



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:

D. V. Esposito, S. T. Hunt, A. L. Stottlemeyer, K. D. Dobson,
B. E. McCandless, R. W. Birkmire, J. G. Chen*

**Low-Cost Hydrogen-Evolution Catalysts Based on Monolayer
Platinum on Tungsten Monocarbide (WC) Substrates**

R. Matsui, K. Seto, K. Fujita, T. Suzuki, A. Nakazaki, S. Kobayashi
**Unusually E-Selective Ring-Closing Metathesis to Form
Eight-Membered Rings**

J. S. Chen, T. Zhu, C. M. Li, X. W. Lou*

Building Hematite Nanostructures Using Oriented Attachment

S. Sun, G. Zhang, D. Geng, Y. Chen, R. Li, M. Cai, X. Sun*
**A New Highly Durable Platinum Nanocatalyst for PEM Fuel
Cells: Multiarmed Star-like Nanowire Single Crystals**

T. J. Hebden, A. J. S. John, D. G. Gusev, W. Kaminsky, K. I. Goldberg,
D. M. Heinekey*

Preparation of a Dihydrogen Complex of Cobalt

S. Vellalath, I. Čorić, B. List*

**N-Phosphinyl Phosphoramidate: A Chiral Brønsted Acid Motif for
the Direct Asymmetric N,O-Acetalization of Aldehydes**

Y. Matsuki, M. T. Eddy, R. G. Griffin, J. Herzfeld*

Rapid 3D MAS NMR Spectroscopy at Critical Sensitivity

Y. Zhang, G. M. Miyake, E. Y.-X. Chen*

**Alane-Based Classical and Frustrated Lewis Pairs in Polymer
Synthesis: Rapid Polymerization of Methyl Methacrylate and
Naturally Renewable Methylene Butyrolactones to
High-Molecular-Weight Polymers**

K. Breuker,* S. Brüscheweiler, M. Tollinger

**Electrostatic Stabilization of Native Protein Structure in the Gas
Phase**

J. Zeng, X. Xia, M. Rycenga, P. Henneghan, Q. Li, Y. Xia*

**Successive Deposition of Silver on Silver Nanoplates: Lateral
Versus Vertical Growth**

M. Mastalerz,* M. W. Schneider, I. M. Oppel, O. Presly

**A Salicylbisimine Cage Compound with a High Surface Area and
Selective CO₂/CH₄ Adsorption**



*“When I wake up I go to our kitchen and prepare the
lunches of my daughters.
The biggest problem that scientists face is the increasing
pressure put on our planet by humanity...”*
This and more about François P. Gabbaï can be found
on page 9318.

Author Profile

François P. Gabbaï _____ 9318



J.-L. Brédas



L. Fabbriizzi



H.-D. Arndt



N. Cramer

Model Systems in Catalysis

Robert M. Rioux

News

Charles H. Stone Award:
J.-L. Brédas _____ 9319

Izatt–Christensen Award:
L. Fabbriizzi _____ 9319

Organic Chemistry Young
Investigator Awards:
H.-D. Arndt and N. Cramer _____ 9319

Books

reviewed by C. Friend _____ 9320

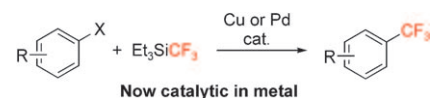
Highlights

Cross-Coupling

R. J. Lundgren,
M. Stradiotto* _____ 9322–9324

Transition-Metal-Catalyzed
Trifluoromethylation of Aryl Halides

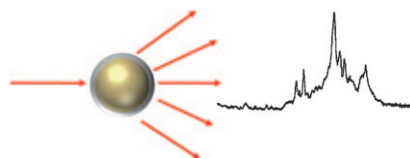
Making inroads into ArCF_3 : Recent advances in the copper- and palladium-catalyzed cross-coupling of aryl halides and the trifluoromethyl anion, derived from (trifluoromethyl)silanes, are highlighted.



Nanoparticle SERS

D. Graham* _____ 9325–9327

The Next Generation of Advanced
Spectroscopy: Surface Enhanced Raman
Scattering from Metal Nanoparticles



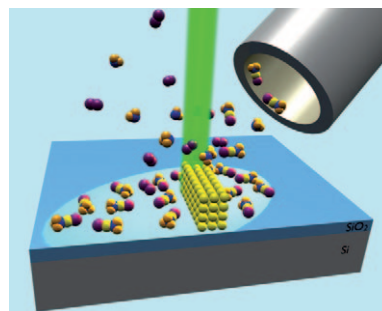
Shining light: Surface enhanced Raman scattering (SERS) offers much in terms of molecularly specific information at ultra-sensitive levels. Two recent breakthroughs have occurred in this field. First, a new surface was developed that provides SERS information previously inaccessible, and second, a nanoparticle SERS label was introduced to image antigens relating to cancer in tissue.

Surface Modifications

I. Utke, A. Götzhäuser* _____ 9328–9330

Small, Minimally Invasive, Direct:
Electrons Induce Local Reactions of
Adsorbed Functional Molecules on the
Nanoscale

Double duty: Apart from imaging and analysis purposes, modern electron microscopes can be exploited for focused electron beam induced processing (FEBIP) on the nanometer scale using adsorbed functional volatile molecules. Depending on the nature of injected molecules and substrates, the electron-impact dissociation products form solid deposits (metals, dielectrics, semiconductors, nanocomposites) or remove substrate material locally.

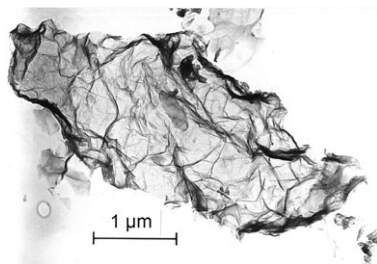


Essays

Graphene Research

H.-P. Boehm* _____ 9332–9335

Graphene—How a Laboratory Curiosity
Suddenly Became Extremely Interesting

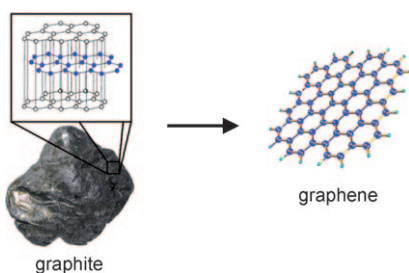


Thanks to its unusual electronic properties graphene has received considerable attention in recent years. It is less known, however, that research in this area goes much further back: At the start of the 1960s H.-P. Boehm et al. reduced graphite oxide with formation of thin films, which today, on account of their content of foreign atoms, would be called “chemically modified graphenes” (figure: electron microscopy image from that time).

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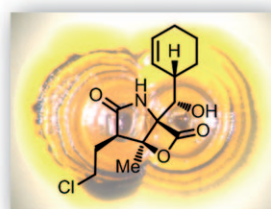
A transformation for the ages: There has been a surge in interest in graphene in recent years; however, graphene-like materials derived from graphite oxide were reported in 1962, and related chemical modifications of graphite were described as early as 1840. This account reveals that the rich history of graphene chemistry, the development of its synthesis and characterization, has laid the foundation for research that continues to this day.

Minireviews

Genealogy of Graphene

D. R. Dreyer, R. S. Ruoff,*
C. W. Bielawski* _____ **9336–9344**

From Conception to Realization: An Historical Account of Graphene and Some Perspectives for Its Future



A young family: The salinosporamides (picture: salinosporamide A), γ -lactam- β -lactone marine natural products isolated from *Salinispora tropica*, are irreversible proteasome inhibitors and constitute a potent new class of small molecules for cancer drugs. This Review highlights the impressive achievements of recent multi-disciplinary research on the discovery, biosynthesis, bioengineering, total synthesis, and biomedical evaluation of this young natural product family.

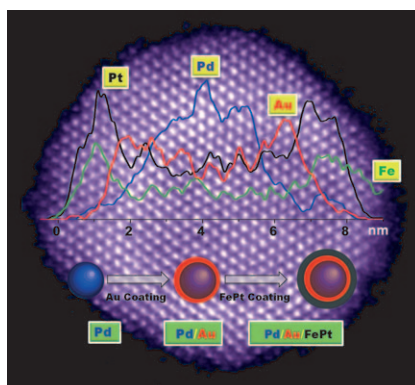
Reviews

Salinosporamides

T. A. M. Gulder,
B. S. Moore* _____ **9346–9367**

Salinosporamide Natural Products: Potent 20S Proteasome Inhibitors as Promising Cancer Chemotherapeutics

Multimetallic dreamcoat: Core/shell nanoparticles of Pd/Au and Pd/Au/FePt were synthesized with palladium (5 nm diameter), a gold shell (1–2 nm), and a FePt shell (2 nm). The synthetic control allowed the Pd/Au catalytic properties to be tuned by the shell thickness. The synthesis provides an indication for future development of multicomponent nanoparticles for advanced catalytic applications.



Communications

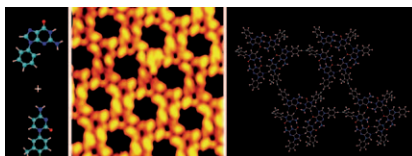
Core/Shell Nanoparticles

V. Mazumder, M. Chi, K. L. More,
S. Sun* _____ **9368–9372**

Synthesis and Characterization of Multimetallic Pd/Au and Pd/Au/FePt Core/Shell Nanoparticles

Molecular Recognition

W. Xu,* J.-g. Wang, M. F. Jacobsen,
M. Mura, M. Yu, R. E. A. Kelly, Q.-q. Meng,
E. Lægsgaard, I. Stensgaard,
T. R. Linderorth, J. Kjems,
L. N. Kantorovich, K. V. Gothelf,
F. Besenbacher* ————— **9373 – 9377**



In a stable relationship: Watson–Crick hydrogen bonding plays a key role in stabilizing the highly ordered supra-molecular porous structure formed by co-deposition of biomimetically modified nucleobases cytosine and guanine onto a Au(111) surface under ultrahigh vacuum conditions. A combination of high-resolution STM imaging and density functional theory has been used to determine the structure of the network (see picture).



Supramolecular Porous Network Formed by Molecular Recognition between Chemically Modified Nucleobases Guanine and Cytosine

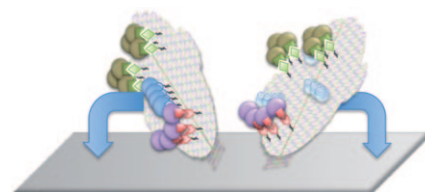
DNA Nanotechnology

B. Saccà, R. Meyer, M. Erkelenz, K. Kiko,
A. Arndt, H. Schroeder, K. S. Rabe,
C. M. Niemeyer* ————— **9378 – 9383**



Orthogonal Protein Decoration of DNA Origami

If the face fits: Self-labeling fusion proteins have been used for the site-specific decoration of DNA origami. This method even allows individual faces of the quasi-two-dimensional plane of the nanostructure to be specifically decorated (see picture), thereby enabling directional immobilization and thus control over the accessibility of distinct proteins presented on the structure.

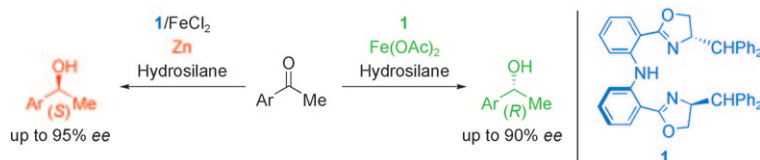


Iron Catalysis

T. Inagaki, A. Ito, J.-i. Ito,
H. Nishiyama* ————— **9384 – 9387**



Asymmetric Iron-Catalyzed Hydrosilane Reduction of Ketones: Effect of Zinc Metal upon the Absolute Configuration



Just a little bit: The **1**/FeCl₂ complex was activated in the presence of Zn and exhibited catalytic activity for the hydrosilane reduction of ketones to give the *S*-configured alcohol. In contrast, the mixed-

catalyst system of **1** and Fe(OAc)₂ provides the *R* enantiomer. This approach provides both enantiomers from a single chiral source by the addition of a small amount of Zn.

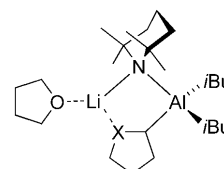
Organometallic Reagents

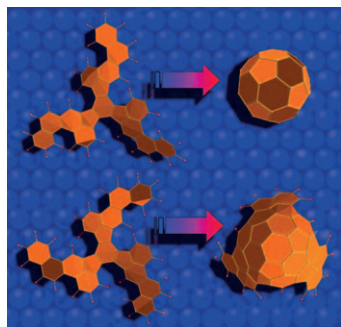
E. Crosbie, P. García-Álvarez,
A. R. Kennedy, J. Klett, R. E. Mulvey,*
S. D. Robertson ————— **9388 – 9391**



Structurally Engineered Deprotonation/Alumination of THF and THTP with Retention of Their Cycloanionic Structures

Engagement ring: α -Metalated by a lithium bisamido-bisalkylaluminate base, the sensitive cycloanion ring of THF or THTP remains intact by engaging with both metal centers of the base residue (see structure; X = O, S).



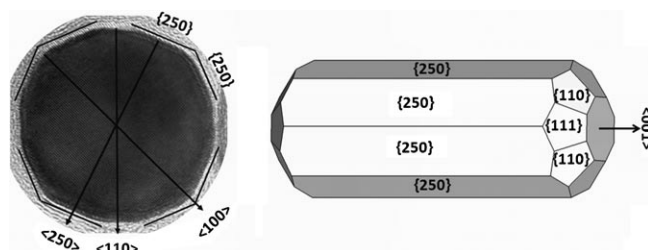


Fullerenes on a plate: A surface-catalyzed cyclodehydrogenation reaction enabled selective fullerene-cage formation from polycyclic organic precursors. As no C–C bond rearrangement occurred during the reaction, only specifically designed precursors gave the desired fullerene (see picture). This efficient and selective condensation process opens new horizons in the directed synthesis of fullerenes and related structures.

Fullerene Synthesis

K. Amsharov,* N. Abdurakhmanova,* S. Stepanow, S. Rauschenbach, M. Jansen, K. Kern _____ **9392 – 9396**

Towards the Isomer-Specific Synthesis of Higher Fullerenes and Buckybowls by the Surface-Catalyzed Cyclodehydrogenation of Aromatic Precursors



A new face of nanorod crystallinity: The structure of single-crystal gold nanorods is reinterpreted on the basis of high-resolution transmission electron micros-

copy on standing rods. The studies provided evidence for eight identical higher-index {250} lateral facets (see picture for TEM image and proposed model).

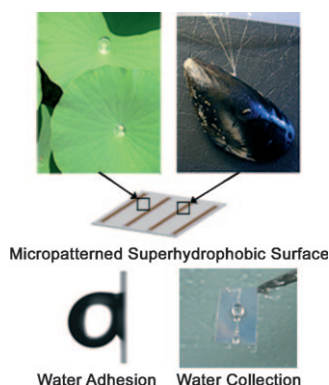
Nanorods

E. Carbó-Argibay, B. Rodríguez-González, S. Gómez-Graña, A. Guerrero-Martínez, I. Pastoriza-Santos, J. Pérez-Juste, L. M. Liz-Marzán* _____ **9397 – 9400**

The Crystalline Structure of Gold Nanorods Revisited: Evidence for Higher-Index Lateral Facets



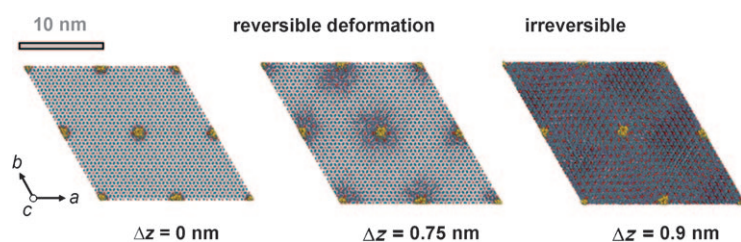
Science MIMIC-king nature: Hydrophilic conversion of superhydrophobic surfaces can be easily achieved through a bio-inspired approach to produce an alternating superhydrophobic–hydrophilic surface by using established soft-lithographic techniques, such as micromolding in capillaries (MIMIC). The resulting patterned surface showed high water adhesion properties as well as superhydrophobic properties.



Surface Modification

S. M. Kang, I. You, W. K. Cho, H. K. Shon, T. G. Lee, I. S. Choi, J. M. Karp, H. Lee* _____ **9401 – 9404**

One-Step Modification of Superhydrophobic Surfaces by a Mussel-Inspired Polymer Coating



Once bitten: Compression along the *c* axis of apatite–collagen composites (see picture), such as that on tooth enamel during biting, reveals a molecular mechanism that accounts for the steel-like characteristics of these composites. Simulations

reveal that before eventual failure, inelastic deformation is initiated near the collagen molecules followed by pseudo-elastic deformation. The composite may undergo self-healing after release of the mechanical load.

Biocomposites

D. Zahn* _____ **9405 – 9407**

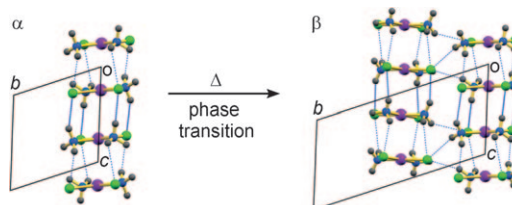
A Molecular Rationale of Shock Absorption and Self-Healing in a Biomimetic Apatite–Collagen Composite under Mechanical Load

Drug Polymorphism

V. P. Ting, M. Schmidtman, C. C. Wilson,
M. T. Weller* 9408–9411



Cisplatin: Polymorphism and Structural
Insights into an Important
Chemotherapeutic Drug



The changing face of cisplatin: The complete crystal structures, including the details of extensive intermolecular hydrogen bonding in two enantiotropic polymorphs of the chemotherapeutic drug

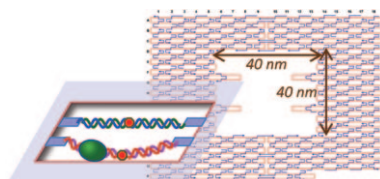
cisplatin, have been elucidated. A massive thermal hysteresis effect exists between the two polymorphs, α and β , that are active at ambient temperatures.

Single-Enzyme Analysis

M. Endo,* Y. Katsuda, K. Hidaka,
H. Sugiyama* 9412–9416



A Versatile DNA Nanochip for Direct
Analysis of DNA Base-Excision Repair



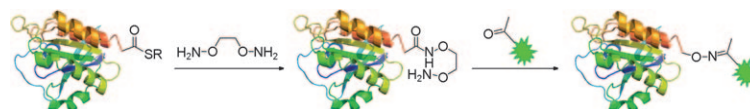
Repair kit: The single DNA-repair enzymes 8-oxoguanine glycosylase and T4 pyrimidine dimer glycosylase were analyzed by a nanoscale DNA chip containing two double-stranded DNA molecules (see picture). Dynamic movement of the enzymes and the single DNA-repair reaction on the DNA nanochip was visualized by fast-scanning atomic force microscopy.

Protein Chemistry

L. Yi, H. Sun, Y.-W. Wu, G. Triola,
H. Waldmann,*
R. S. Goody* 9417–9421



A Highly Efficient Strategy for
Modification of Proteins at the
C Terminus



A new linker: In a facile, chemoselective, and potentially general method for protein modification at the C terminus oxamino-modified proteins obtained from protein thioesters react rapidly with ketones

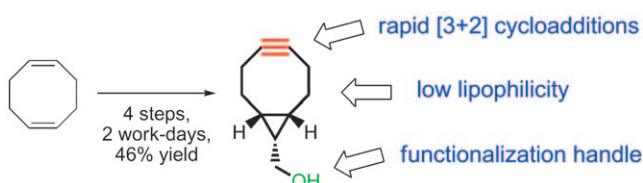
under mild conditions. This strategy was used for fluorescence labeling, for example with modified coumarin and fluorescein (see scheme).

Bimolecular Imaging

J. Dommerholt, S. Schmidt, R. Temming,
L. J. A. Hendriks, F. P. J. T. Rutjes,
J. C. M. van Hest, D. J. Lefeber, P. Friedl,
F. L. van Delft* 9422–9425

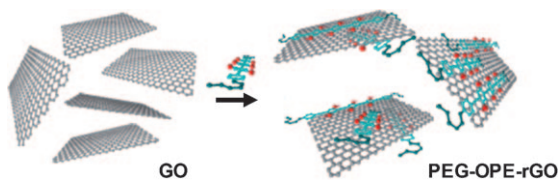


Readily Accessible Bicyclononynes for
Bioorthogonal Labeling and Three-
Dimensional Imaging of Living Cells



I can see clearly now: Bicyclo[6.1.0]non-4-yne, an easily prepared, symmetrical cycloalkyne, displays excellent reaction kinetics in strain-promoted cycloaddition reactions with azides and nitrones (see scheme). Highly specific protein

modifications are demonstrated in vitro and subcellular-resolved imaging of glycan expression was achieved in metastatic melanoma cells during invasive migration into three-dimensional collagen lattices.



Both kinds of solubility: An amphiphilic reduced graphene oxide (rGO) composite is synthesized by using a novel coil-rod-coil conjugated triblock copolymer as the π - π binding stabilizer. Such a graphene-

based composite can be dissolved not only in organic solvents with low polarity (such as toluene and chloroform) but also in water-miscible solvents with high polarity (for example methanol).

Amphiphilic Graphene

X. Qi, K.-Y. Pu, H. Li, X. Zhou, S. Wu, Q.-L. Fan, B. Liu,* F. Boey, W. Huang,* H. Zhang* ————— 9426–9429

Amphiphilic Graphene Composites

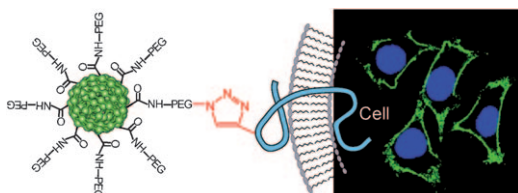


Don't stress: Maradolipids (see picture; red O, grey C, white H) are the first diacyltrehaloses found to be produced in animal organisms. The nematode *Caenorhabditis elegans* synthesizes maradolipids for the highly stress-resistant dauer larvae. Genetic knockout studies result in the improper morphology of the gut lumen of dauer larvae. Maradolipids might be important for understanding the chemical basis for the resistance of dauer larvae to extreme environmental stress.

Natural Products

S. Penkov, F. Mende, V. Zagoriy, C. Erkut, R. Martin, U. Pässler, K. Schuhmann, D. Schwudke, M. Gruner, J. Mäntler, T. Reichert-Müller, A. Shevchenko, H.-J. Knölker,* T. V. Kurzchalia* ————— 9430–9435

Maradolipids: Diacyltrehalose Glycolipids Specific to Dauer Larva in *Caenorhabditis elegans*



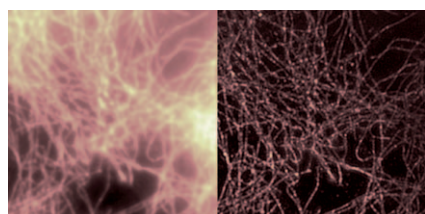
All aboard! A facile conjugation method allows covalent linking of functional molecules to semiconducting polymer dots for bioorthogonal labeling of cellular tar-

gets. Targeting of the polymer dots to newly synthesized proteins and glycoproteins in mammalian cells by click chemistry is highly efficient and specific.

Polymer Dots

C. Wu, Y. Jin, T. Schneider, D. R. Burnham, P. B. Smith, D. T. Chiu* — 9436–9440

Ultrabright and Bioorthogonal Labeling of Cellular Targets Using Semiconducting Polymer Dots and Click Chemistry



SOFI's choice: Amongst the variety of superresolution far-field microscopy techniques, the most recently established method is superresolution optical fluctuation imaging, SOFI. SOFI can be quickly performed on samples labeled with conventional organic dyes.

Superresolution Imaging

T. Dertinger,* M. Heilemann,* R. Vogel, M. Sauer, S. Weiss* ————— 9441–9443

Superresolution Optical Fluctuation Imaging with Organic Dyes

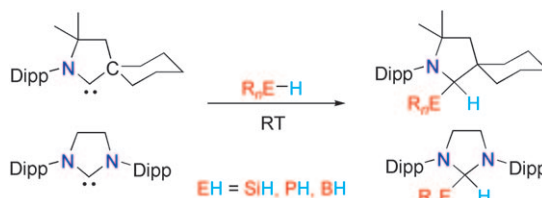


Carbenes

G. D. Frey, J. D. Masuda, B. Donnadieu,
G. Bertrand* 9444–9447



Activation of Si–H, B–H, and P–H Bonds
at a Single Nonmetal Center



Carbenes more than measure up: Singlet stable carbenes compete with transition metals in the activation of enthalpically strong bonds, as shown by the cleavage of the E–H bonds of silanes, boranes, and

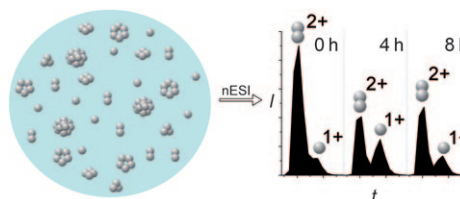
phosphanes (see scheme). However, in contrast with the electrophilic mode of activation observed with metals, carbenes act as nucleophiles towards these substrates. Dipp = 2,6-diisopropylphenyl.

Prefibrillar Aggregates

H. L. Cole, J. M. D. Kalapothakis,
G. Bennett, P. E. Barran,*
C. E. MacPhee* 9448–9451



Characterizing Early Aggregates Formed
by an Amyloidogenic Peptide by Mass
Spectrometry



What floats in the soup? Time-course and ion-mobility nano-electrospray ionization (nESI) mass spectrometry probes the early aggregation states of an amyloidogenic endecapeptide derived from amino

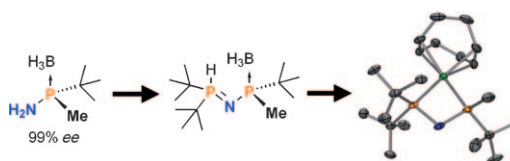
acid residues 105–115 of the human plasma protein transthyretin. A wide range of densely packed prefibrillar oligomers $1 \leq n \leq 13$ are observed in dynamic populations over 8 h.

P Ligands

M. Revés, C. Ferrer, T. León, S. Doran,
P. Etayo, A. Vidal-Ferran, A. Riera,*
X. Verdaguer* 9452–9455



Primary and Secondary Aminophosphines
as Novel P-Stereogenic Building Blocks
for Ligand Synthesis



Set the N free! The reactivity of the amino group of P-stereogenic aminophosphines allows the further elaboration of the aminophosphine unit whilst preserving the original chirality of the phosphorus atom (see picture; Rh green). P-stereo-

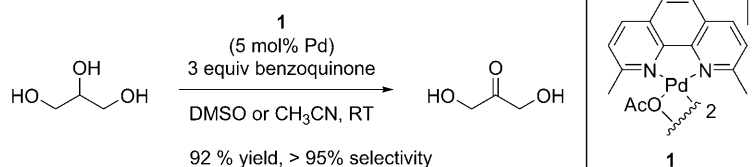
genic aminodiphosphine ligands can easily be prepared in optically pure forms, feature distinct structural and electronic characteristics, and can be used in asymmetric hydrogenation reactions.

Glycerol Oxidation

R. M. Painter, D. M. Pearson,
R. M. Waymouth* 9456–9459

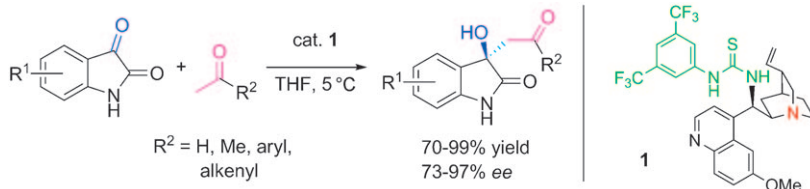


Selective Catalytic Oxidation of Glycerol to
Dihydroxyacetone



High selectivity and high yield characterize the oxidation of glycerol into dihydroxyacetone using catalyst **1**, with benzoquinone or air as the oxidant. The

mechanism proposed involves reversible palladium-alkoxide formation with the turnover-limiting reoxidation of the palladium complex.



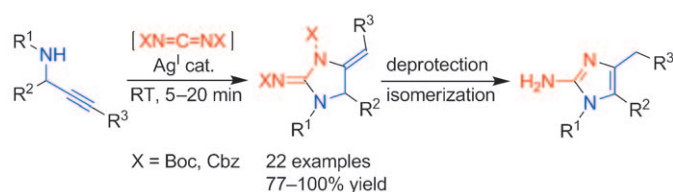
New catalysis mechanism! The asymmetric aldol reaction of unactivated ketones and activated carbonyl compounds is realized with a quinidine-derived thiourea catalyst (see scheme), and involves an enolate mechanism

instead of the widely used enamine mechanism. With isatins as the substrate, the reaction can be applied to the enantioselective synthesis of biologically active 3-hydroxyindolin-2-ones.

Organocatalysis

Q. Guo, M. Bhanushali,
C.-G. Zhao* 9460–9464

Quinidine Thiourea-Catalyzed Aldol Reaction of Unactivated Ketones: Highly Enantioselective Synthesis of 3-Alkyl-3-hydroxyindolin-2-ones



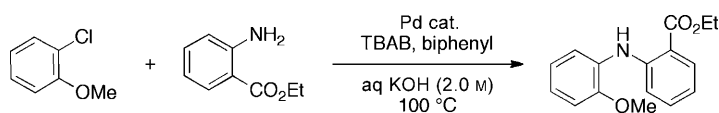
Alkaloids of the naamine family were synthesized from diverse propargylamines in just two steps (see scheme: $R^1 = \text{Me}$, $R^2 = \text{substituted benzyl}$, $R^3 = \text{Ar}$). Thus, the addition to a propargylamine of a carbodiimide generated in situ, silver(I)-

catalyzed intramolecular hydroamidation, and subsequent deprotection provide access to the heterocyclic core of numerous natural products and biologically active compounds. Boc = *tert*-butoxycarbonyl, Cbz = carbobenzyloxy.

Heterocycle Synthesis

D. S. Ermolat'ev, J. B. Bariwal,
H. P. L. Steenackers,
S. C. J. De Keersmaecker,
E. V. Van der Eycken* 9465–9468

Concise and Diversity-Oriented Route toward Polysubstituted 2-Aminoimidazole Alkaloids and Their Analogues



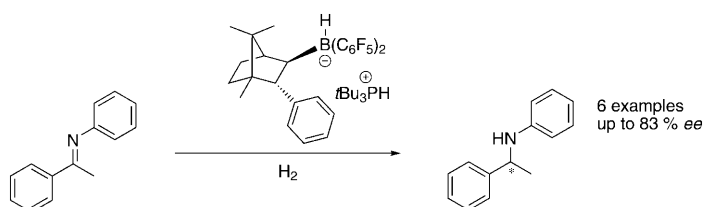
Take a C–N bond and make it better: The optimized conditions for continuous-flow palladium-catalyzed C–N bond-forming reactions have been determined. They require the use of aqueous KOH, toluene as the solvent, tetrabutylammonium bro-

mide as a phase-transfer catalyst, and a packed-bed microreactor (see scheme; TBAB = tetrabutylammonium bromide). In some cases, performing these reactions under harsh conditions led to greatly enhanced reaction rates.

Continuous Flow

J. R. Naber, S. L. Buchwald* 9469–9474

Packed-Bed Reactors for Continuous-Flow C–N Cross-Coupling



No subsequent frustration: Frustrated Lewis pairs (FLPs) have been recently introduced as an unprecedented possibility to activate hydrogen. On the basis of

this concept the first example of highly enantioselective catalytic hydrogenation of imines using chiral FLPs has been demonstrated (see scheme).

Asymmetric Hydrogenation

D. Chen, Y. Wang,
J. Klankermayer* 9475–9478

Enantioselective Hydrogenation with Chiral Frustrated Lewis Pairs

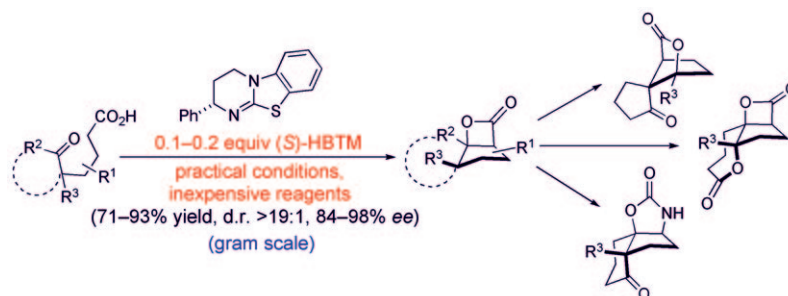


Synthetic Methods

C. A. Leverett, V. C. Purohit,
D. Romo* 9479–9483



Enantioselective, Organocatalyzed,
Intramolecular Aldol Lactonizations with
Keto Acids Leading to Bi- and Tricyclic β -
Lactones and Topology-Morphing
Transformations



Quickly emerging complexity characterizes the asymmetric, nucleophile-catalyzed aldol lactonization (NCAL) process with keto acid substrates and subsequent topology-altering reactions. The utility of chiral cyclic isothiourea catalysts as

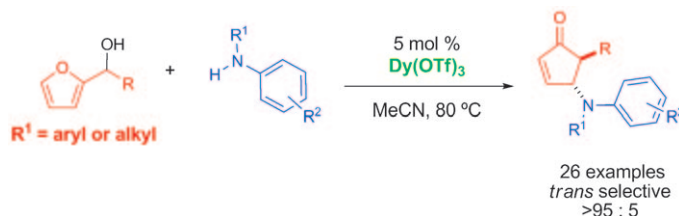
nucleophilic promoters (Lewis bases) for desymmetrization reactions through scalable NCAL processes is demonstrated (see picture; HBTM = homoben-zotetramisole).

Rearrangement Reactions

G. K. Veits, D. R. Wenz,
J. Read de Alaniz* 9484–9487



Versatile Method for the Synthesis of 4-
Aminocyclopentenones: Dysprosium(III)
Triflate Catalyzed Aza-Piancatelli
Rearrangement



A sweet dysproposition: A dysprosium(III) trifluoromethanesulfonate catalyzed rearrangement of furylcarbinols into 4-aminocyclopentenones by a 4π electro-

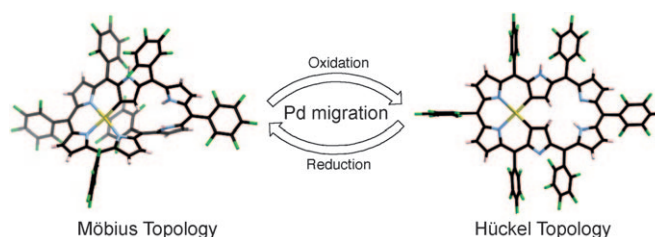
cyclization has been developed. The aza-Piancatelli rearrangement affords a single *trans* diastereomer from both aryl- and alkyl-substituted furylcarbinols.

Aromaticity

M. Inoue, A. Osuka* 9488–9491



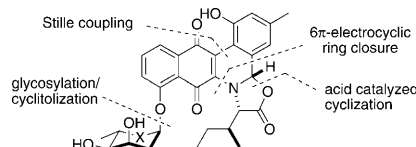
Redox-Induced Palladium Migrations that
Allow Reversible Topological Changes
between Palladium(II) Complexes of
Möbius Aromatic [28]Hexaphyrin and
Hückel Aromatic [26]Hexaphyrin



Plane twisted: A twisted Möbius aromatic [28]hexaphyrin/ Pd^{II} complex and a planar Hückel aromatic [26]hexaphyrin/ Pd^{II} complex are reversibly interconvertible by an unprecedented palladium migration through oxidation and reduction (see

scheme). The [26]hexaphyrin/ Pd^{II} complex is a precursor to [26]hexaphyrin hetero-bis(metal) complexes having Pd^{II} / Cu^{III} or Pd^{II} / Ag^{III} centers. C gray, N blue, H white, F green, Pd yellow.

One's trash is another one's treasure: The first syntheses of jadomycin A and the carbasugar analogue of jadomycin B have been achieved in 6 and 20 longest linear steps, respectively. The key ring system of the aglycone was prepared by a 6 π -electron electrocyclic ring closure and subsequent hemiaminal ring closure. Acid sensitivity of the glycosidic bond in jadomycin B (see structure; X=O) precluded its synthesis but led to the carbasugar analogue (X=CH₂).



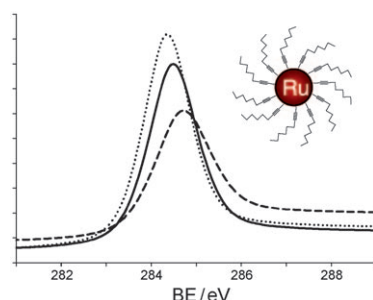
Synthetic Methods

M. Shan, E. U. Sharif,
G. A. O'Doherty* — 9492 – 9495

Total Synthesis of Jadomycin A and a Carbasugar Analogue of Jadomycin B



Particles in charge: Ruthenium nanoparticles passivated by Ru≡C interfacial bonding interactions exhibit apparent intraparticle charge delocalization, which can be manipulated by the nanoparticle charge state. Control of the back-bonding occurs by interactions between ruthenium core electrons and sp-hybridized carbon atoms of the alkynyl ligands (see picture: C_{sp} 1s binding energy (BE): reduced, ----- oxidized form, — as-prepared nanoparticles).



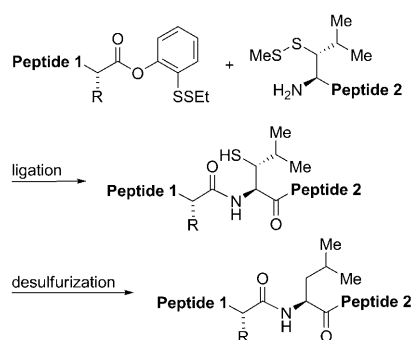
Nanomaterials

X. W. Kang, N. B. Zuckerman,
J. P. Konopelski,
S. W. Chen* — 9496 – 9499

Alkyne-Stabilized Ruthenium Nanoparticles: Manipulation of Intraparticle Charge Delocalization by Nanoparticle Charge States



Maximizing by minimizing: An efficient and broadly useful two-step ligation protocol was developed. Important mechanistic issues of ligation were probed from competition studies on the formation of diastereomeric ligation products. This study provides a valuable approach to facilitate polypeptide synthesis by minimizing protecting group manipulations and intermediate isolations.



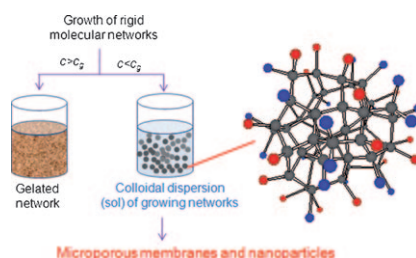
Peptide Coupling

Z. Tan, S. Shang,
S. J. Danishefsky* — 9500 – 9503

Insights into the Finer Issues of Native Chemical Ligation: An Approach to Cascade Ligations



Concentration is critical: Amine/isocyanate polycondensation below the critical gelation concentration c_g affords a sol of growing microporous molecular-network nanoparticles rather than a gelated network (see picture, for model of particle: NCO red, NH₂ blue, tetrahedral cross-link point gray). Further growth to form monolithic networks occurs on solvent evaporation, analogous to sol-gel synthesis of inorganic oxide networks.



Organic Sol-Gel Process

S. Y. Moon, J. S. Bae, E. Jeon,
J. W. Park* — 9504 – 9508

Organic Sol-Gel Synthesis: Solution-Processable Microporous Organic Networks

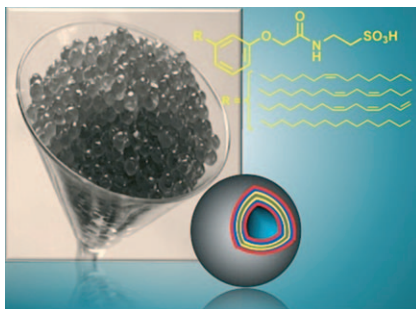


Vesicular Adhesion

V. S. Balachandran, S. R. Jadhav,
P. Pradhan, S. De Carlo,
G. John* ————— 9509–9512



Adhesive Vesicles through Adaptive Response of a Biobased Surfactant



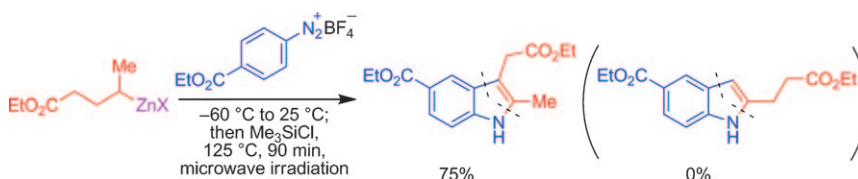
Chemist's caviar: Stimuli-responsive fusogenic vesicles from a cardanol-aurine surfactant are reported. The thermo-responsive behavior of the unsaturations in the alkyl chains, reminiscent of homeoviscous alterations, lead to a micelle-to-vesicle transformation and to the formation of caviar-like adhesive vesicles (see photograph).

Indole Synthesis

B. A. Haag, Z.-G. Zhang, J.-S. Li,
P. Knochel* ————— 9513–9516



Fischer Indole Synthesis with Organozinc Reagents



Updated classic: Primary and secondary alkylzinc reagents add to various aryl-diazonium salts leading regioselectively to polyfunctional indoles by means of a [3,3]-sigmatropic shift and subsequent aroma-

tization. This organometallic variation of the Fischer indole synthesis tolerates a wide range of functional groups and displays absolute regioselectivity.

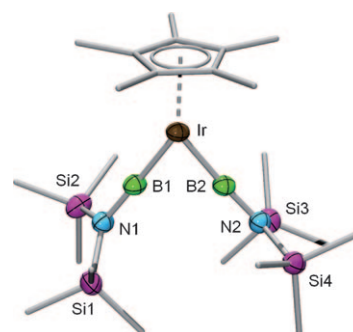
Bis(borylene) Complexes

S. Bertsch, H. Braunschweig,* B. Christ,
M. Forster, K. Schwab,
K. Radacki ————— 9517–9520



Towards Homoleptic Borylene Complexes: Incorporation of Two Borylene Ligands into a Mononuclear Iridium Species

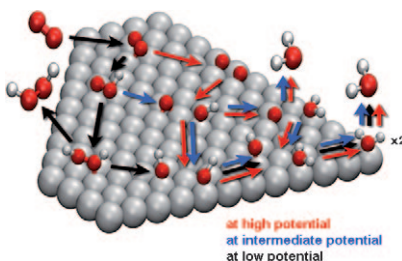
Place two B: The isolation of the first terminal, mononuclear bis(borylene) complex (see structure) represents a significant step towards the synthesis of homoleptic borylene complexes, and also provides deeper insight into the bonding characteristics of borylene complexes in general. A preliminary elucidation of the question of how two terminal BR ligands affect each other when bound to the same metal center is presented.



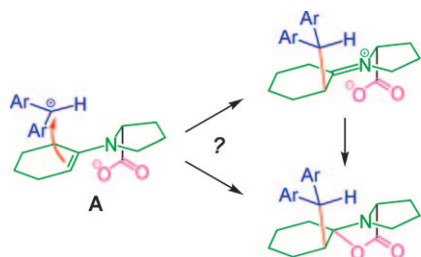
Oxygen Reduction

J. A. Keith, T. Jacob* ————— 9521–9525

Theoretical Studies of Potential-Dependent and Competing Mechanisms of the Electrocatalytic Oxygen Reduction Reaction on Pt(111)



This way ORR that: Theoretical investigations on the oxygen reduction reaction (ORR) mechanism using first-principles quantum chemistry are presented. Explicit analysis of potential-dependent mechanisms shows how subtle changes in conditions alter ORR reaction processes. Importantly, a kinetics-based model reproduces experimental observations for products and quantitative potential ranges.

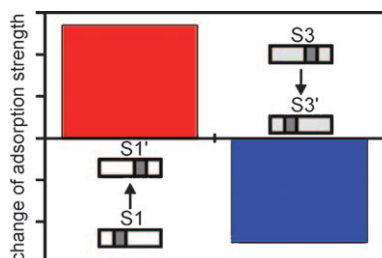


Neighboring-group participation: Anchimeric assistance of the carboxylate group accelerates the attack of the electrophiles at the double bond of the proline-derived enamine **A** by a factor of about 50.

Organocatalysis

T. Kanzian, S. Lakhdar,
H. Mayr* _____ **9526–9529**

Kinetic Evidence for the Formation of Oxazolidinones in the Stereogenic Step of Proline-Catalyzed Reactions



On the surface of it: Experimental and computational analyses for a hybrid peptide–substrate system showed that changing the position of a proline residue in synthetic peptides changes their adsorption onto semiconductors substantially and predictably (see picture with a Si(100) surface). Such information is essential for the formation of novel peptide–solid interfaces for nanotechnological applications.

Hybrid Interfaces

M. Bachmann, K. Goede,*
A. G. Beck-Sickinger, M. Grundmann,
A. Irback, W. Janke _____ **9530–9533**

Microscopic Mechanism of Specific Peptide Adhesion to Semiconductor Substrates



Supporting information is available on www.angewandte.org (see article for access details).



A video clip is available as Supporting Information on www.angewandte.org (see article for access details).

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Spotlight on Angewandte's Sister Journals _____ **9314–9316**

Keywords _____ **9534**

Authors _____ **9535**

Vacancies _____ **9321**

Preview _____ **9537**

Retraction

The following article from *Angewandte Chemie International Edition*, “Stable Aziridinium Salts as Versatile Intermediates: Isolation and Regio- and Stereoselective Ring-Opening and Rearrangement”, published online on January 13, 2009 in Wiley Online Library (www.onlinelibrary.wiley.com, DOI: 10.1002/anie.200805244) and in print (*Angew. Chem. Int. Ed.* **2009**, *48*, 1328–1330), has been retracted by agreement between the corresponding author, the journal Editor, Dr. Peter Göltz, and Wiley-VCH. The retraction has been agreed upon because by performing additional NMR analyses and preparing authentic reference compounds, the authors discovered that the structures of the aziridinium ions **3** were incorrectly assigned.

Stable Aziridinium Salts as Versatile Intermediates: Isolation and Regio- and Stereoselective Ring-Opening and Rearrangement

H. A. Song, M. Dadwal, Y. Lee, E. Mick,
H.-S. Chong* _____ **1328–1330**

Angew. Chem. Int. Ed. **2009**, *48*

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