, practical reaction makes it ideal for synthetic preparations on an industrial scale.

Germanium



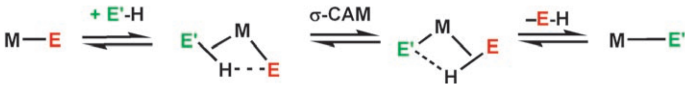
Homoatomic Zintl ions (for example, $[Ge_9]^{4-}$; see picture, left) have long been discussed as precursors for the formation of more complicated structures. The characterization of "$\square_{24}Ge_{136}$" with the (unfilled) clathrate-II structure (right; orange, gray, yellow: pentagonal dodecahedra, pink: hexakaidecahedra) and other porous germanium-based materials supports this hypothesis.

Reviews

Reaction Mechanisms

R. N. Perutz,*
S. Sabo-Etienne* ________ **2578 – 2592**

The σ-CAM Mechanism: σ Complexes as the Basis of σ-Bond Metathesis at Late-Transition-Metal Centers



Dynamic processes provide the clue that it is possible to interconvert σ ligands in complexes of the form [ME′(η^2-E-H)] (E, E′ = H, B, Si, C) without a change in oxidation state (see scheme). This σ-complex-assisted metathesis (σ-CAM) is distinct from the familiar σ-bond metathesis and from oxidative addition/reductive elimination mechanisms. σ-CAM mechanisms are significant in catalytic and stoichiometric reactions.

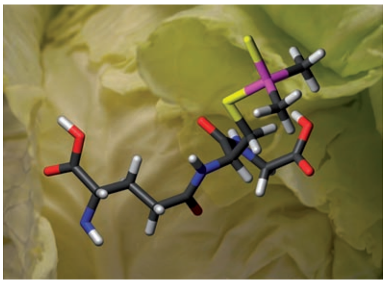
Communications

Bioinorganic Chemistry

A. Raab, S. H. Wright, M. Jaspars,
A. A. Meharg, J. Feldmann* **2594 – 2597**

Pentavalent Arsenic Can Bind to Biomolecules

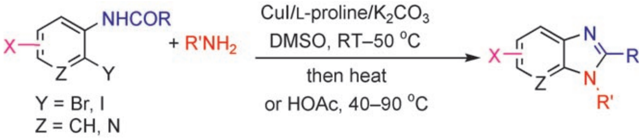
As biomolecules go: By identifying the dimethylarsinothioyl glutathione complex in arsenic-exposed cabbage, it was shown that pentavalent arsenic can bind to biomolecules when it is activated by sulfide (see picture; As^V purple, S yellow, O red, N blue). The result highlights that sulfide reactions may play a role in the reactivity of arsenic intermediates and the metabolic pathway of arsenic in organisms.



Nitrogen Heterocycles

B. Zou, Q. Yuan, D. Ma* ___ **2598 – 2601**

Synthesis of 1,2-Disubstituted Benzimidazoles by a Cu-Catalyzed Cascade Aryl Amination/Condensation Process



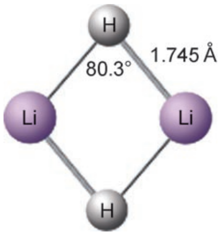
Helpful neighbors: A wide range of 1,2-disubstituted benzimidazoles can be assembled from 2-haloanilides and primary amines by using a copper-catalyzed amination reaction promoted by an *ortho*-substituent effect of an NHCOR group (see scheme, DMSO = dimethyl sulfoxide). The strategy also permits a broad array of substituents X at different positions of the benzimidazole phenyl ring.

Hydrogen Activation

X. Wang, L. Andrews* _____ **2602 – 2606**

The Activation of Hydrogen by Li Atoms To Form [$(LiH)_2$]

Dimers are a girl's best friend: The rhombic dimer [$(LiH)_2$] (see calculated structure) is the major product of the reaction of laser-ablated lithium atoms in solid H_2 upon annealing or irradiation with visible light. Irradiation also produces the higher clusters [$(LiH)_n$] ($n = 3,4$). Like the more stable lithium halide dimers, the rhombic dimer [$(LiH)_2$] is highly ionic.



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Multi Component Reaction

J. Barluenga,* L. Álvarez-Rodrigo,
F. Rodríguez, F. J. Fañanás, T. L. Sordo,
P. Campomanes ——— **2607–2609**

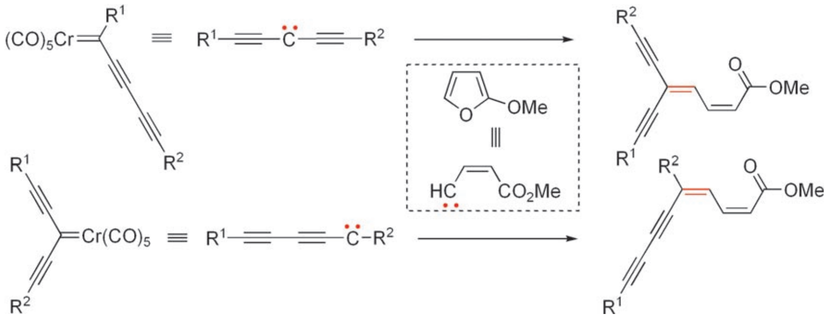
Synthesis of Cyclohexanol Derivatives by Zirconocene-Mediated Ring-Contraction Reactions of Seven-Membered Cyclic Enol Ethers

Shrinking the circle: Complex cyclohexanol derivatives with up to four new stereogenic centers are easily obtained by simple one-pot, three-component, zirconium-mediated coupling of an alkyllithium or Grignard reagent, a seven-membered cyclic enol ether, and an electrophile (E, see scheme).

Extended Enyne Structures

J. Barluenga,* P. García-García, D. de Sáa,
M. A. Fernández-Rodríguez,
R. Bernardo de la Rúa, A. Ballesteros,
E. Aguilar, M. Tomás ——— **2610–2612**

Chromium(0) Alkynylcarbene Complexes as C_β-Electrophilic Carbene Equivalents: Regioselective Access to Dienynes and Dienediynes

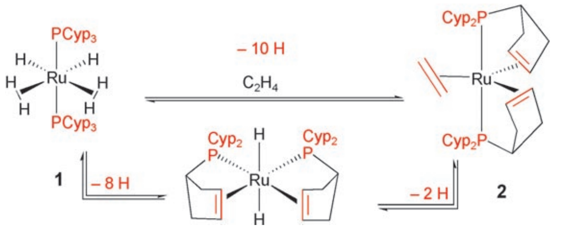


Just one step is all that is needed for a direct, selective, and easy synthesis of different conjugated enyne frameworks from simple chromium alkynylcarbene complexes and commercially available 2-methoxyfuran (see scheme).

Hydrogen Release

M. Grellier,* L. Vendier,
S. Sabo-Etienne* ——— **2613–2615**

Ruthenium Complexes Carrying Hydride, Dihydrogen, and Phosphine Ligands: Reversible Hydrogen Release

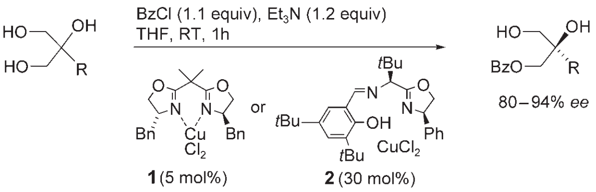


If it's meant to be, set it free: The bis(dihydrogen) complex **1**, which is stabilized by two tricyclopentylphosphine ligands (PCyp₃), can release up to ten hydrogen atoms, ultimately forming the new zerovalent ruthenium complex **2**. This facile hydrogen release is totally reversible. The first step of the dehydrogenation process leads to various dihydride isomers of formula $[RuH_2\{(PCyp_2(\eta^2\text{-}C_5H_7)\}_2]$.

Asymmetric Catalysis

B. Jung, M. S. Hong,
S. H. Kang* ——— **2616–2618**

Enantioselective Synthesis of Tertiary Alcohols by the Desymmetrizing Benzoylation of 2-Substituted Glycerols



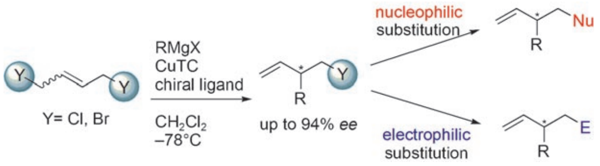
Complementary catalysts have been found for the enantioselective desymmetrization of 2-substituted glycerols by monobenzoylation with benzoyl chloride and Et_3N to give chiral tertiary alcohols with 80 to 94% *ee* (see Scheme; Bn = benzyl, Bz = benzoyl). The dibenzylbisoxazoline–$CuCl_2$ complex **1** is remarkably effective for substrates with an alkyl substituent in the 2-position, the iminooxazoline–$CuCl_2$ complex **2** for those with vinyl, phenyl, and benzyl substituents.

Contents

Asymmetric Catalysis

C. A. Falciola, A. Alexakis* — **2619 – 2622**

1,4-Dichloro- and 1,4-Dibromo-2-butenes as Substrates for Cu-Catalyzed Asymmetric Allylic Substitution

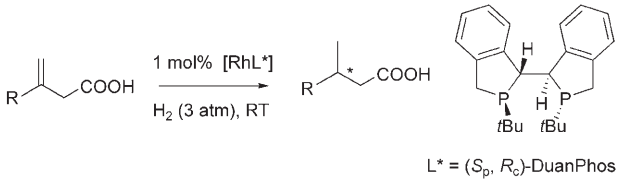


Cu at the AAA meeting: Difunctionalized allylic substrates can undergo Cu-catalyzed asymmetric allylic alkylation (AAA) reactions with high enantioselectivities. The products have a functional group that remains for further transformation through substitution with a nucleophile (Nu) or electrophile (E) with conservation of optical purity (see scheme; TC = thiophene carboxylate).

Asymmetric Hydrogenation

X. Sun, L. Zhou, C.-J. Wang, X. Zhang* —————— **2623 – 2626**

Rh-Catalyzed Highly Enantioselective Synthesis of 3-Arylbutanoic Acids

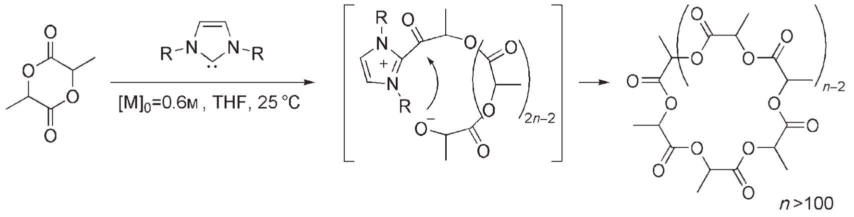


It's in the mix: The reaction conditions—catalyst, additive, and solvent—have been optimized for the asymmetric hydrogenation of 3-aryl-3-butenoic acids. The rigid, chiral bisphospholane ligand (S_p,R_c)-DuanPhos is crucial to achieving high enantioselectivity.

Cyclic Polymers

D. A. Culkin, W. Jeong, S. Csihony, E. D. Gomez, N. P. Balsara, J. L. Hedrick, R. M. Waymouth* ———— **2627 – 2630**

Zwitterionic Polymerization of Lactide to Cyclic Poly(Lactide) by Using N-Heterocyclic Carbene Organocatalysts

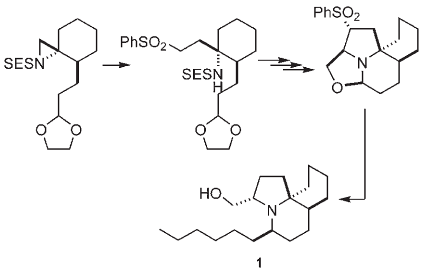


Closing the loop: The zwitterionic ring-opening polymerization of lactide in the presence of N-heterocyclic carbenes generates well-defined cyclic poly(lactide) (see scheme). The polymerization is rapid and produces macrocyclic polymers with high purity and exceptional control of molecular weight and polydispersity.

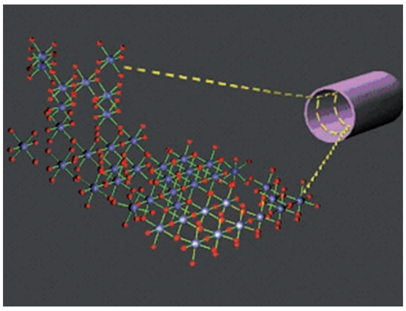
Natural Products Synthesis

J. J. Caldwell, D. Craig* ——— **2631 – 2634**

Sulfone-Mediated Total Synthesis of (±)-Lepadiformine



Key steps in the total synthesis of the marine alkaloid (±)-lepadiformine (**1**) include regioselective opening of a spirocyclic aziridine ring with a sulfone-stabilized carbanion, cyclocondensation of the N,C dianion of the resulting γ-sulfonamidosulfone with an aldehyde, and highly stereoselective alkynylation by nucleophilic substitution of an aminal. SES = 2-(trimethylsilyl)ethylsulfonyl.



Order locally: ^{17}O magic-angle-spinning NMR spectroscopy of bulk sol–gel-prepared Nb_2O_5 and mesoporous, template-free Nb_2O_5 (see picture) shows very high local order in the mesoporous sample. The oxygen atoms are coordinated only as ONb_2 in contrast with bulk phases in which the oxygen atoms are always present in a mixture of ONb_2 and ONb_3 coordination environments.

Mesoporous Materials

B. O. Skadtchenko, Y. Rao, T. F. Kemp,
P. Bhattacharya, P. A. Thomas,
M. Trudeau, M. E. Smith,*
D. M. Antonelli* **2635 – 2638**

A Solid-State ^{17}O NMR Study of Local Order and Crystallinity in Amine-Templated Mesoporous Nb Oxide

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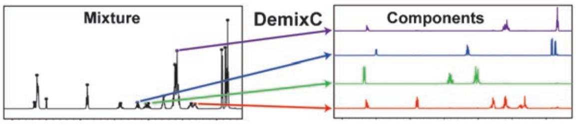

Reliable analysis of complex mixtures has been achieved with a new analytical method, dubbed DemixC, for the deconvolution of the NMR spectrum of a mixture into individual components (see scheme). The method, which is based on covariance total correlation spectroscopy (TOCSY) spectra, identifies traces with minimal spectral overlap with other spin systems that can be scanned against an NMR database.

NMR Spectroscopy

F. Zhang, R. Brüschweiler* **2639 – 2642**

Robust Deconvolution of Complex Mixtures by Covariance TOCSY Spectroscopy

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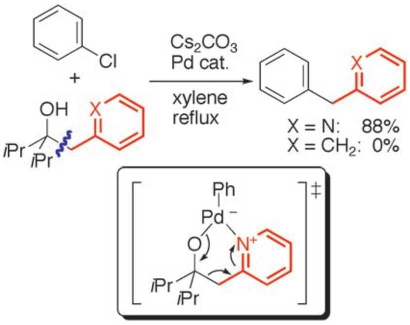


Making a break for it: Treatment of 2-(2-pyridyl)ethanol derivatives with aryl chlorides in the presence of a palladium catalyst results in the transfer of the pyridylmethyl moiety of the alcohol to yield the corresponding (2-pyridylmethyl)arene. The reaction proceeds by chelation-assisted cleavage of an C_{sp^3}–C_{sp^3} bond (see scheme) followed by formation of a carbon–carbon bond.

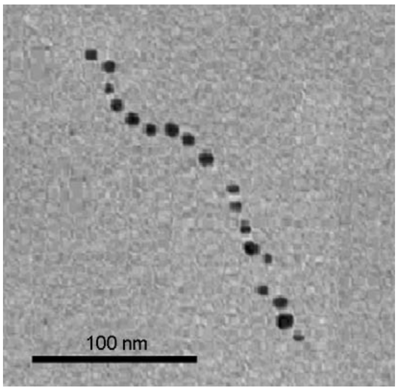
Homogeneous Catalysis

T. Niwa, H. Yorimitsu,*
K. Oshima* **2643 – 2645**

Palladium-Catalyzed 2-Pyridylmethyl Transfer from 2-(2-Pyridyl)ethanol Derivatives to Organic Halides by Chelation-Assisted Cleavage of Unstrained C_{sp^3}–C_{sp^3} Bonds

---

All wired up: Robust 1D scaffolds have been designed based on the i tetraplex by a strategy of inducing bidirectional growth on “slipped” tetraplexes. The growth propagates through non-Watson–Crick base-pairing and leads to nanowires more than 3 μm long. These nanowires have been characterized by microscopy (AFM and TEM, see picture), surface-enhanced Raman spectroscopy, and circular dichroism spectroscopy.



Nanowires

H. B. Ghodke, R. Krishnan, K. Vignesh,
G. V. P. Kumar, C. Narayana,
Y. Krishnan* **2646 – 2649**

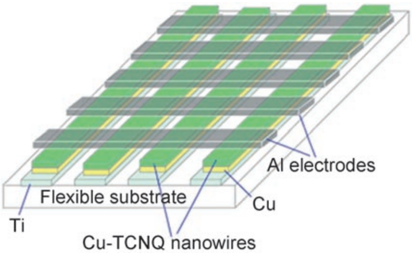
The I-Tetraplex Building Block: Rational Design and Controlled Fabrication of Robust 1D DNA Scaffolds through Non-Watson–Crick Interactions

Molecular Devices

K. Xiao,* J. Tao, Z. Pan, A. A. Puretzky,
I. N. Ivanov, S. J. Pennycook,
D. B. Geohegan* ________ 2650 – 2654

Single-Crystal Organic Nanowires of Copper–Tetracyanoquinodimethane: Synthesis, Patterning, Characterization, and Device Applications

Current events: Nanowires of the organic semiconductor copper–tetracyanoquinodimethane (Cu–TCNQ) have been synthesized in a controlled manner and patterned on a variety of substrates by chemical vapor deposition. A cross-point memory device based on a network of Cu–TCNQ nanowires (see picture) has been constructed that repeatedly switches electrically between two states with a conductivity difference of more than two orders of magnitude.

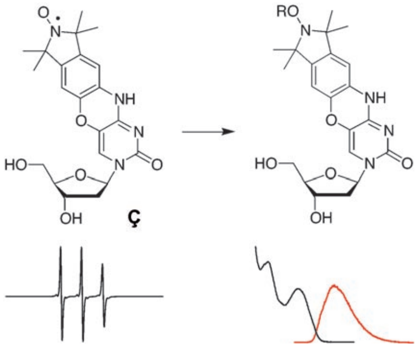


Spectroscopic Probes

N. Barhate, P. Cekan, A. P. Massey,
S. Th. Sigurdsson* ________ 2655 – 2658

A Nucleoside That Contains a Rigid Nitroxide Spin Label: A Fluorophore in Disguise

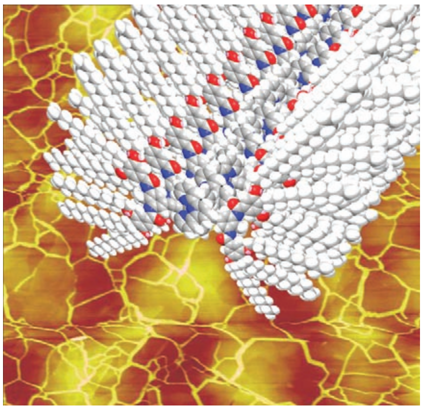
Take a spin: The nucleoside **Ç** (C-spin), which contains a rigid nitroxide spin label, allows the structure and dynamics of nucleic acids into which it is incorporated to be studied by EPR spectroscopy (left spectrum). Reduction of the nitroxide with a mild reducing agent renders the nucleoside fluorescent (right spectrum). Thus, the same nucleic acid can be studied with two complementary spectroscopic techniques.



Self-Assembly Processes

F. Camerel, R. Ziessel,* B. Donnio,
C. Bourgogne, D. Guillon, M. Schmutz,
C. Iacovita, J.-P. Bucher ____ 2659 – 2662

Formation of Gels and Liquid Crystals Induced by Pt···Pt and π–π* Interactions in Luminescent σ-Alkynyl Platinum(II) Terpyridine Complexes

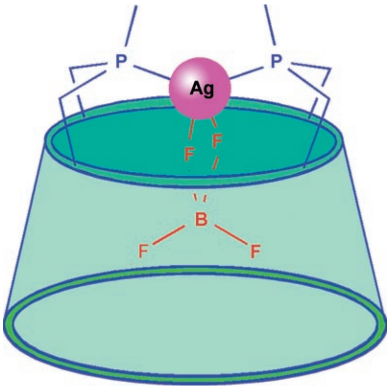


Well organized! A new class of phosphorescent materials was obtained by the coupling of trialkylgallate-functionalized alkynes to a planar Pt^{II} terpyridine unit. Pt···Pt interactions in these complexes lead to the formation of highly colored organogels and columnar liquid crystals (see picture). Amide groups linking the gallate and alkyne units provide additional stabilization of the structures through hydrogen bonding.

Anion Inclusion

L. Poorters, D. Armspach,* D. Matt,*
L. Toupet, P. G. Jones _____ 2663 – 2665

A Metallocavitand Functioning as a Container for Anions: Formation of Noncovalent Linear Assemblies Mediated by a Cyclodextrin-Entrapped NO$_3^-$ Ion

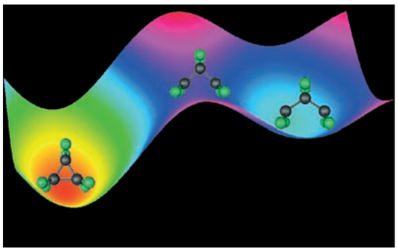


Containing the negativity: A cyclodextrin-based complex substituted with two phosphine groups is able to fully embrace medium sized anions such as BF$_4^-$ (see picture), NO$_3^-$, AcO$^-$, or X$^-$ (X = Cl, Br, I). Besides conventional electrostatic cation···anion interactions, complex formation has been shown to involve weak interactions with the lipophilic host environment.

Theoretical Chemistry

H. Wei, D. A. Hrovat, W. R. Dolbier, Jr., B. E. Smart, W. T. Borden* — **2666 – 2668**

The “Bond-Stretched Invertomer” of Hexafluorocyclopropane—a New Type of Reactive Intermediate

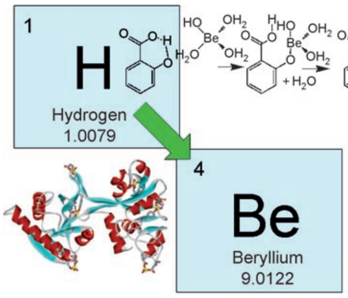


It all adds up: Calculations show the “bond-stretched invertomer” of hexafluorocyclopropane to be an energy minimum with a barrier to ring closure of 9.8 kcal mol^{-1} (see potential-energy surface). The bond-stretched invertomer is a likely intermediate in the reactions of hexafluorocyclopropane with halogens to form 1,3-dihalo-1,1,2,2,3,3-hexafluoropropanes.

Bioinorganic Chemistry

T. M. McCleskey,* D. S. Ehler, T. S. Keizer, D. N. Asthagiri, L. R. Pratt, R. Michalczyk, B. L. Scott* — **2669 – 2671**

Beryllium Displacement of H$^+$ from Strong Hydrogen Bonds

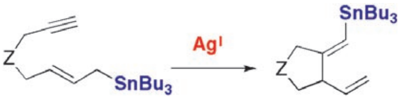


It’s bound to Be: The binding of beryllium to the iron transport protein transferrin proceeds by displacement of H$^+$ from strong hydrogen bonds in the protein (see picture). This new view of beryllium binding, in which beryllium as a “tetrahedral proton” is thermodynamically preferred, provides insight into the transport mechanism of beryllium in chronic beryllium disease.

Cyclization

S. Porcel, A. M. Echavarren* — **2672 – 2676**

Intramolecular Carbostannylation of Alkynes Catalyzed by Silver(I) Species

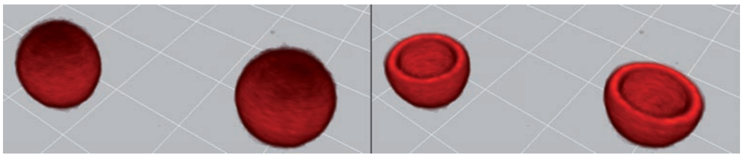


Joined at the hip: The intramolecular carbostannylation of alkynes catalyzed by silver(I) stereoselectively gives *E*-alkenylstannanes as single isomers (see scheme, Z = C(CO$_2$Me)$_2$, C(SO$_2$Ph)$_2$, C(CH$_2$OR)$_2$). The mechanism of the reaction appears to be similar to that of the reaction of enynes with other electrophilic transition-metal complexes.

Colloids

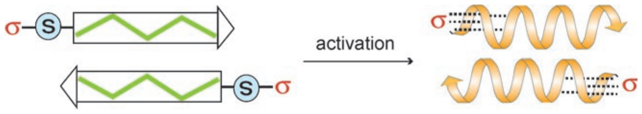
A. P. R. Johnston, F. Caruso* — **2677 – 2680**

Exploiting the Directionality of DNA: Controlled Shrinkage of Engineered Oligonucleotide Capsules



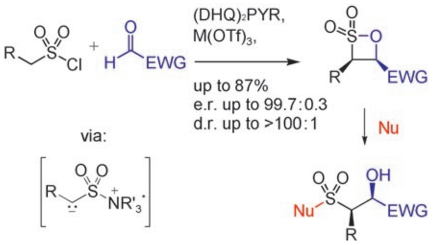
Shrinking capsules: Using the directionality of DNA hybridization, DNA capsules with controllable shrinkage properties are formed (see picture). The degree of shrinkage ranges from 35–90 % of the original particle volume, depending on the oligonucleotide sequences used to assemble the capsules. These capsules could find use in drug delivery and diagnostic applications.

Peptide Structures



Most problems are soluble: Reversal of amyloid formation through a controlled induced transformation from β-sheet to soluble α-helix structures through the use of a switch element S (see scheme, σ is a helix-inducing template) could have an important consequences understanding the mechanisms of amyloid formation and clearance.

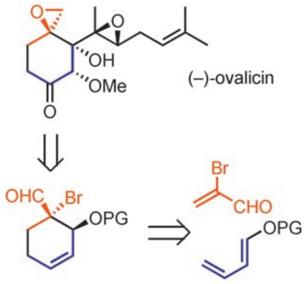
β-Sultones



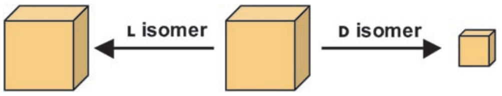
Sultones swing! Sulfenes, the highly reactive sulfonyl equivalents of ketenes, were used for the first time as substrates in asymmetric catalysis. A [2+2] cyclocyclocondensation reaction catalyzed by a tertiary amine enabled the asymmetric synthesis of β-sultones, which are convenient precursors of β-hydroxysulfonyl derivatives (EWG: electron-withdrawing group; Tf: triflate, (DHQ)$_2$PYR: dihydroquinine-2,5-diphenyl-4,6-pyrimidinediyl diether, Nu: nucleophile).

Natural Product Synthesis

A round at the Oval: The antiangiogenic activity of the natural product ovalicin has sparked significant interest. A highly efficient enantio- and diastereoselective total synthesis of ovalicin proved successful in which the key step involved an *endo* selective Diels–Alder reaction (see scheme, PG = protecting group).



Chemomechanics

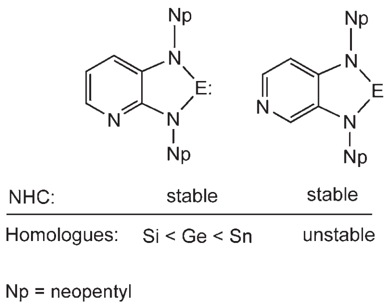


Small cause, large effect: The D and L enantiomers of diphenyltartaric acid incur different interactions with chitosan hydrogels and lead to a chemomechanical effect (see scheme), which is expressed through clear differences in the volume of the polymer particles. Increased sensitivity is possible by reducing the size of the polymer particles.

N-Heterocyclic Carbenes

F. Ullah, G. Bajor, T. Veszprémi, P. G. Jones, J. W. Heinicke* **2697 – 2700**

Stabilization of Unsymmetrically Annelated Imidazol-2-ylidenes with Respect to Their Higher Group 14 Homologues by n-/π-HOMO Inversion



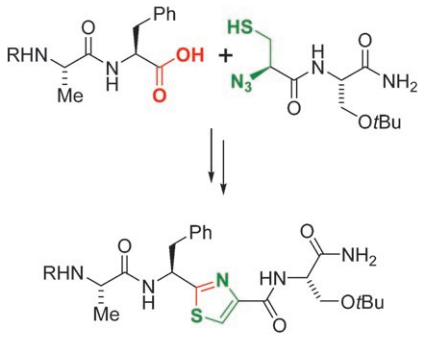
From annelation to an elation: The surprising stability of pyridoannelated imidazol-2-ylidenes (see scheme) in comparison with the heavier Group 14 homologues suggests broad tuning potential and control of the reactivity by the lone pair of electrons at the carbon atom. The asymmetric distribution of π-electron density, which destabilizes the heavier homologues, does not markedly diminish the kinetic stability of the N-heterocyclic carbenes (NHCs).

Heterocycles in Biomolecules

M. Riedrich, S. Harkal, H.-D. Arndt* **2701 – 2703**

Peptide-Embedded Heterocycles by Mild Single and Multiple Aza-Wittig Ring Closures

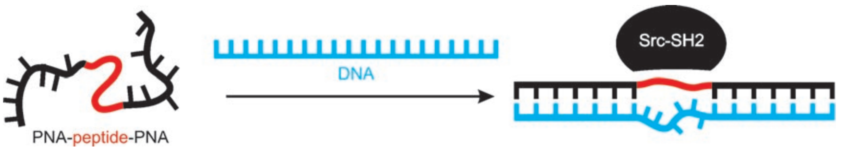
Ring a ring o'azoles: The aza-Wittig cyclization of amino acids and peptides is extremely mild, selective, and versatile. The reaction of amino acid esters and amino acid thioester azides delivers peptidic 1,3-azolines and 1,3-azoles with unsurpassed functional-group tolerance. This method allows multiple ring closures and tolerates aqueous solvents.



Control of Peptide Activity

L. Röglin, M. R. Ahmadian, O. Seitz* **2704 – 2707**

DNA-Controlled Reversible Switching of Peptide Conformation and Bioactivity



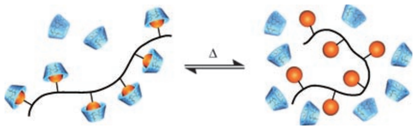
A DNA switch: Hybridization with DNA controls the conformation of a peptide nucleic acid (PNA)–peptide conjugate. This reversible process can activate (see scheme) or deactivate the binding propensity of the peptide for a protein target involved in cellular signal transduction.

Host–Guest Systems

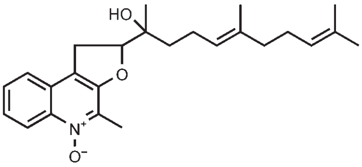
O. Kretschmann, C. Steffens, H. Ritter* **2708 – 2711**

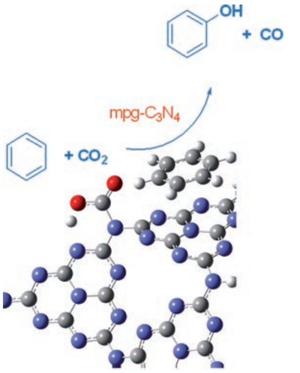
Cyclodextrin Complexes of Polymers Bearing Adamantyl Groups: Host–Guest Interactions and the Effect of Spacers on Water Solubility

Thermoresponsive polymer inclusion complexes were prepared by radical polymerization in water of acrylamides bearing adamantyl groups by the use of randomly methylated β-cyclodextrin (Me-β-CD). Aqueous solutions of the resulting polymer complexes show a temperature-dependent transparency arising from a reversible dissociation above a critical temperature. The rate of the process strongly depends on the distance between the adamantyl groups and the polymer main chain.



Contents





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

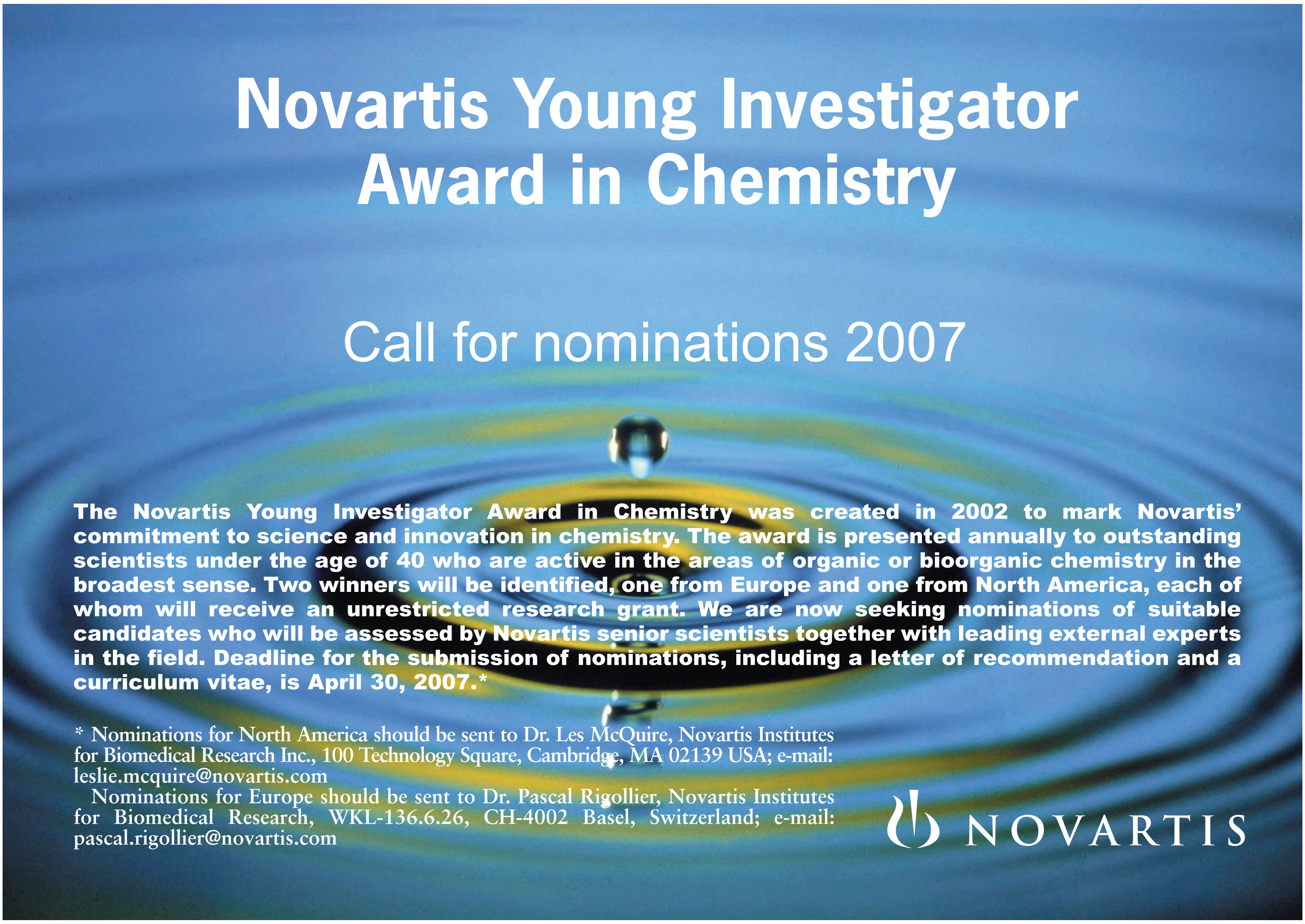
The authors of this Communication recently noted that a key word in a sentence in their publication appeared incorrectly. Thus, the penultimate sentence in the penultimate paragraph on page 2369 should read: Hence, it is safe to conclude that the number of nanocrystals (nuclei) formed in the initial nucleation stage increased significantly with *decreasing* initial oleic acid concentration.

Formation of High-Quality CdS and Other II–VI Semiconductor Nanocrystals in Noncoordinating Solvents: Tunable Reactivity of Monomers

W. W. Yu, X. Peng* ________ **2368–2371**

Angew. Chem. Int. Ed. **2002**, *41*

DOI 10.1002/1521-3773-(20020703)41:13<2368::AID-ANIE2368>3.0.CO;2-G



Novartis Young Investigator Award in Chemistry

Call for nominations 2007

The Novartis Young Investigator Award in Chemistry was created in 2002 to mark Novartis' commitment to science and innovation in chemistry. The award is presented annually to outstanding scientists under the age of 40 who are active in the areas of organic or bioorganic chemistry in the broadest sense. Two winners will be identified, one from Europe and one from North America, each of whom will receive an unrestricted research grant. We are now seeking nominations of suitable candidates who will be assessed by Novartis senior scientists together with leading external experts in the field. Deadline for the submission of nominations, including a letter of recommendation and a curriculum vitae, is April 30, 2007.*

* Nominations for North America should be sent to Dr. Les McQuire, Novartis Institutes for Biomedical Research Inc., 100 Technology Square, Cambridge, MA 02139 USA; e-mail: leslie.mcquire@novartis.com

Nominations for Europe should be sent to Dr. Pascal Rigollier, Novartis Institutes for Biomedical Research, WKL-136.6.26, CH-4002 Basel, Switzerland; e-mail: pascal.rigollier@novartis.com

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