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:

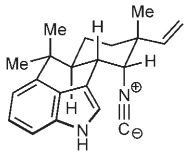
Obituary

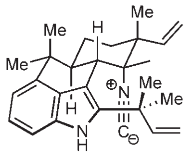
Books

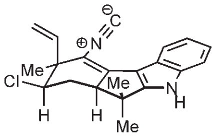
Highlights

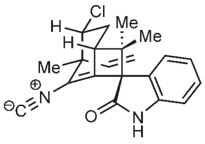
Synthetic Methods

It also works without: The marine alkaloids hapalindole U, ambiguine, fischerindole, and welwitindolinone (see structures) were synthesized without using any protecting groups. In an elegant approach the intrinsic reactivity of the sensitive isonitrile group was utilized instead to establish the molecular skeleton.


(−)-hapalindole U


(+)-ambiguine H


(−)-fischerindole I


(+)-welwitindolinone A

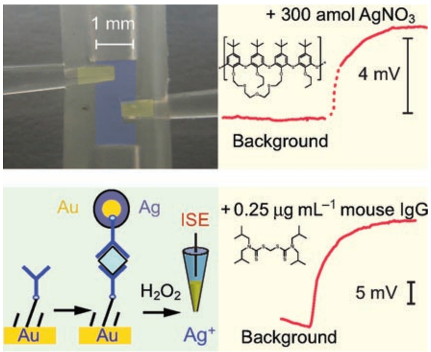
Contents

Minireviews

Sensors

E. Bakker,* E. Pretsch* ____ **5660 – 5668**

Modern Potentiometry



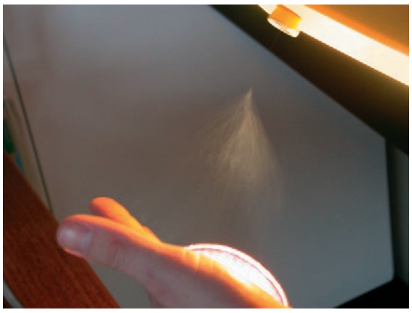
Pushing the limits: A silent revolution of ion-selective electrodes (ISEs) took place during the past decade. Polymeric membrane electrodes are now routinely used to determine complex formation constants between lipophilic guests and ionic hosts. Ultratrace level measurements have become possible even in samples of very small volumes, with detection limits in the attomole range.

Reviews

Nanotechnology

A. Greiner,* J. H. Wendorff* **5670 – 5703**

Electrospinning: A Fascinating Method for the Preparation of Ultrathin Fibers



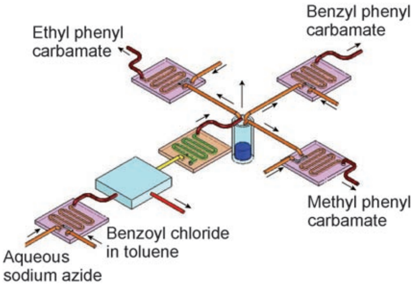
Weaving webs: Electrospinning is a highly versatile method for the preparation of polymer and metal nanofibers. Fibers with complex morphologies or specific functions for various applications (for example, filtration, textiles, sensors, optics, catalysis, drug delivery, wound dressings, tissue engineering, and plant protection) can be designed through the selection of suitable systems.

Communications

Microreactor Networks

H. R. Sahoo, J. G. Kralj,
K. F. Jensen* ________ **5704 – 5708**

Multistep Continuous-Flow Microchemical Synthesis Involving Multiple Reactions and Separations



All for one and one for all: A continuous-flow, multistep microchemical synthesis of carbamates starting from aqueous azide and organic azoyl chloride by using the Curtius rearrangement reaction is described. The procedure involves three reaction steps and two separation steps (one gas–liquid and one liquid–liquid). Formation of a microreactor network for parallel synthesis of analogous compounds is also demonstrated.

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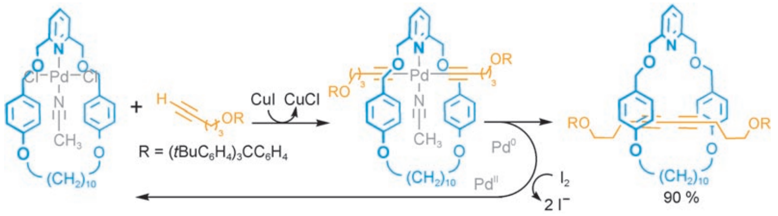
Rotaxanes

J. Berná, J. D. Crowley, S. M. Goldup,
K. D. Hänni, A.-L. Lee,
D. A. Leigh* ______ 5709 – 5713

A Catalytic Palladium Active-Metal Template Pathway to [2]Rotaxanes

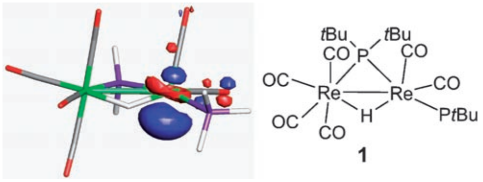


A multitasking template: [2]Rotaxanes have been synthesized with the help of a palladium active-metal template, which acts as both a template for threading and a catalyst for covalent-bond formation (see scheme). The synthesis is high yielding, operates under mild conditions, and is catalytic in palladium.

Rhenium Complexes

R. D. Adams,* B. Captain ______ 5714 – 5716

Saturated Versus Unsaturated: Ligand Addition to the Saturated Metal Site in an Unsaturated Binuclear Metal Complex

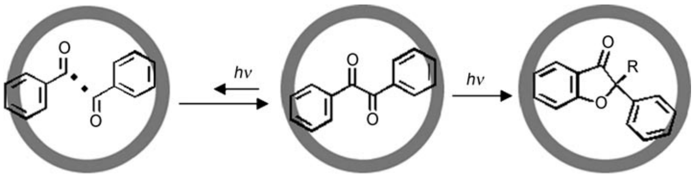


Pretty vacant: The unsymmetrical complex **1** contains one saturated 18-electron rhenium atom and one unsaturated 16-electron rhenium atom with a vacant coordination site. CO and NCMe can add to **1** to yield complexes in which both metal atoms have 18-electron configurations. Surprisingly, the added ligands are coordinated to the metal atom in **1** that originally had the 18-electron configuration.

Photoreactions

T. Furusawa, M. Kawano,
M. Fujita* ______ 5717 – 5719

The Confined Cavity of a Coordination Cage Suppresses the Photocleavage of α-Diketones To Give Cyclization Products through Kinetically Unfavorable Pathways

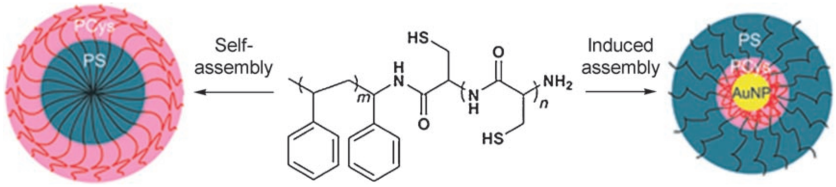


It's a trap: The photochemical homolytic cleavage of an α-diketone leading to degradation products was suppressed through the encapsulation of the diketone in a self-assembled cage. Instead, intramolecular cyclization products were formed through otherwise unfavorable (kinetically hidden) reaction pathways. This provides an approach to find new reactions of photolabile compounds that had been abandoned because of predominant cleavage reactions.

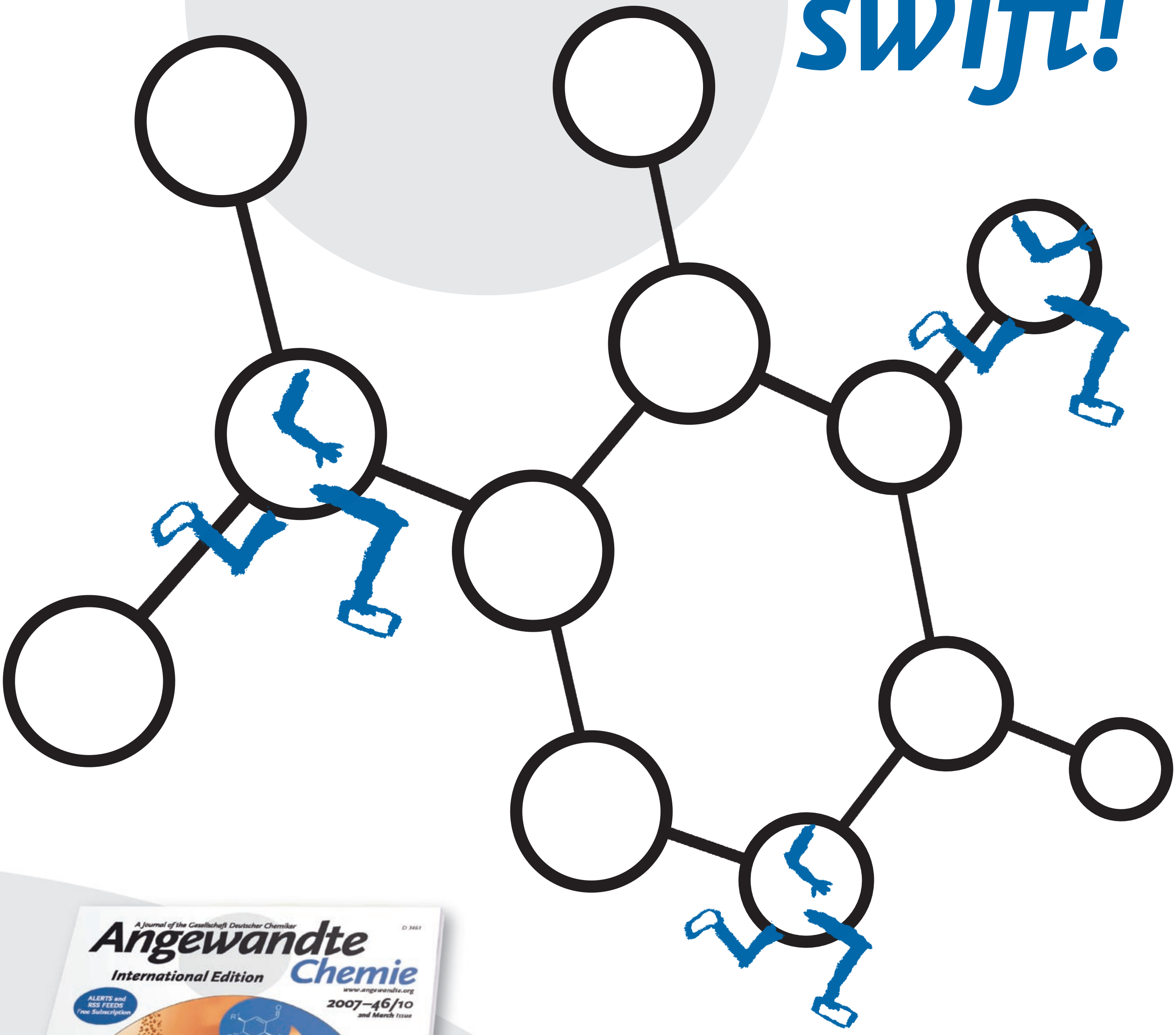
Gold Nanoparticles

S. Abraham, I. Kim,*
C. A. Batt* ______ 5720 – 5723

A Facile Preparative Method for Aggregation-Free Gold Nanoparticles Using Poly(styrene-*block*-cysteine)



In a stable condition: The self-assembly and induced assembly of a new class of block copolymers containing polystyrene (PS) and polycysteine (PCys) is investigated (see picture). The efficiency of these "molecular chimeras" to encapsulate gold nanoparticles (AuNPs), and thereby enhance their stability against aggregation, is also demonstrated.

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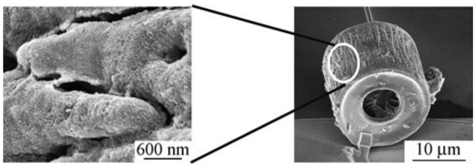
Scanning Electrochemical Microscopy
Organocatalytic Domino Reactions
Inorganic Block Copolymers
WILEY-VCH

Thin Films

M. R. Weatherspoon, M. B. Dickerson, G. Wang, Y. Cai, S. Shian, S. C. Jones, S. R. Marder,* K. H. Sandhage* ______ 5724 – 5727

Thin, Conformal, and Continuous SnO_2 Coatings on Three-Dimensional Biosilica Templates through Hydroxy-Group Amplification and Layer-By-Layer Alkoxide Deposition

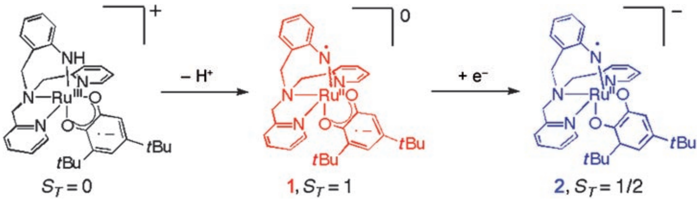


Led to the bioscaffold: A method is developed to coat intricate biosilica structures with functional oxides. Thin coatings of SnO_2 are applied to the silica valves of diatoms (see picture) through dendritic amplification of surface hydroxy groups and subsequent sol–gel processing. The SnO_2-coated valves act as sensitive detectors for NO gas.

Metal–Radical Complexes

Y. Miyazato, T. Wada, J. T. Muckerman, E. Fujita, K. Tanaka* ______ 5728 – 5730

Generation of a Ru^{II}–Semiquinone–Anilino-Radical Complex through the Deprotonation of a Ru^{III}–Semiquinone–Anilido Complex

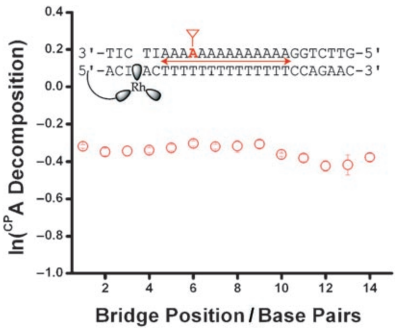


Calming the radicals: Aminyl radicals may one day be useful oxidation catalysts if their thermodynamic instability can be overcome, for example, through complexation with a metal. The semiquinone–anilino-radical and catechol–anilino-radical complexes **1** and **2** have now been prepared and the anilino-radical character of the tetradentate amine ligand proved by electron paramagentic resonance and resonance Raman spectroscopy, as well as DFT calculations.

DNA Charge Transport

K. E. Augustyn, J. C. Genereux, J. K. Barton* ______ 5731 – 5733

Distance-Independent DNA Charge Transport across an Adenine Tract

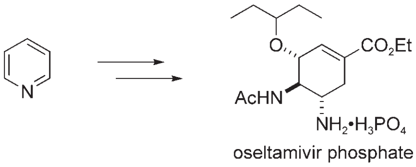


Charging along: DNA-mediated charge transport across adenine tracts is monitored by using a probe interior to the bridge (N^6-cyclopropyladenine (^{CP}A), shown in red). This trap was incorporated serially across the bridge and could be oxidized by a distal rhodium photooxidant without significant attenuation in yield over a distance of 5 nm. These results are consistent with complete delocalization of charge across the DNA bridge.

Drug Synthesis

N. Satoh, T. Akiba, S. Yokoshima, T. Fukuyama* ______ 5734 – 5736

A Practical Synthesis of (−)-Oseltamivir

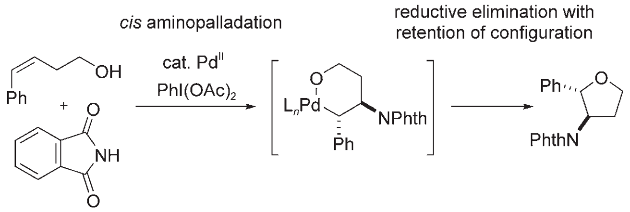


Keep it simple: Still in hot demand, the influenza drug (−)-oseltamivir phosphate (tamiflu; see scheme) has now been synthesized from pyridine by using inexpensive reagents. A strict minimum of purification steps are required in a synthetic route which features an asymmetric Diels–Alder reaction, a bromolactonization, a Hofmann rearrangement, and a domino transformation of a bicyclo[2.2.2] system into an aziridine intermediate.

Palladium Catalysis

L. V. Desai, M. S. Sanford* **5737 – 5740**

Construction of Tetrahydrofurans by Pd^{II}/Pd^{IV}-Catalyzed Aminooxygenation of Alkenes

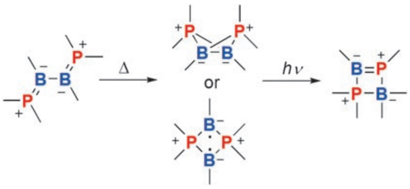


Resolute in the face of elimination: Substituted 3-aminotetrahydrofurans were prepared in good yield and with modest to high diastereoselectivity by the Pd-catalyzed reaction shown in the scheme (Phth = phthaloyl). Mechanistic studies indicate a Pd^{II}/Pd^{IV} catalytic cycle involving *cis* aminopalladation and intramolecular C–O bond-forming reductive elimination with retention of configuration at the carbon atom.

Valence Isomerization

J.-B. Bourg, A. Rodriguez,
D. Scheschkewitz, H. Gornitzka,
D. Bourissou,* G. Bertrand* **5741 – 5745**

Thermal Valence Isomerization of 2,3-Diborata-1,4-diphosphoniabuta-1,3-dienes to Bicyclo[1.1.0]butanes and Cyclobutane-1,3-diyls



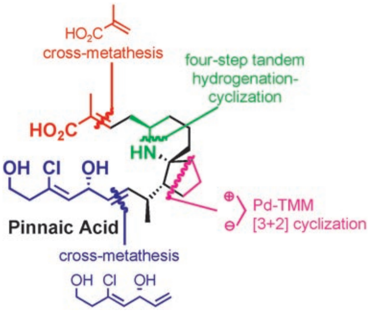
Mind your Ps and Bs: Valence isomerizations of PBBP 1,3-butadienes are investigated and compared to those of PCCP and all-carbon systems. The 2,3-diborata-1,4-diphosphoniabuta-1,3-dienes thermally isomerize to bicyclo[1.1.0]butanes or cyclobutane-1,3-diyls. Under photolytic activation, the bicyclo[1.1.0]butanes rearrange into cyclobutenes.

Natural Product Synthesis

S. Xu, H. Arimoto,*
D. Uemura **5746 – 5749**

Asymmetric Total Synthesis of Pinnaic Acid

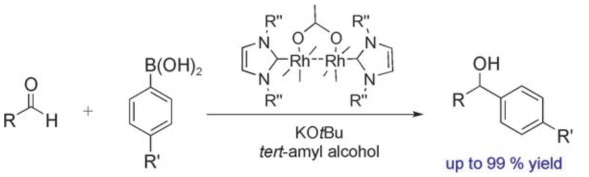
Pinned together: Asymmetric total synthesis of pinnaic acid was accomplished through a stereospecific route that features as key steps a Pd-catalyzed trimethylenemethane (TMM) [3+2] cyclization, a four-step tandem hydrogenation–cyclization, and cross-olefin-metathesis reactions (see scheme).



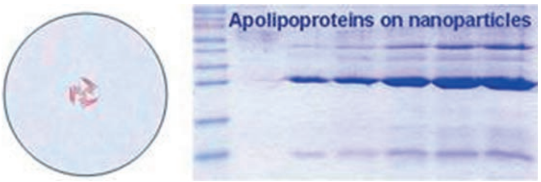
Catalytic Arylation

P. M. P. Gois,* A. F. Trindade, L. F. Veiros,
V. André, M. T. Duarte, C. A. M. Afonso,
S. Caddick, F. G. N. Cloke **5750 – 5753**

Tuning the Reactivity of Dirhodium(II) Complexes with Axial N-Heterocyclic Carbene Ligands: The Arylation of Aldehydes

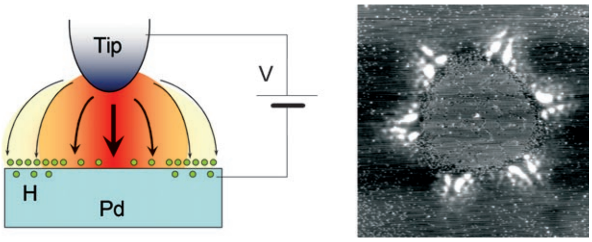


Efficient dinuclear catalysts: A complex of $\{Rh_2(OAc)_4\}$ with two N-heterocyclic carbenes (NHCs) at the axial positions catalyzes the arylation of aldehydes (see picture; R = alkyl, aryl). DFT calculations reveal subtle stereoelectronic effects resulting from the NHC coordination to the dirhodium(II) complex and suggest that complexes with one axial NHC ligand are the catalytically active species.



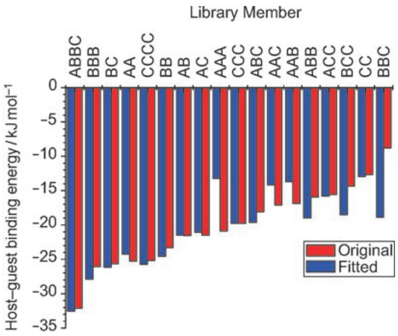
Blood relations: Nanoparticles that enter the bloodstream become coated with proteins. Four apolipoproteins are consistently recovered on model copolymer nanoparticles by using a centrifugation procedure (see electropherogram); their interaction with the nanoparticles is stronger than that of other plasma proteins with higher abundance.

Protein–Nanoparticle Binding



Paint with a field, not a brush: An electric field created by the tip of a scanning tunneling microscope (see picture, left) is used to control the diffusion of hydrogen on and into a palladium surface, creating distinctive patterns. The resulting STM image (see picture, right) shows a triangular region of reduced hydrogen concentration surrounded by white features due to subsurface hydrogen.

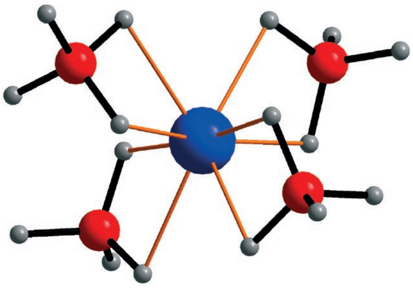
Hydrogen Adsorption



Reading a library without opening the books: It is possible to obtain most host–guest binding affinities, even in libraries of more than 30 components, directly from library product distributions by using a numerical data-fitting procedure. With this technique, it is not necessary to isolate any individual library members or measure binding constants.

Combinatorial Chemistry

Unexpected structural complexity: Well-crystallized $Mg(BH_4)_2$ powder is obtained, allowing the structure to be determined from synchrotron X-ray and neutron diffraction data. $Mg(BH_4)_2$ is a novel and remarkably complex three-dimensional framework in which each Mg^{2+} ion (blue) is tetrahedrally coordinated by four $[BH_4]^-$ tetrahedra (B red, H gray; see picture).



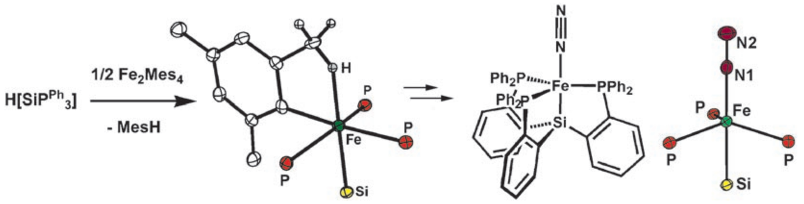
Metal Hydrides

Contents

Dinitrogen Complexes

N. P. Mankad, M. T. Whited,
J. C. Peters* ———— **5768–5771**

Terminal Fe^I–N_2 and $Fe^{II}\cdots H$–C Interactions Supported by Tris(phosphino)silyl Ligands



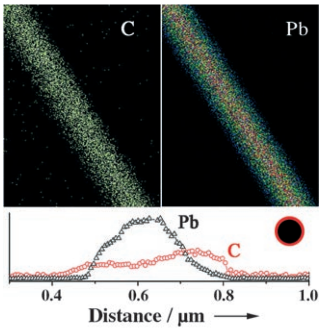
Taking hold: Monoanionic tris(phosphino)silyl ligands ($[SiP^R_3] = [(2\text{-}R_2PC_6H_4)_3Si]^-$) stabilize unusual five-coordinate Fe^I complexes. The silane $[SiP^{Ph}_3]H$ reacts with mesityliron(II) to give $[(SiP^{Ph}_3)Fe^{II}Mes]$, which displays a C–H agostic interaction. Treatment with HCl and reduction affords the terminally bonded Fe^I–N_2 complex $[(SiP^{Ph}_3)FeN_2]$ (see scheme; structures show only donor atoms of $[SiP^{Ph}_3]$), which yields hydrazine under protolytic conditions.

Nanostructures

X. L. Lu, G. Q. Zhang, W. Wang,
X. G. Li* ———— **5772–5774**

Superconducting and Oxidation-Resistant Coaxial Lead–Polymer Nanocables

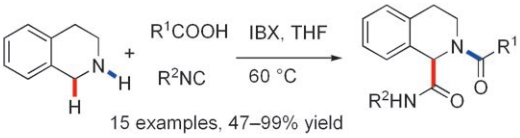
Superthin cables: Superconducting coaxial lead–polymer nanocables (see TEM/EDX element maps (top) and line scan (bottom)) are fabricated by a one-step method. Self-assembled polymer tubes act as both templates and microreactors for the growth of lead cores. The polymer shells also improve the oxidation resistance of the inner nanowires. EDX = energy dispersion X-ray spectroscopy.



Multicomponent Reactions

T. Ngouansavanh, J. Zhu* — **5775–5778**

IBX-Mediated Oxidative Ugi-Type Multicomponent Reactions: Application to the N and C1 Functionalization of Tetrahydroisoquinoline

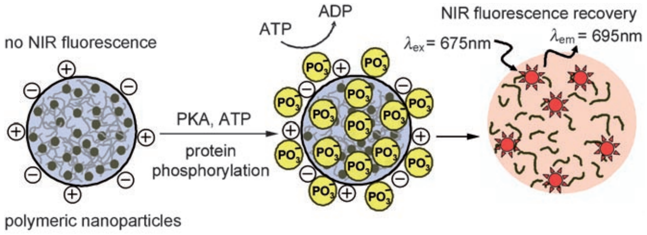


Ugi wonderland: An Ugi-type reaction of tetrahydroisoquinoline with an isocyanide and a carboxylic acid in the presence of iodoxybenzoic acid (IBX) afforded the 1,2-diacylated adduct in good to excellent yields (see scheme).

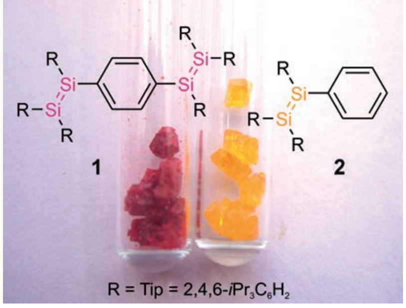
Cell Imaging

J.-H. Kim, S. Lee, K. Park, H. Y. Nam,
S. Y. Jang, I. Youn, K. Kim, H. Jeon,
R.-W. Park, I.-S. Kim, K. Choi,
I. C. Kwon* ———— **5779–5782**

Protein-Phosphorylation-Responsive Polymeric Nanoparticles for Imaging Protein Kinase Activities in Single Living Cells



Take your PIC: Cell-permeable and biocompatible polyion-induced complex (PIC) nanoparticles were developed consisting of a negatively charged polymer along with a positively charged polymer conjugated to a near-infrared fluorophore and a protein-kinase-specific peptide. Owing to profound changes in fluorescence, the PIC nanoparticle is an attractive probe for protein kinase A (PKA) in single living cells. ATP = adenosine triphosphate, ADP = adenosine diphosphate.

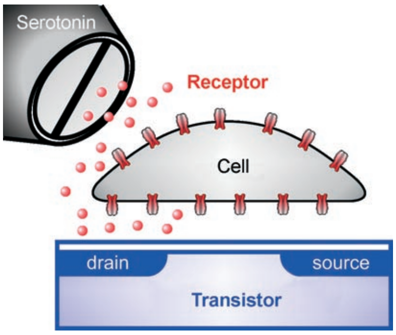


Electronic communication between two Si=Si double bonds is enabled by a phenylene linkage and expressed in a large red shift of the longest-wavelength UV/Vis absorptions of deep red tetrasiladiene **1** compared to yellow phenyldisilene **2**.

Silicon–Silicon Double Bonds

I. Bejan, D. Scheschkewitz* **5783 – 5786**

Two Si=Si Double Bonds Connected by a Phenylene Bridge

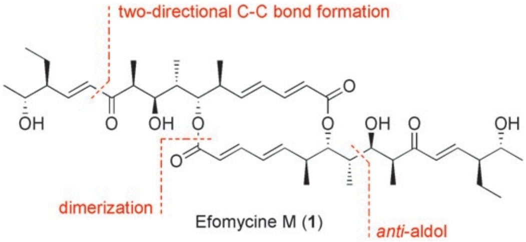


An unlike pair: A serotonin receptor is functionally coupled to a silicon chip by means of cell–transistor interfacing. The transistor signal is proportional to the membrane cell current of activated receptors. The development of this receptor-cell–transistor biosensor provides the physicochemical basis for noninvasive drug screening.

Serotonin–Transistor Biosensor

I. Peitz, M. Voelker,
P. Fromherz* **5787 – 5790**

Recombinant Serotonin Receptor on a Transistor as a Prototype for Cell-Based Biosensors

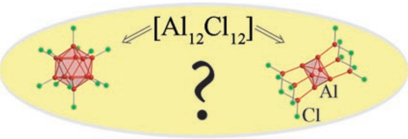


Two-directional synthesis: Key steps in the first total synthesis of the anti-inflammatory agent efomycine M (**1**) are a two-directional C11–C12 chain elongation and an early-stage dimerization reaction. The central stereopentad is synthesized by a highly stereoselective sequence consisting of an *anti*-aldol reaction and a diastereoselective reduction.

Polyketides

R. Barth, J. Mulzer* **5791 – 5794**

Total Synthesis of Efomycine M



In a dead end? The value of applying Wade's rules to neutral and dianionic [Al$_{12}$Cl$_{12}$] and [Ga$_{12}$Cl$_{12}$] species is diminishing: According to DFT calculations, [Al$_6$(AlCl$_2$)$_6$] clusters with an octahedral (metalloid) {Al$_6$} core (right) are energetically favored over icosahedral compounds (left) as is also found for several structurally examined subhalides (e.g. [Al$_{22}$Cl$_{20}$]). In addition it is not the postulated centered icosahedral isomers of [Al$_{13}$I$_{12}$]$^-$ clusters that constitute the energetic minima, but the metalloid isomers.

Cluster Compounds

K. Koch, R. Burgert,
H. Schnöckel* **5795 – 5798**

From Icosahedral Boron Subhalides to Octahedral Metalloid Aluminum and Gallium Analogues: Quo vadis, Wade's Rules?

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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Corrigenda

Since publication of their Communication, the authors have noticed that the definition of $\{Mo_{51}V_9\}$ given in the footnote at the bottom of the first page is incorrect. The correct definition is $\{Mo_{51}V_9\} = (NH_4)_{21}[Mo_{51}V_9(NO)_{12}O_{165}(OH)_3(H_2O)_3(NHMe_2)_3]\cdot x\,H_2O$ ($x \approx 60$).

A Large, Bowl-Shaped $\{Mo_{51}V_9\}$ Polyoxometalate

S. Wang,* X. Lin, Y. Wan, W. Yang, S. Zhang, C. Lu, H. Zhuang **3490–3493**

Angew. Chem. Int. Ed. **2007**, *46*

DOI 10.1002/anie.200700076

In the reference section of this Communication, some citations were listed wrongly. The references concerned should be read as follows: for Ref. [14], read Ref. [20]; for Ref. [16], read Ref. [22]; for Ref. [18], read Ref. [24]; for Ref. [20], read Ref. [26]; for Ref. [22], read Ref. [14]; for Ref. [24], read Ref. [16]; and for Ref. [26], read Ref. [18]. For the large-scale preparation of aromatic aldehydes from the corresponding aryl methyl chloride according to the described oxidation procedure, the chloride should be added dropwise or in small portions. The optimized yield of the aldehyde based on the consumption of chloride was over 95 %, with about 45 % of the chloride recovered. The reaction is exothermic, so external heating is not necessary. **WARNING: The reaction is explosive if a large amount of chloride is added in one portion.**

The Dual Roles of Oxodiperoxovanadate Both as a Nucleophile and an Oxidant in the Green Oxidation of Benzyl Alcohols or Benzyl Halides to Aldehydes and Ketones

C. Li,* P. Zheng, J. Li, H. Zhang, Y. Cui, Q. Shao, X. Ji, J. Zhang, P. Zhao, Y. Xu **5063–5066**

Angew. Chem. Int. Ed. **2003**, *42*

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