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:

M. Mascal, E. B. Nikitin*
Direct, High-Yield Conversion of Cellulose into Biofuel

P. García-Álvarez, D. V. Graham, E. Hevia, A. R. Kennedy, J. Klett, R. E. Mulvey, C. T. O Hara, S. Weatherstone*
Unmasking Representative Structures of TMP-Active Hauser and Turbo Hauser Bases

*T. Robert, J. Velder, H.-G. Schmalz**
Enantioselective Copper-Catalyzed 1,4-Addition of Grignard Reagents to Cyclohexenone Using Taddol-Derived Phosphine–Phosphite Ligands and 2-Methyl-THF as a Solvent

*A. D. Shaller, W. Wang, H. Gan, A. D. Q. Li**
Tunable Molecular Assembly Codes Direct Reaction Pathways

D. Staack, A. Fridman, A. Gutsol, Y. Gogotsi, G. Friedman**
Nanoscale Corona Discharge in Liquids Enabling Nanosecond Optical Emission Spectroscopy

*C. Hawner, K. Li, V. Cirriez, A. Alexakis**
Copper-Catalyzed Asymmetric Conjugate Addition of Aryl Aluminum Reagents to Trisubstituted Enones: Construction of Aryl-Substituted Quaternary Centers

*K. W. Eberhardt, C. L. Degen, A. Hunkeler, B. H. Meier**
One- and Two-Dimensional NMR Spectroscopy with a Magnetic-Resonance Force Microscope

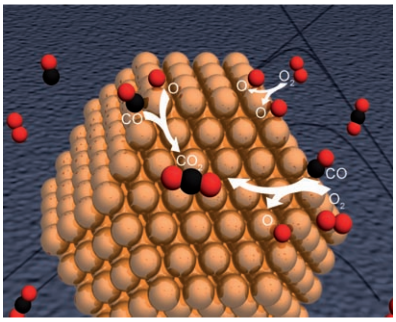
*S. Wan, J. Guo, J. Kim, H. Ihee, D. Jiang**
A Belt-Shaped, Blue-Luminescent and Semiconducting Covalent Organic Framework

N. Ziemert, K. Ishida, A. Liaimer, C. Hertweck, E. Dittmann**
Ribosomal Synthesis of Tricyclic Depsipeptides in Bloom-Forming Cyanobacteria

Books

Highlights

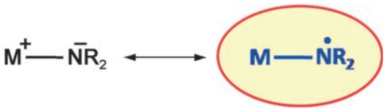
Nanocatalysis



All that glitters is not gold: A powerful computational approach using density functional theory and kinetic modeling leads the field of nanoparticle catalysis into a new era. Not only gold exhibits unique properties on the nanoscale, but also other noble and transition metals should show similar effects for a variety of catalytic reactions.

Radical Ligands

Innocent until proven ... non-innocent! Until recently, metal complexes of neutral aminyl radicals have proven very elusive in comparison to the more common metal amide valence isomer. Recent publications are discussed in which the synthesis and elucidation of genuine, isolable metal aminyl radical complexes have been realized.



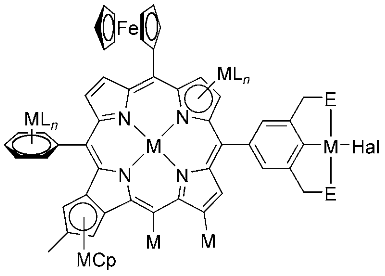
$$\overset{+}{M}-\overset{-}{N}R_2 \longleftrightarrow M-\dot{N}R_2$$

Reviews

Metalated Porphyrins

B. M. J. M. Suijkerbuijk,
R. J. M. Klein Gebbink* ____ **7396 – 7421**

Merging Porphyrins with Organometallics: Synthesis and Applications



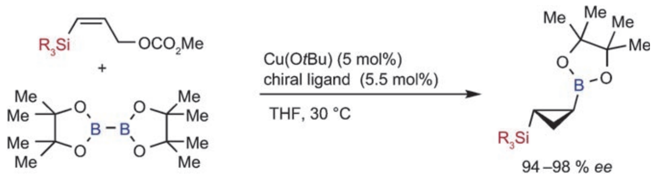
Ringing the changes: The combination of organometallic structural elements with porphyrin systems has led to many molecular metalloporphyrins with fascinating properties. This Review presents an overview of the syntheses and structural diversity of such compounds.

Communications

Asymmetric Cyclopropanation

H. Ito,* Y. Kosaka, K. Nonoyama,
Y. Sasaki, M. Sawamura* __ **7424 – 7427**

Synthesis of Optically Active Boron–Silicon Bifunctional Cyclopropane Derivatives through Enantioselective Copper(I)-Catalyzed Reaction of Allylic Carbonates with a Diboron Derivative



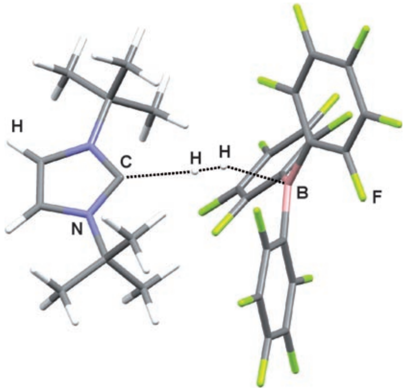
Two for the show: A copper(I)-catalyzed reaction forms boron–silicon bifunctional cyclopropane derivatives from γ-silylated allylic carbonates and a diboron species (see scheme). The reaction is highly enantioselective when a chiral bisphosphine ligand is used. The stereoelectronic effect of the silyl group induces unusual regioselectivity of the borylcopper(I) addition across the C=C double bond.

H_2 Activation

D. Holschumacher, T. Bannenberg,
C. G. Hrib, P. G. Jones,
M. Tamm* ______________ **7428 – 7432**

Heterolytic Dihydrogen Activation by a Frustrated Carbene–Borane Lewis Pair

Relief from frustration: The sterically demanding carbene 1,3-di-*tert*-butylimidazolin-2-ylidene and B(C_6F_5)$_3$, a "frustrated" Lewis pair, is a viable system for the activation of C–O, H–H, and C–H bonds. However, slow rearrangement to an abnormal carbene–borane adduct allows the irreversible formation of a strong B–C bond and enables this system to circumvent frustration at the expense of its activity.



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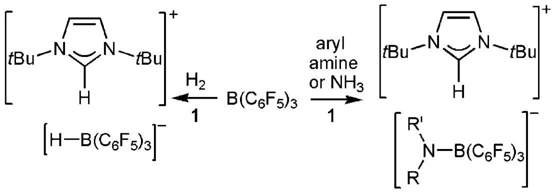
H_2 Activation

P. A. Chase, D. W. Stephan* **7433 – 7437**

Hydrogen and Amine Activation by a Frustrated Lewis Pair of a Bulky N-Heterocyclic Carbene and $B(C_6F_5)_3$

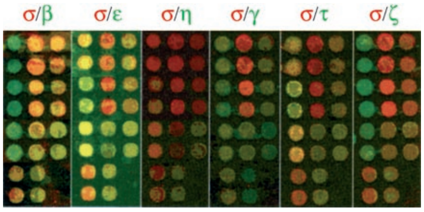


Size matters: The frustrated Lewis pair derived from $B(C_6F_5)_3$ and the sterically encumbered N-heterocyclic carbene *N*,*N*′-$tBu_2C_3H_2N_2$ (**1**) cleaves dihydrogen heterolytically to give a imidazolium borate (see scheme, left), and cleaves amine N−H bonds to form aminoborate salts (right) or aminoboranes.

Peptide Microarrays

C. H. S. Lu, H. Sun, F. B. Abu Bakar, M. Uttamchandani, W. Zhou, Y.-C. Liou, S. Q. Yao* **7438 – 7441**

Rapid Affinity-Based Fingerprinting of 14-3-3 Isoforms Using a Combinatorial Peptide Microarray

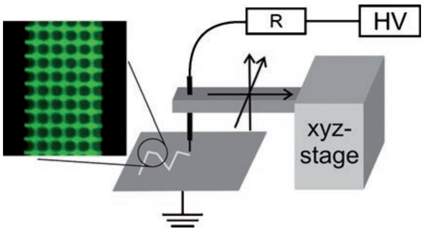


Specifying 14-3-3: A fragment-based combinatorial peptide microarray generates affinity-based fingerprints of seven mammalian 14-3-3 isoforms. High-affinity motifs are identified against the highly homologous isoforms. Putative 14-3-3σ-specific peptides were also delineated by a dual-color ratiometric screening strategy (see picture).

Surface Patterning

N. M. Suni, M. Haapala, A. Mäkinen, L. Sainiemi, S. Franssila, E. Färm, E. Puukilainen, M. Ritala, R. Kostiainen* **7442 – 7445**

Selective Surface Patterning with an Electric Discharge in the Fabrication of Microfluidic Structures



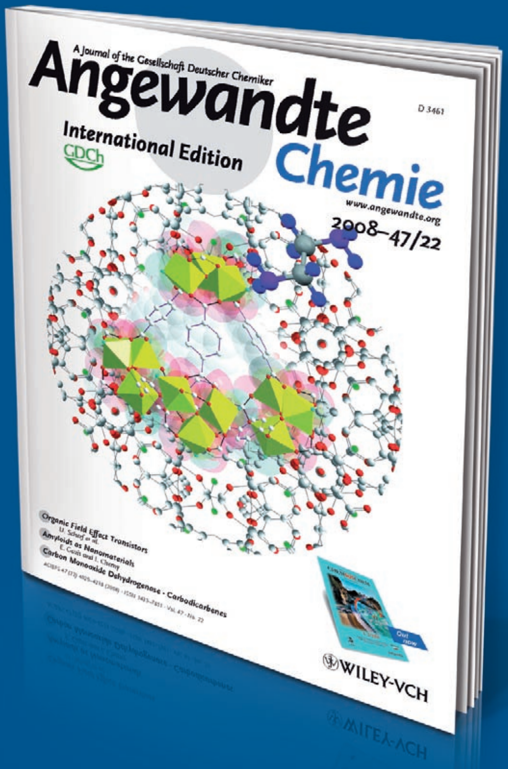
Patterned chips: Organic self-assembled monolayers on Si–SiO_2 surfaces are patterned with an electric discharge between a patterning tip and the silicon substrate (see picture). The method allows rapid patterning with simple equipment on planar, curved, and textured surfaces. It is used in the fabrication of microfluidic structures for microchip-based mass spectrometric drug analysis.

Heteroaromatic Oxidation

H. Takikawa, A. Takada, K. Hikita, K. Suzuki* **7446 – 7449**

Formation of α-Hydroxy-β-diketones through Hydroxylation of Isoxazolium Salts: Stereoselective Approach to Angular *cis*-Diols in Polycyclic Systems

Only two steps were needed for the unprecedented oxidation of isoxazoles, which is exploited in the stereocontrolled introduction of an "angular *cis*-diol" characteristic of polyketide-derived polycyclic natural products, such as **3**. In this two-step process, 1) N-methylation of isoxazole **1** and 2) stereoselective epoxidation of isoxazolium salt **2** with sodium hypochlorite followed by hydrolysis are carried out (Bn: benzyl).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Angewandte Chemie
International Edition
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D 3461
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2008–47/22
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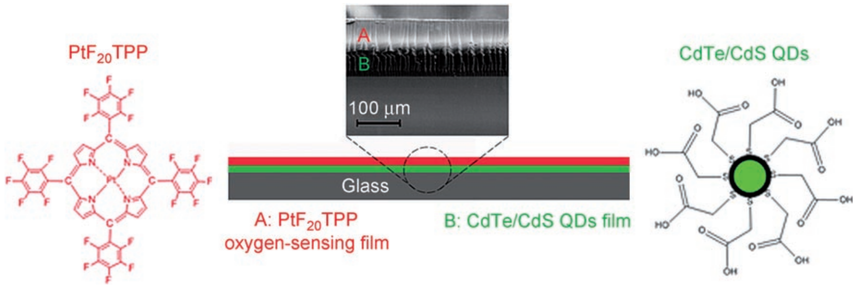
Oxygen Sensors

X. Wang, X. Chen,* Z. Xie,
X. Wang ——— **7450 – 7453**

Reversible Optical Sensor Strip for Oxygen

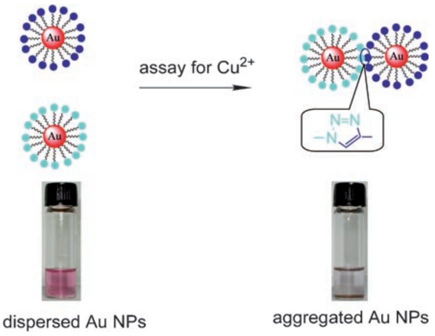


Seeing red: An optical sensor based on CdTe quantum dots (QDs) and [*meso*-tetrakis(pentafluorophenyl)porphyrinato]-platinum(II) ($PtF_{20}TPP$; $\lambda_{em,max} = 648$ nm, red), achieves both colorimetric and quantitative determination of oxygen. The sensor strip is reversible in its response and can be reused.

Click Chemistry

Y. Zhou, S. Wang, K. Zhang,
X. Jiang* ——— **7454 – 7456**

Visual Detection of Copper(II) by Azide- and Alkyne-Functionalized Gold Nanoparticles Using Click Chemistry

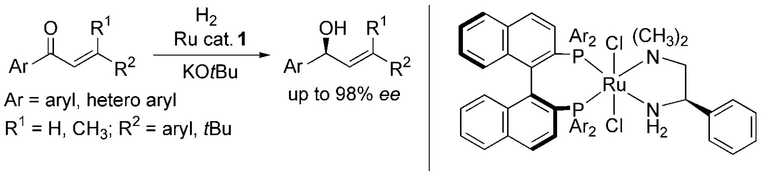


Just one click, and the color's gone: In the presence of Cu^{2+} with sodium ascorbate as a reductant, gold nanoparticles that have azide- and alkyne-terminated groups undergo aggregation as the result of Cu^{I}-catalyzed click chemistry. This process can be monitored by eye without the aid of instruments (NPs = nanoparticles).

Asymmetric Hydrogenation

N. Arai, K. Azuma, N. Nii,
T. Ohkuma* ——— **7457 – 7460**

Highly Enantioselective Hydrogenation of Aryl Vinyl Ketones to Allylic Alcohols Catalyzed by the Tol-Binap/Dmapen Ruthenium(II) Complex



1

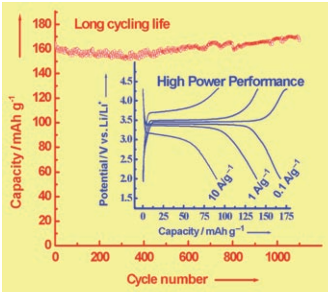
Binap catalyst doesn't dmapen expectations: In basified 2-propanol, $[RuCl_2\{(S)\text{-tol-binap}\}\{(R)\text{-dmapen}\}]$ (**1**, see picture, Ar = $4\text{-}CH_3C_6H_4$) catalyzes the highly enantioselective hydrogenation of a series of aryl vinyl ketones and affords the allylic alcohols in high yields with up to 98 % *ee*. Formation of the saturated ketones and alcohols is suppressed with triphenylphosphine when necessary.

Lithium Batteries

Y. G. Wang, Y. R. Wang, E. Hosono,
K. X. Wang, H. Zhou* ——— **7461 – 7465**

The Design of a $LiFePO_4$/Carbon Nanocomposite With a Core–Shell Structure and Its Synthesis by an In Situ Polymerization Restriction Method

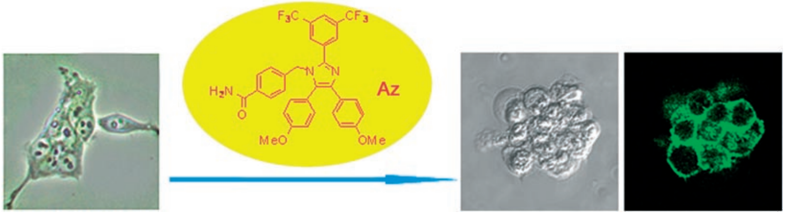
Truly long-life: A $LiFePO_4$/carbon composite containing a highly crystalline $LiFePO_4$ core with a size of about 20–40 nm and a semi-graphitic carbon shell with a thickness of about 1–2 nm provides both high power and very long cycling life (see picture). The synthetic method can be extended to the preparation of other materials, such as $Li_4Ti_5O_{12}$/carbon and Mn_3O_4/carbon composites.



Bioorganic Chemistry

D. R. Williams, S.-K. Ko, S. Park, M.-R. Lee, I. Shin* ——— **7466 – 7469**

An Apoptosis-Inducing Small Molecule That Binds to Heat Shock Protein 70

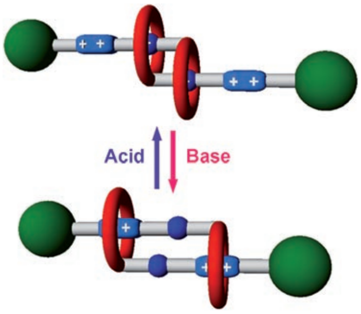


A cell-based screening approach in which annexin V was used as a staining agent identified apoptozole (Az; see scheme) as an imidazole-based molecule which induces apoptosis. Az binds to Hsc70 and Hsp70 (anti-apoptotic chaperone proteins), with dissociation constants of 0.21 and 0.14 μM, respectively, thereby inhibiting their function. Thus, Az possesses antitumor activity and is, therefore, a potential cancer therapeutic agent.

Interlocked Molecules

J. Wu, K. C.-F. Leung, D. Benítez, J.-Y. Han, S. J. Cantrill, L. Fang, J. F. Stoddart* ——— **7470 – 7474**

An Acid–Base-Controllable [c2]Daisy Chain

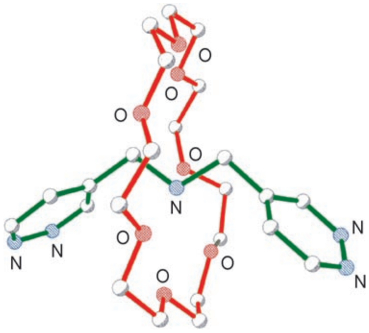


The long and the short of it: A bistable molecular muscle, based on a doubly threaded Janus-type [2]rotaxane, is assembled using a template-directed self-assembly process. Under the influence of changes in the pH value, the two identical matching components glide along one another through terminal crown ether moieties, bringing about expansion and contraction of the molecule.

Supramolecular Chemistry

C.-C. Hsu, N.-C. Chen, C.-C. Lai, Y.-H. Liu, S.-M. Peng, S.-H. Chiu* ——— **7475 – 7478**

Solvent-Free Synthesis of the Smallest Rotaxane Prepared to Date

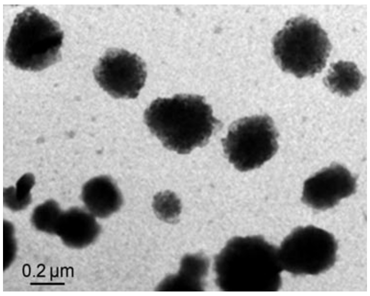


Small is beautiful: The [2]pseudorotaxane formed from dipropargylammonium tetrafluoroborate and the crown ether [21]crown-7 on SiO$_2$ was stoppered with 1,2,4,5-tetrazine in a ball-milling process (see X-ray structure). This new and efficient solvent-free reaction led to the isolation in high yield (81 %) of the smallest [2]rotaxane reported to date.

Cell Recognition

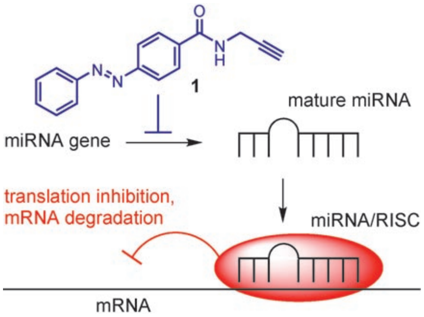
K. Cai,* Y. Hu, Z. Luo, T. Kong, M. Lai, X. Sui, Y. L. Wang, L. Yang, L. H. Deng ——— **7479 – 7481**

Cell-Specific Gene Transfection from a Gene-Functionalized Poly(D,L-lactic acid) Substrate Fabricated by the Layer-by-Layer Assembly Technique



The surface matters: Along with the degradation of the multilayer structure, galactosylated chitosan/plasmid DNA complexes (see picture) were simultaneously formed in situ for cell uptake and gene transfection. Surface-induced cell-specific recognition and in situ gene transfection were achieved.

Short, but significant, microRNAs (miRNAs) are an important class of gene regulators. Small-molecule modifiers of miRNA function, such as **1** (see schematic representation), were identified in a cellular screen for miRNA-pathway inhibitors. Such compounds are expected to be useful tools for the elucidation of detailed mechanisms of miRNA action and may serve as lead structures for the development of new therapeutic agents.

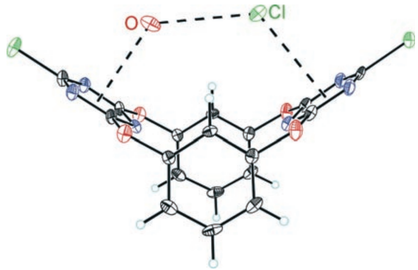


Medicinal Chemistry

K. Gumireddy, D. D. Young, X. Xiong,
J. B. Hogenesch, Q. Huang,*
A. Deiters* ________ **7482 – 7484**

Small-Molecule Inhibitors of MicroRNA miR-21 Function

Cleft of center: The self fine-tuning π-deficient cleft of 1,3-dichloro-substituted tetraoxacalix[2]arene[2]triazine forms noncovalent π–halide and π–lone-pair-electron interactions with halides Cl^- and Br^-, and water, giving rise to ternary complexes in the solid state (see structure, N blue). In solution, the host molecule, formed by a different mechanism, complexes with fluoride, giving K_a (1:1) of over 4000 M^{-1}.



Host–Guest Complexes

D.-X. Wang, Q.-Y. Zheng, Q.-Q. Wang,
M.-X. Wang* ________ **7485 – 7488**

Halide Recognition by Tetraoxacalix[2]arene[2]triazine Receptors: Concurrent Noncovalent Halide–π and Lone-pair–π Interactions in Host–Halide–Water Ternary Complexes

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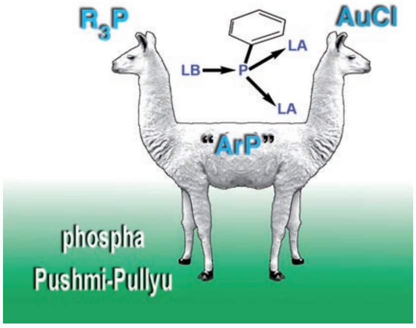
Unlike the mythical Pushmi–Pullyu beast, push–pull stabilization of phosphinidenes is a reality. $[ArP(AuCl)_2PMe_3]$ (Ar = aryl) represent interesting examples of phosphinidenes having both main group Lewis acid (LA) and Lewis base (LB) adducts. These materials have been structurally authenticated and show longer P—P bonds and greater stabilization than of purely base-stabilized phosphinidenes (in $ArP{=}PMe_3$).



Phosphanylidenes

D. V. Partyka, M. P. Washington,
J. B. Updegraff III, R. A. Woloszynek,
J. D. Protasiewicz* ________ **7489 – 7492**

Synergistic Binding of Both Lewis Acids and Bases to Phosphinidenes

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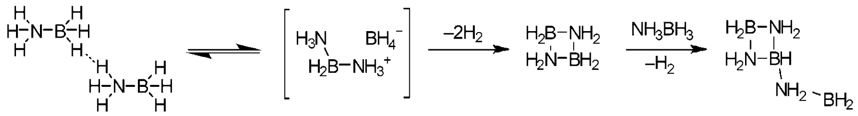


Looking to the future: The decomposition in solution of a potential hydrogen-storage compound, ammonia borane (AB), was investigated by in situ ^{11}B NMR spectroscopy and ex situ ^{15}N NMR spectroscopy. The reaction was found to be second order in AB with an activation barrier of (25 ± 2) kcal mol^{-1}. The second-order kinetics have implications for the use of solutions containing AB in high concentrations for hydrogen storage.

Hydrogen Storage

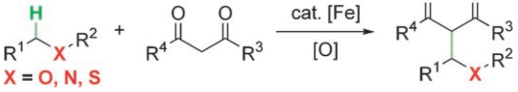
W. J. Shaw,* J. C. Linehan, N. K. Szymczak,
D. J. Heldebrant, C. Yonker,
D. M. Camaioni, R. T. Baker,
T. Autrey* ________ **7493 – 7496**

In Situ Multinuclear NMR Spectroscopic Studies of the Thermal Decomposition of Ammonia Borane in Solution

Synthetic Methods

Z. Li,* R. Yu, H. Li ________ **7497 – 7500**

Iron-Catalyzed C–C Bond Formation by Direct Functionalization of C–H Bonds Adjacent to Heteroatoms

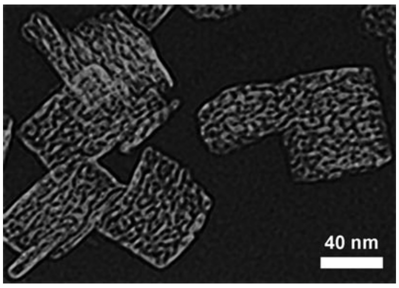


Iron/oxidant can do: Heteroatom-containing molecules are abundant in natural products, pharmaceuticals, and materials. It is highly desirable to synthesize these molecules and their derivatives by direct C–H functionalization. The novel title reaction provides a simple and efficient method to construct such molecules by using 1,3-dicarbonyl compounds (see scheme).

Transition Alumina Phases

Z. Zhang, T. J. Pinnavaia* __ **7501 – 7504**

Mesostructured Forms of the Transition Phases η- and χ-Al_2O_3

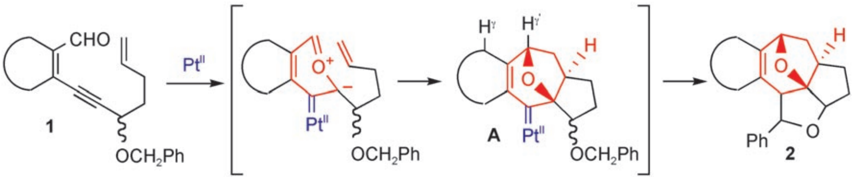


A surfactant-templated route to mesostructured forms of the transition alumina phases η-Al_2O_3 and χ-Al_2O_3 is described. The surface areas and pore-size distributions of these novel forms of alumina are substantially improved with respect to those of conventional forms of these phases. Wormholelike pores are visible in the TEM image shown of mesostructured η-Al_2O_3.

Synthetic Methods

C. H. Oh,* J. H. Lee, S. J. Lee, J. I. Kim, C. S. Hong ________ **7505 – 7507**

Intramolecular Huisgen-Type Cyclization of Platinum-Bound Pyrylium Ions with Alkenes and Subsequent Insertion into a Benzylic C–H Bond

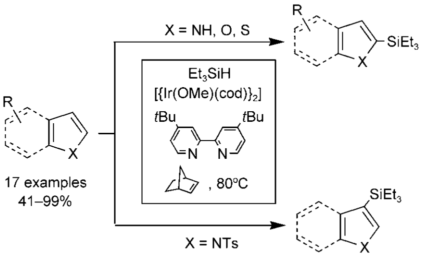


Access granted: The platinum-catalyzed cyclization of enynals **1**, which contain an additional alkene bond in their side chain, through a [3+2] cycloaddition to give tetracyclic platinum–carbene complexes **A** was followed by C–H insertion at the δ position to afford highly complex products **2**. These polycyclic compounds and related products of the title transformation are extremely difficult to access by other means.

Synthetic Methods

B. Lu, J. R. Falck* ________ **7508 – 7510**

Efficient Iridium-Catalyzed C–H Functionalization/Silylation of Heteroarenes

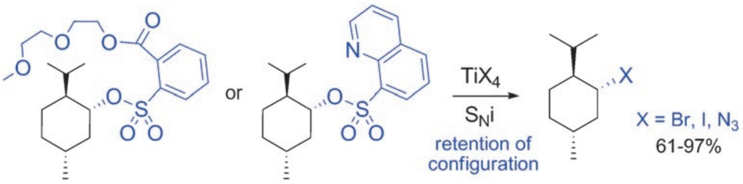


CSi investigation: The efficient iridium-catalyzed C–H functionalization/silylation of a wide variety of N-, S-, and O-heteroarenes, including N-unsubstituted indoles, is promoted by 2-norbornene and features a high level of regioselectivity (see scheme; Ts = *p*-toluenesulfonyl, cod = cyclooctadiene).

Synthetic Methods

S. D. Lepore,* D. Mondal, S. Y. Li,
A. K. Bhunia ______ **7511–7514**

Stereoretentive Halogenations and Azidations with Titanium(IV) Enabled by Chelating Leaving Groups

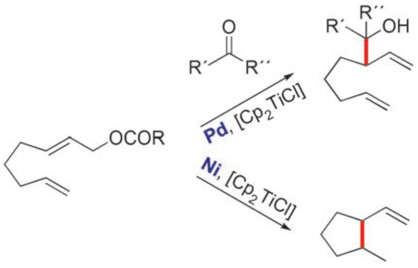


Titanium does it again! With the help of nucleophile-assisting leaving groups (NALGs), alkyl bromides, iodides, and, for the first time, azides are obtained from sulfonates with complete retention of configuration. Critical to the design of these new titanium(IV) reactions has been the use of NALGs which are thought to chelate the Lewis acid reagent in the transition state promoting an S_Ni-type mechanism.

Synthetic Methods

A. G. Campaña, B. Bazdi, N. Fuentes,
R. Robles, J. M. Cuerva,*
J. E. Oltra,* S. Porcel,
A. M. Echavarren* ______ **7515–7519**

Divergent Titanium-Mediated Allylations with Modulation by Nickel or Palladium

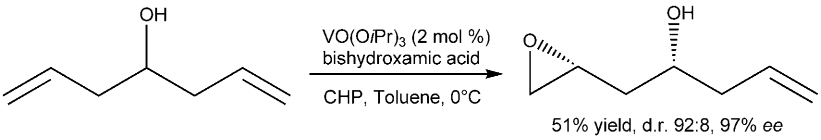


Palladium and nickel are used in conjunction with titanocene(III) complexes to perform selective allylations of carbonyl compounds and alkenes, respectively. Pd/Ti-catalyzed allylation of ketones proceeds diastereoselectively under mild conditions, whereas Ni/Ti-promoted cyclizations provide polyalkyl-substituted carbo- and heterocycles with excellent control over regio- and stereoselectivity.

Asymmetric Catalysis

Z. Li, W. Zhang,
H. Yamamoto* ______ **7520–7522**

Vanadium-Catalyzed Enantioselective Desymmetrization of *meso* Secondary Allylic Alcohols and Homoallylic Alcohols

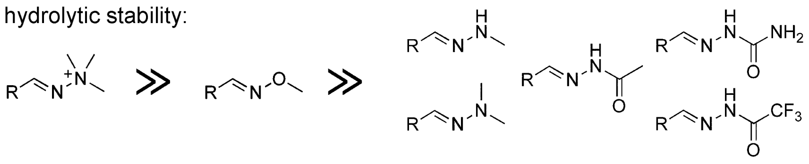


Desymmetrization isn't complex: The substrate scope for vanadium-catalyzed epoxidation has been extended. In addition to various allylic alcohols, homoallylic alcohols can also be desymmetrized by using vanadium/bishydroxamic acid complexes (see scheme; CHP = cumene hydroperoxide).

Conjugate Stability

J. Kalia, R. T. Raines* ______ **7523–7526**

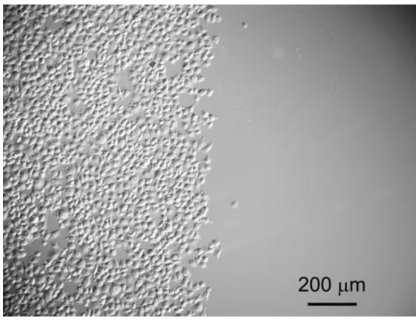
Hydrolytic Stability of Hydrazones and Oximes



Watching C 'n' N: Hydrazones and oximes are common conjugates but are labile to hydrolysis. The hydrolytic stabilities of isostructural hydrazones and one oxime were determined at pD 5.0–9.0. The rate constant for the acid-catalyzed hydrolysis of the oxime was nearly 10^3-fold lower than those for simple hydrazones, and a trialkylhydrazonium ion (formed after condensation) was even more stable than the oxime.

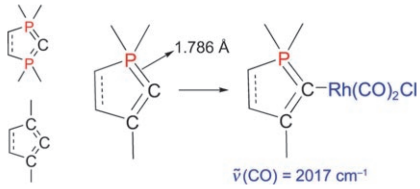
Cell Adhesion

Sticking to the time and the place: Cell adhesion can be photocontrolled spatiotemporally on a photoresponsive culture dish functionalized with a caged cell-adhesion motif, namely a nitrobenzyl-substituted argine-glycine-aspartate peptide. Photolysis of the dish cleaves the nitrobenzyl group to produce the active peptide to which HeLa cells can adhere (see micrograph: left half, irradiated).

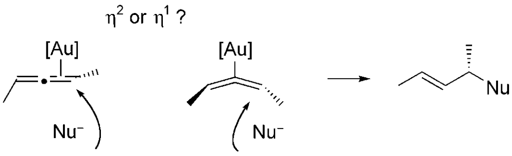


Cyclic Heteroallenes

Best of both worlds: Related to carbodiphosphoranes and carbodicarbenes (bent allenes), a cyclic vinylidenephosphorane has been isolated and is stable at room temperature (see scheme). It features a very long phosphorus ylide bond, much longer than in the acyclic version, which leaves the carbon lone pair fully available. Accordingly, this species behaves as a strong electron-donating ligand, giving rise to very robust transition-metal complexes.

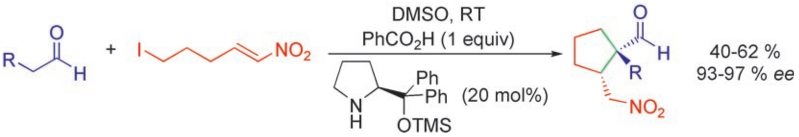


Gold Catalysis



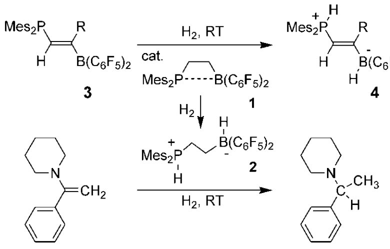
Activation of allenes toward nucleophilic attack by gold complexes ([Au], see scheme) often proceeds with axis-to-center chirality transfer. The stereochemical information is shown to be maintained in not only η^2 allene complexes, but also in bent η^1 allene complexes.

Organocatalysis



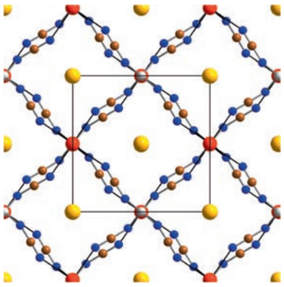
A direct approach to cyclic γ-nitroaldehydes with an all-carbon-substituted quaternary stereocenter is provided by a novel organocatalytic diastereo- and enantioselective cascade consisting of a Michael addition and an aldehyde α-alkylation (see scheme). The corresponding γ-amino acids are available in two steps.

H_2 Activation



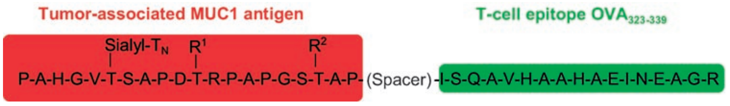
The metal-free hydrogen activator 1 catalyzes the unique P/B hydrogenation of the frustrated Lewis pair **3**, which itself is inactive toward H_2 under the applied conditions, to yield the hydrogenation product **4**. System **1**/**2** (5 mol %) also catalyzes the hydrogenation of a bulky ketimine and of enamines under mild conditions (2.5 bar H_2, RT) to yield the respective amines.

Solid-State Reactions



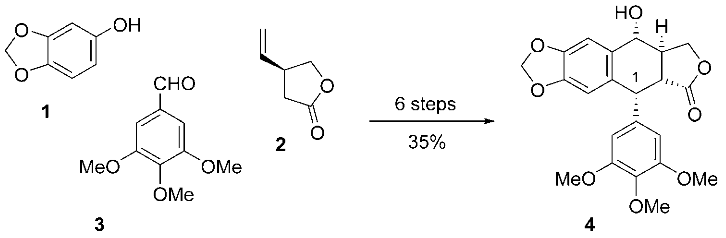
Adjustable networks: The tetracyanamidosilicates $A(RE)[Si(CN_2)_4]$ are formed by solid-state metathesis reactions and contain the novel $[Si(CN_2)_4]^{4-}$ ion. Depending on the alkali metal ion (A = K or Rb), orthorhombic or tetragonal network structures are formed in which the rare-earth (RE) ions have differently distorted trigonal-dodecahedral environments. The crystal structure of $RbLa[Si(CN_2)_4]$ is shown (Rb yellow, La red, Si gray, C brown, N blue).

Synthetic Vaccines



Selective response: The fully synthetic vaccine shown, which contains a glycopeptide antigen from the tumor-associated mucin MUC1 and an immunostimulating T-cell epitope from ovalbumin, induces a highly specific immune response in mice. The induced antibody reacts with the glycopeptides and analogues that carry additional tumor-associated T_N antigen monosaccharides in their sequence.

Natural Product Synthesis



Without further ado, the building blocks **1**–**3** were combined in three C–C bond-forming reactions to provide the enantiomerically pure natural product (−)-podophyllotoxin (**4**). The stereogenic center at C1 was generated in the key reaction, a diastereoselective iron(III)-catalyzed intermolecular Friedel–Crafts alkylation.

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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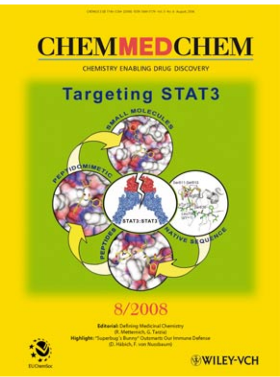

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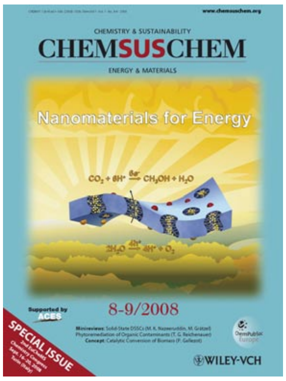

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