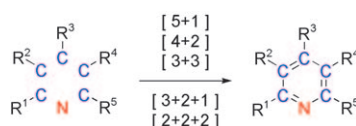


Closing the ring: Modification of traditional condensation strategies continues to be a recurrent theme in contemporary literature. Advancements in transition-metal-catalyzed cyclization and cross-coupling procedures offer new routes to functionalized pyridine derivatives (see scheme).

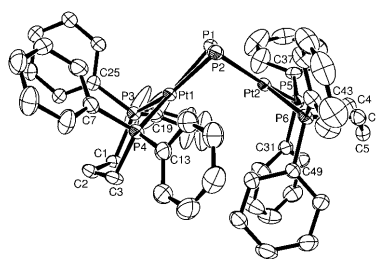


Heterocycles

*M. D. Hill** 12052–12062

Recent Strategies for the Synthesis of Pyridine Derivatives

Mind your P's and Pt's! Reaction of a 14-electron [Pt(dppp)] (dppp = 1,3-bis-(diphenylphosphino)propane) fragment, generated in situ at low temperature, or a 16-electron species [Pt(dppp)-(diphenylacetylene)] with 0.5 equivalents of P₄ resulted in the formation of a single complex, incorporating a dinuclear {Pt₂(μ,η^{2,2}-P₂)} fragment (see graphic). A charge decomposition analysis showed four of the five highest occupied orbitals to possess between 39 and 52% of the electron density on the P₂ fragment.

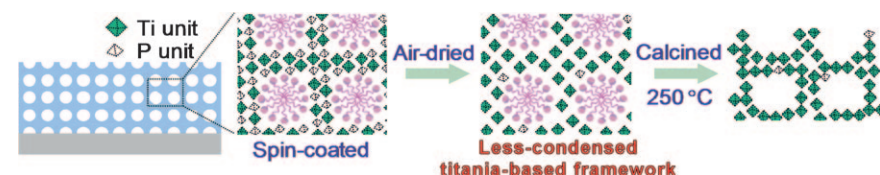


COMMUNICATIONS

Main Group Elements

*M. Demange, X.-F. Le Goff, P. Le Floch, N. Mézailles** 12064–12068

P₄ Activation with Pt⁰ Metal Centers: Selective Formation of a Dinuclear {Pt₂(μ,η^{2,2}-P₂)} Complex



Framework management: A method of preventing the continuous condensation of transition-metal species in solution by adding triethyl phosphite is proposed. Condensation reactions between titanium species are inhibited by the presence of the phosphite,

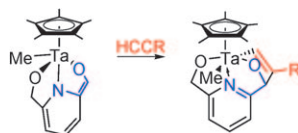
which results in less-condensed titania-based frameworks (see figure). The calcination temperature controls the framework crystallinity and mesoporosity to give anatase nanocrystal films with high photocatalytic performance.

Mesoporous Materials

T. Kimura, Y. Yamauchi, N. Miyamoto* 12069–12073

Condensation- and Crystallinity-Controlled Synthesis of Titanium Oxide Films with Assessed Mesopores

Cleavage and coupling: The sequential C–H activation/C–C coupling processes on a tantalum-bound pincer ligand render a variety of tetradentate ligands (see scheme).



Organometallic Complexes

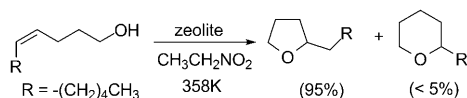
A. Conde, R. Fandos, C. Hernández, A. Otero,* A. Rodríguez* 12074–12078

C–H Bond Cleavage and Regioselective C–C Coupling on a Tantalum-Bound Pincer Ligand

Zeolites

E. Pérez-Mayoral, I. Matos, I. Fonseca, J. Čejka* 12079–12082

Zeolites Efficiently Promote the Cyclization of Nonactivated Unsaturated Alcohols



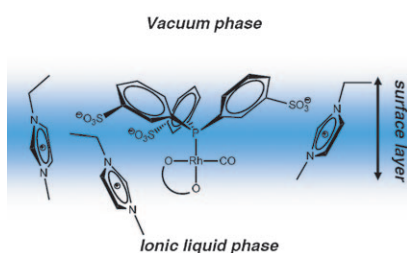
Excellent cyclization: Zeolites H-BEA, H-MFI, H-FAU, and H-STF were found to be efficient, selective, and reusable catalysts in the cyclization of *cis*-4-decenol, affording the corresponding tetrahydrofuran with excel-

lent yields to provide a new synthetic route to alkylfurans. Brønsted and Lewis acid sites in the zeolites under study are probably the active sites, because both of them catalyze this reaction.

Ionic Liquids

C. Kolbeck, N. Paape, T. Cremer, P. S. Schulz, F. Maier, H.-P. Steinrück,* P. Wasserscheid 12083–12087

Ligand Effects on the Surface Composition of Rh-Containing Ionic Liquid Solutions Used in Hydroformylation Catalysis

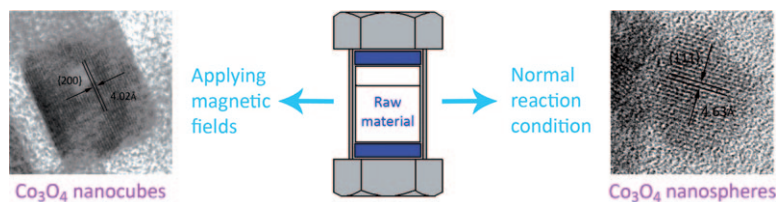


The chemical surface composition of Rh-containing ionic liquid solutions has been studied by angle-resolved X-ray photoelectron spectroscopy (ARXPS). Rh–tppts complexes of high relevance for multiphase hydroformylation catalysis showed remarkable surface activity, whereas non-tppts containing systems showed Rh depleting from the surface (tppts = tris(3-sodium sulfonatophenyl)phosphine).

Magnetic Properties

M. Wang, Q. Chen* 12088–12090

Experimental and Theoretical Investigations on the Magnetic-Field-Induced Variation of Surface Energy of Co_3O_4 Crystal Faces



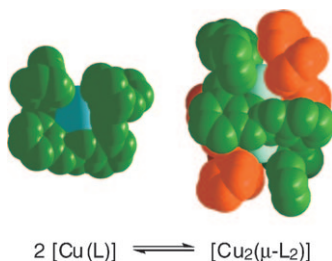
Morphological control by magnetic fields: The application of magnetic fields is found to result in fluctuation of the energy of the Co_3O_4 crystal surface, which hinders the growth of {100} faces, and thus leads to the preferred

formation of Co_3O_4 nanocubes. However, in the absence of external magnetic fields during synthesis, only irregular Co_3O_4 nanospheres can be obtained (see graphic).

Helicates

G. Bauer, Z. Benkő, J. Nuss, M. Nieger, D. Gudat* 12091–12095

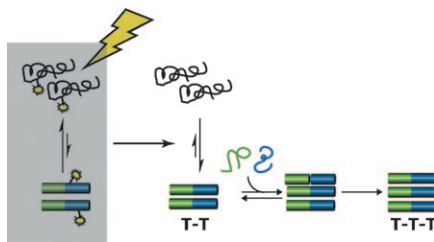
Assembly and Disassembly of a Metastable Bis-phosphine-Based Copper(I) Helicate



Taking turns: Reaction of an anionic bis-phosphine with Cu^+ produces a monomeric complex that crystallizes as a dimeric helicate (see picture). The helicate dissolves again in non-coordinating solvents, but disassembles upon addition of a donor solvent. The observed behavior implies that the helicate is metastable in solution, and persists only because its disassembly is impeded by a high kinetic barrier.

Light up the replication, please!

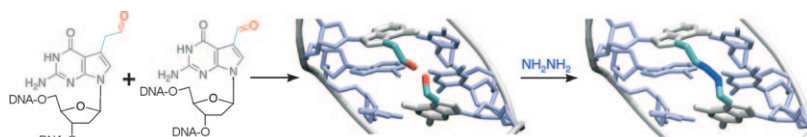
De novo designed coiled coil proteins can be triggered by light (see figure) to control their self-replication of the templates (**T**) and thereby induce selective product formation within small chemical networks.



Self-Replication

Z. Dadon, M. Samiappan,
E. Y. Safranchik,
G. Ashkenasy* 12096–12099

Light-Induced Peptide Replication Controls Logic Operations in Small Networks



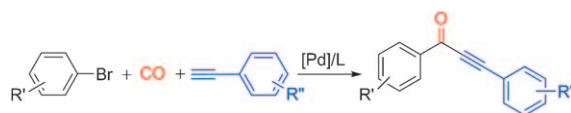
Nitrogen mustard reloaded: Over 60 years after nitrogen mustards (NMs) were the first agents used to treat tumors by chemotherapy, we provide a method to generate the main DNA

adduct formed by NMs and validate them by using molecular dynamics simulations (see graphic). We are able to provide amounts that permit extensive structural and biological studies.

Oligonucleotide Synthesis

A. Guainazzi, A. J. Campbell,
T. Angelov, C. Simmerling,*
O. D. Schärer* 12100–12103

Synthesis and Molecular Modeling of a Nitrogen Mustard DNA Interstrand Crosslink



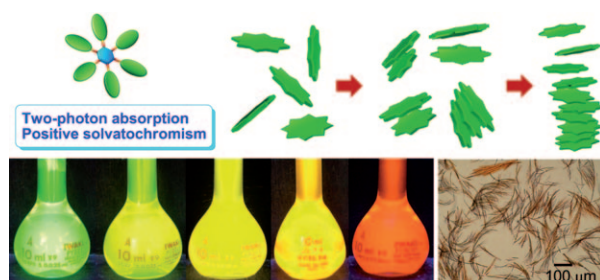
Convenient carbonylations: An efficient methodology for the carbonylative Sonogashira reaction of aryl bromides has been developed (see scheme). Contrary to known proce-

dures, inexpensive aryl bromides can be applied as substrates to give the desired compounds in moderate to good yields (47–88 %).

Carbonylation

X.-F. Wu, H. Neumann,
M. Beller* 12104–12107

A General and Convenient Palladium-Catalyzed Carbonylative Sonogashira Coupling of Aryl Bromides



Shining star: Star-shaped hexakis(oligothienylethynyl)benzene with C_6 symmetry shows solvatochromic fluorescence with a marked redshift in emission. Furthermore, the star-shaped molecule shows a fairly large two-

photon absorption property. Interestingly, the molecule forms fluorescent fibrous materials from hexane, DMF, and isopropyl alcohol owing to its disc-like structure (see graphic).

Supramolecular Chemistry

T. Narita, M. Takase, T. Nishinaga,
M. Iyoda,* K. Kamada,*
K. Ohta 12108–12113


Star-Shaped Oligothiophenes with Unique Photophysical Properties and Nanostructured Polymorphs

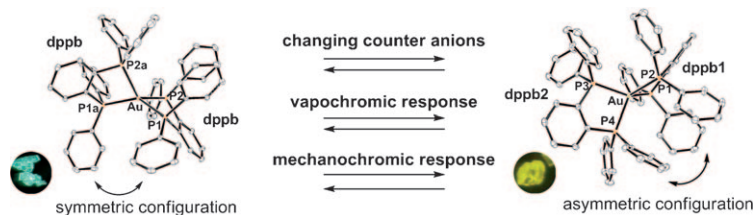


FULL PAPERS

Phosphorescence

M. Osawa,* I. Kawata, S. Igawa,
M. Hoshino, T. Fukunaga,
D. Hashizume 12114–12126

 **Vapochromic and Mechanochromic Tetrahedral Gold(I) Complexes Based on the 1,2-Bis(diphenylphosphino)benzene Ligand**




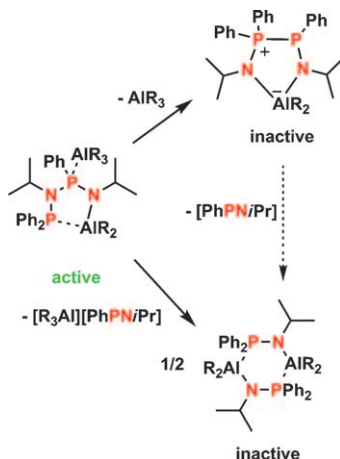
Phosphorescence color alteration: A small conformational change of two 1,2-bis(diphenylphosphino)benzene (dppb) ligands in tetrahedral Au^I complexes is caused by changing the coun-

ter anion or by external stimuli (volatile organic compounds and mechanical grinding), giving rise to the remarkable phosphorescence color alteration (see scheme).

Coordination Chemistry

S. Peitz, N. Peulecke, B. R. Aluri,
B. H. Müller, A. Spannenberg,
U. Rosenthal,* M. H. Al-Hazmi,
F. M. Mosa, A. Wöhl,
W. Müller* 12127–12132

 **Activation and Deactivation by Temperature: Behavior of Ph₂PN-(iPr)P(Ph)N(iPr)H in the Presence of Alkylaluminum Compounds Relevant to Catalytic Selective Ethene Trimerization**

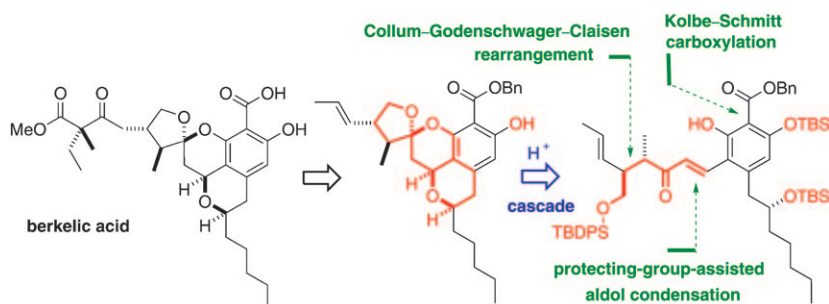


Chemical transformer: Coordination, deprotonation, rearrangement, and cleavage of Ph₂PN(*i*Pr)P(Ph)N(*i*Pr)H (**1**) by R₃Al (R = Me, Et) are all relevant for a selective ethene trimerization system consisting of **1**, CrCl₃·(THF)₃, and Et₃Al that produces 1-hexene in more than 90% yield and high purity (see scheme). This chemistry gives an insight into possible activation and deactivation pathways, which have to be considered for a better understanding of the catalytic system and technical requirements of the trimerization process.

Total Synthesis

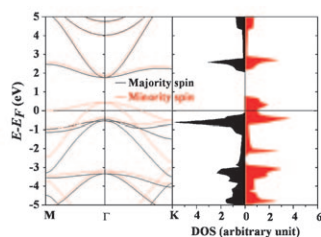
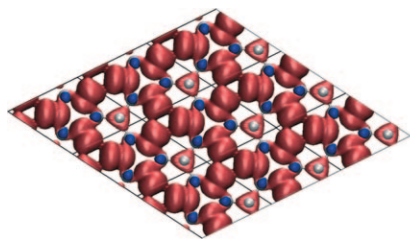
T. N. Snaddon, P. Buchgraber,
S. Schulthoff, C. Wirtz, R. Mynott,
A. Fürstner* 12133–12140

 **Total Synthesis of Berkelic Acid**



Queue up: Three deprotection and three bond-forming reactions, all of which are effected just by a trace of HCl, zip an easily attained enone to the polycyclic core of berkelic acid in diastereomerically pure form and

essentially quantitative yield. This cascade process paves the way to a concise and effective total synthesis of this alleged metalloproteinase-3 inhibitor and cytotoxic metabolite derived from an extremophilic fungus.



Half the metal! A new 2D organic half metal, the 2,4,6-tri-(1,3,5-triazinyl)-methyl radical polymer, is predicted to be a candidate for a complete spin-

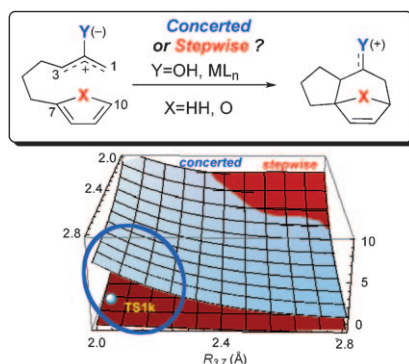
polarized carrier source (see graphic). It should not only be a half metal, but it should also show spontaneous magnetic ordering behavior.

Organic Half Metals

*E. C. Lee, Y. C. Choi, W. Y. Kim, N. J. Singh, S. Lee, J. H. Shim, K. S. Kim** 12141–12146

A Radical Polymer as a Two-Dimensional Organic Half Metal

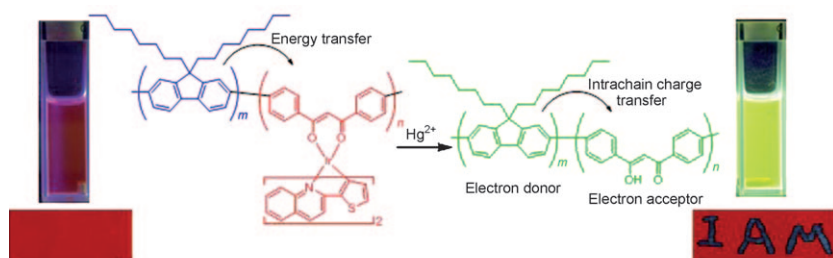
Concerted or stepwise? We present a comparison between classical oxyallyl cation–diene cycloadditions and the analogous reaction involving a metal moiety (see scheme) in terms of activation barriers, synchronicity, and aromaticity of the corresponding transition states. The factors that control the concertedness of the process are analyzed theoretically and discussed.



Reaction Mechanisms

I. Fernández, F. P. Cossío,* A. de Cózar, A. Lledós, J. L. Mascareñas* 12147–12157

Concerted and Stepwise Mechanisms in Metal-Free and Metal-Assisted [4+3] Cycloadditions Involving Allyl Cations



A mercurial disposition: A series of simple conjugated polymers that contain iridium(III) complexes in their backbones have been designed and synthesized. They are capable of ratio-

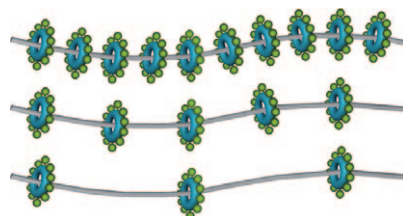
metric optical sensing of mercury(II) with high sensitivity and selectivity and can function as polymer chemodosimeters (see image).

Conjugated Polymers

H.-F. Shi, S.-J. Liu, H.-B. Sun, W.-J. Xu, Z.-F. An, J. Chen, S. Sun, X.-M. Lu, Q. Zhao, W. Huang** 12158–12167

Simple Conjugated Polymers with On-Chain Phosphorescent Iridium(III) Complexes: Toward Ratiometric Chemodosimeters for Detecting Trace Amounts of Mercury(II)

Wheels on a string: Pseudopolyrotaxane carbohydrate clusters can be prepared by threading cucurbit[6]uril-based mannose wheels on a polyviologen polymer string through host–guest interactions (see graphic). The mannose units of the clusters selectively bind to the FimH proteins on *E. coli* ORN 178 to induce efficient aggregation of the bacteria. Moreover, the clusters show effective inhibition of bacterial adhesion to urinary epithelial cells.




Pseudopolyrotaxanes

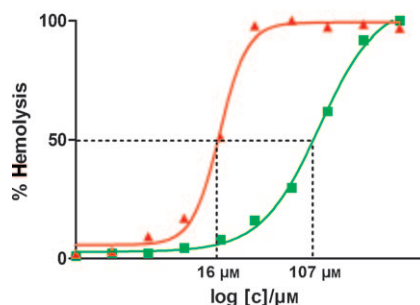
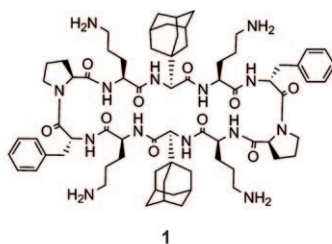
*J. Kim, Y. Ahn, K. M. Park, D.-W. Lee, K. Kim** 12168–12173

Glyco-pseudopolyrotaxanes: Carbohydrate Wheels Threaded on a Polymer String and Their Inhibition of Bacterial Adhesion

Peptide Antibiotics

V. V. Kapoerchan, A. D. Knijnenburg,
M. Niamat, E. Spalburg,
A. J. de Neeling, P. H. Nibbering,
R. H. Mars-Groenendijk, D. Noort,
J. M. Otero, A. L. Llamas-Saiz,
M. J. van Raaij, G. A. van der Marel,
H. S. Overkleef, M. Overhand* 12174–12181


 **An Adamantyl Amino Acid Containing Gramicidin S Analogue with Broad Spectrum Antibacterial Activity and Reduced Hemolytic Activity**



Fighting the resistance: Nine analogues of the cyclic antimicrobial peptide gramicidin S (GS) were synthesized, each with a different amphiphilic profile. These peptides were evaluated for their antibacterial and hemolytic activity. Peptide **1** (■) displayed improved antibacterial activity and reduced hemolytic activity relative to that of the natural product (▲).

Microwave Chemistry

B. Gutmann, D. Obermayer,
B. Reichart, B. Prekodravac, M. Irfan,
J. M. Kremsner,
C. O. Kappe* 12182–12194

 **Sintered Silicon Carbide: A New Ceramic Vessel Material for Microwave Chemistry in Single-Mode Reactors**



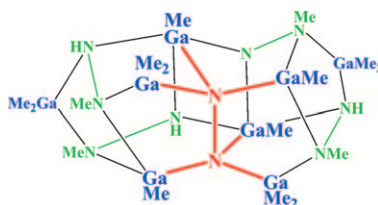
- High corrosion resistance
- Melting point 2700 °C
- High microwave absorptivity
- High thermal conductivity and effusivity
- Hardness second only to diamond

Simulating conductive heat transfer in a microwave: Using reaction vials made out of strongly microwave-absorbing silicon carbide (SiC) in a microwave reactor simulates a conductively heated autoclave experiment due to efficient shielding of the electromagnetic field by the SiC vial. Advantages of SiC vials for microwave processing include their excellent corrosion resistance, thermal stability, and high thermal effusivity and conductivity.

Cage Compounds

W. Uhl,* B. Rezaeirad, M. Layh,
E. Hagemeyer, E.-U. Würthwein,
N. Ghavtadze, I. Kuzu ... 12195–12198


Synthesis of a GaN Cage Compound with a Hydrazinetetraide Fragment, [N–N]⁴⁻, Stabilised by Six Gallium Atoms

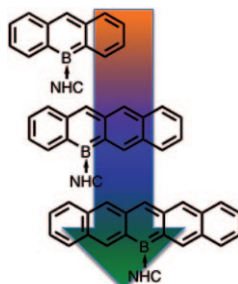


Completely deprotonated hydrazine (“pernitride”) encapsulated in a molecular framework was obtained by thermolysis of an organogallium hydrazide. The unique molecular structure comprises an [N–N]⁴⁻ group stabilised by coordination to six gallium atoms (see graphic).

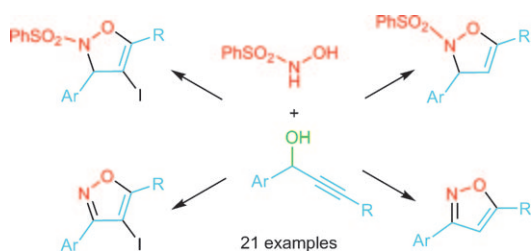
Higher Boraacenes

T. K. Wood, W. E. Piers,* B. A. Keay,
M. Parvez 12199–12206

 **Synthesis and Comparative Characterization of 9-Boraanthracene, 5-Boranaphthalene, and 6-Borapentacene Stabilized by the H₂IMes Carbene**



Just add boron: Synthetic routes to the N-heterocyclic-carbene-stabilized 5-boranaphthalene and 6-borapentacene are described and complement that previously developed for 9-boraanthracene. Comparative structural, photo-physical, and redox properties reveal narrow HOMO–LUMO gaps relative to the all-carbon acene analogues.



Strike while the iron is hot! Iron-catalyzed protocols for the selective, one-pot synthesis of four classes of substituted isoxazoles or isoxazolines from

the same propargylic alcohols, with yields of up to 94%, are described (21 examples; see scheme).

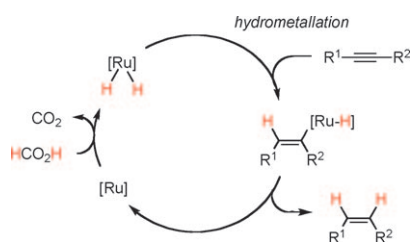
Alkyne Cyclization

O. Debleds, E. Gayon, E. Ostaszuk, E. Vrancken,
J.-M. Campagne** 12207–12213

A Versatile Iron-Catalyzed Protocol for the One-Pot Synthesis of Isoxazoles or Isoxazolines from the Same Propargylic Alcohols



A discerning transformation: *Z*-Configured C=C bonds are stereoselectively formed from alkynes in the presence of a Ru catalyst with formic acid as the sole H₂ source at room temperature (see scheme). A variety of functional groups are compatible with this novel procedure. Operational simplicity and the lack of overreduction products are characteristics for this unprecedented process.



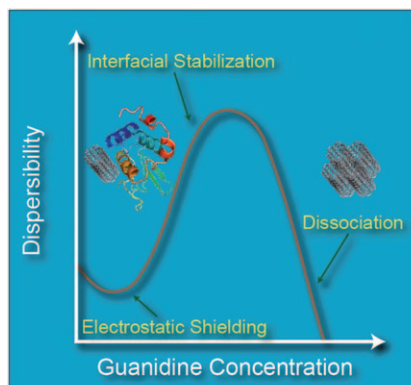
Transition-Metal Catalysis

*C. Belger, N. M. Neisius, B. Plietker** 12214–12220

A Selective Ru-Catalyzed Semireduction of Alkynes to *Z* Olefins under Transfer-Hydrogenation Conditions



Nanotube conjugates: Medium concentrations of guanidine hydrochloride (Gdn·HCl) enhance the dispersibility of protein-SWNT (single-walled carbon nanotube) conjugates without denaturation or dissociation of the protein, whereas high concentrations of Gdn·HCl dissociate the protein from the SWNT surfaces, leading to the precipitation of pristine SWNTs (see picture). The difference in the effective concentrations of Gdn·HCl is accounted for by a difference in the folding and binding stabilities of the protein on SWNTs.



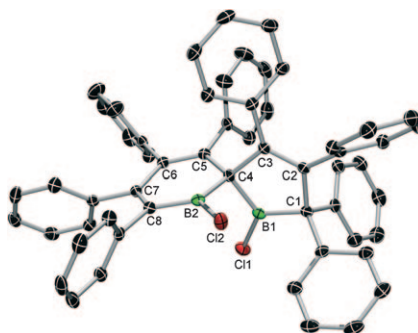
Hybrid Materials

*A. Hirano, Y. Maeda, X. Yuan, R. Ueki, Y. Miyazawa, J.-i. Fujita, T. Akasaka, K. Shiraki** 12221–12228

Controlled Dispersion and Purification of Protein–Carbon Nanotube Conjugates Using Guanidine Hydrochloride



As an extension of borole chemistry, the reduction of 1-chloro-2,3,4,5-tetraphenylborole (**1**) leads to the corresponding dianionic derivative. Dimerization of **1** under thermal conditions results in the formation of a spiro-bicyclic compound that features a boracyclohexadiene and a borolene ring (see picture). Solid-state molecular structures of all three compounds are also reported.



Boron Compounds

H. Braunschweig, C.-W. Chiu, J. Wahler, K. Radacki, T. Kupfer* 12229–12233

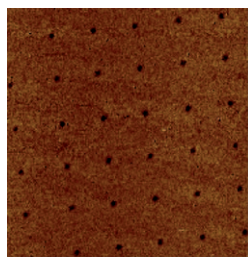
Chemical Reduction and Dimerization of 1-Chloro-2,3,4,5-tetraphenylborole



Bionanotechnology

L. S. Wong, S. J. Janusz, S. Sun,
G. J. Leggett,
J. Micklefield* 12234–12243

Nanoscale Biomolecular Structures on Self-Assembled Monolayers Generated from Modular Pegylated Disulfides



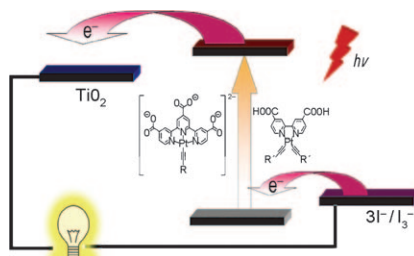
Photopatterned self-assembled monolayer array

Play it again SAM! A synthetically expedient method for the assembly of functionalised pegylated alkyldisulfides employing an alternative solid-phase synthetic strategy was successfully demonstrated. Self-assembled monolayers (SAMs) of the synthesised disulfides were characterised and shown to possess a number of desirable properties that were relevant for biological applications and amenable to near-field photolithography.

Sensitizers

E. C.-H. Kwok, M.-Y. Chan,
K. M.-C. Wong, W. H. Lam,
V. W.-W. Yam* 12244–12254

Functionalized Alkynylplatinum(II) Polypyridyl Complexes for Use as Sensitizers in Dye-Sensitized Solar Cells

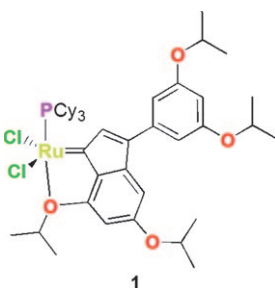


Electric company: A series of platinum(II) alkynyl-based sensitizers has been synthesized and found to show light-to-electricity conversion properties (see graphic). A dye-sensitized solar cell based on one of the complexes shows a fill factor of 0.65 and a power-conversion efficiency of 3.6%.

Transition-Metal Catalysis

A. Kabro, T. Roisnel, C. Fischmeister,*
C. Bruneau* 12255–12261

Ruthenium–Indenylidene Olefin Metathesis Catalyst with Enhanced Thermal Stability



Hot catalysts! Two new ruthenium complexes bearing a bidentate (κ^2O,C)-isopropoxy–indenylidene ligand and a PPh_3 or PCy_3 (**1**, Cy = cyclohexyl; see picture) ligand are thermally stable catalysts. Complex **1** displays a latent behavior in olefin-metathesis transformations and possesses a very high thermal stability with a half life of six days at 110 °C in $[D_8]$ toluene. This complex features very low activity at room temperature and higher activity upon thermal activation.

* Author to whom correspondence should be addressed

Supporting information on the WWW (see article for access details).

VIP Full Papers labeled with this symbol have been judged by two referees as being “very important papers”.

Video A video clip is available as Supporting Information on the WWW (see article for access details).

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