Angewandte Chemie
International Edition

Editorial

Service

Author Profile

"If I were not a scientist, I would be a carpenter or a goldsmith.
My favorite food is the Bratwurst at the Göttingen Christmas market …"
This and more about Dietmar Stalke can be found on page 9730.

News

G. P. Winter

R. A. Lerner

W. Uhl

H. Waldmann

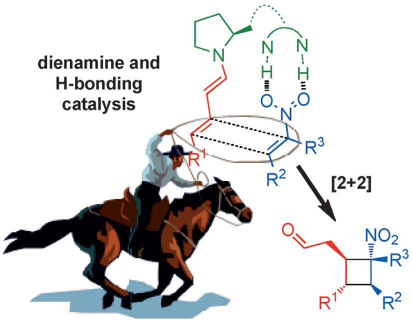
F. Schüth

Books

Highlights

Organocatalysis

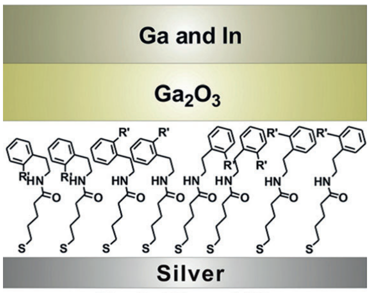
Trap it: A combination of aminocatalysis with H-bonding activation is used in two new approaches to carry out formal enantioselective organocatalyzed [2+2] cycloaddition reactions. This cooperative catalysis solves the inconveniences associated with this transformation. These two new reactions will open opportunities to find reactivities involving other organocatalytic cycloadditions.



Conducting Materials

S. L. Bernasek* ____________ **9737 – 9738**

Can We Understand the Molecule in Molecular Electronics?



R' = -H, $-NO_2$ or $-OCH_3$

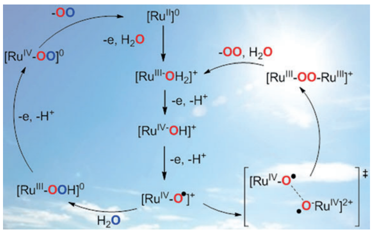
Using molecules as individual components in electronic devices promises the ultimate in miniaturization coupled with the flexibility of organic synthesis to tune the individual component. Examination of metal/molecule/metal junctions (see figure) show that organic functionality has little effect on the conductivity and rectification behavior of molecular electronic junctions, thus questioning the possible tunability of molecular electronic devices.

Minireviews

Water Chemistry

D. G. H. Hetterscheid,*
J. N. H. Reek ____________ **9740 – 9747**

Mononuclear Water Oxidation Catalysts



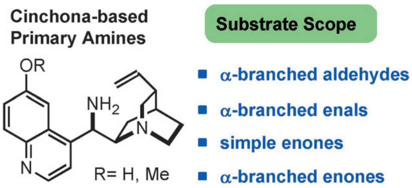
One is enough: Mononuclear water oxidation catalysts are noteworthy as they can achieve turnover frequencies similar to those of the oxygen-evolving center of Photosystem II. Several of these mononuclear catalysts are highlighted, as well as studies on their incorporation into a device that splits water upon irradiation with visible light (see scheme)—an important first step towards efficient solar energy to fuel conversion.

Reviews

Asymmetric Organocatalysis

P. Melchiorre* ____________ **9748 – 9770**

Cinchona-based Primary Amine Catalysis in the Asymmetric Functionalization of Carbonyl Compounds



Primary choice: In only five years, cinchona-based primary amine catalysis has almost equaled the high level of efficiency and reliability of aminocatalysis by proline-derived catalysts, offering the unique possibility of effecting reactions between sterically demanding carbonyl compounds (see picture).

For the USA and Canada:
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Communications

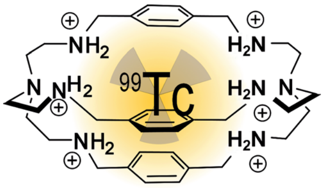
Molecular Receptors

R. Alberto, G. Bergamaschi, H. Braband, T. Fox, V. Amendola* ______ 9772 – 9776

$^{99}TcO_4^-$: Selective Recognition and Trapping in Aqueous Solution

Frontispiece

Too hot to handle: Unprecedented affinity and specificity for $^{99}TcO_4^-$ in aqueous solution was shown with the *p*-xylyl azacryptand in the hexaprotonated form (see scheme). A crystal structure of the complex reveals how the anion fits within the cavity of the cage, and the formation of multiple H-bond interactions with protonated amino groups stabilize the adduct.

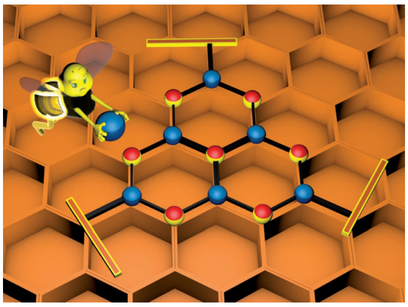


Cluster Compounds

M. C. Blanco,* J. Cámara, M. C. Gimeno, A. Laguna, S. L. James, M. C. Lagunas, M. D. Villacampa ______ 9777 – 9779

Synthesis of Gold–Silver Luminescent Honeycomb Aggregates by Both Solvent-Based and Solvent-Free Methods

Heterometallic clusters with strong luminescence have been synthesized (see picture: $Au(C\equiv CPh)_2$ yellow-red, Ag_2 blue, O red) from the metalloligand unit $[Au(C\equiv CPh)PPh_3]$ (yellow/red bars) by using both standard solvent-based and solvent-free reactions. The aggregates are stabilized only by acetylide–metal or metal–metal interactions, and their nuclearity is controlled through the addition of different donor ligands.



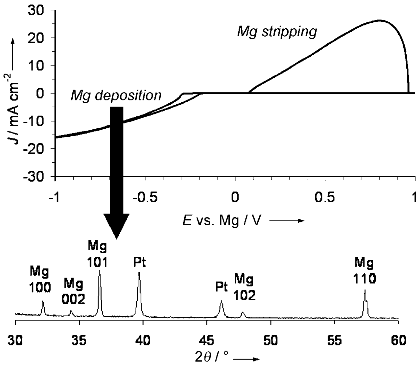
Electrochemistry

R. Mohtadi,* M. Matsui, T. S. Arthur, S.-J. Hwang ______ 9780 – 9783

Magnesium Borohydride: From Hydrogen Storage to Magnesium Battery

Front Cover

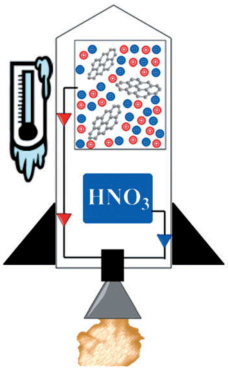
Beyond hydrogen storage: The first example of reversible magnesium deposition/stripping onto/from an inorganic salt was seen for a magnesium borohydride electrolyte. High coulombic efficiency of up to 94 % was achieved in dimethoxyethane solvent. This $Mg(BH_4)_2$ electrolyte was utilized in a rechargeable magnesium battery.



Hypergolicity

P. D. McCrary, P. A. Beasley, S. A. Alaniz, C. S. Griggs, R. M. Frazier, R. D. Rogers* ______ 9784 – 9787

Graphene and Graphene Oxide Can “Lubricate” Ionic Liquids based on Specific Surface Interactions Leading to Improved Low-Temperature Hypergolic Performance

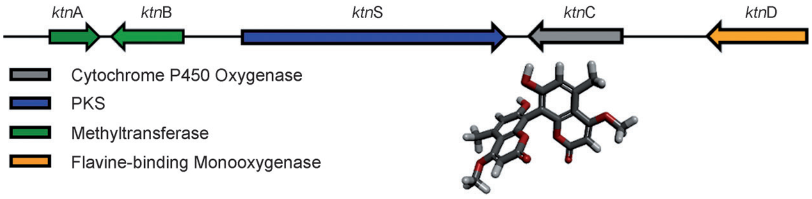


Space-qualified lubricants: Graphene and graphene oxide (r-GO) can strongly improve the low-temperature performance of hypergolic ionic liquids by reduction of viscosity. Key to success is to match the graphene type to the specific ionic-liquid functionality.

Biosynthesis

C. Gil Girol, K. M. Fisch, T. Heinekamp,
S. Günther, W. Hüttel, J. Piel,
A. A. Brakhage, M. Müller* **9788 – 9791**

Regio- and Stereoselective Oxidative Phenol Coupling in *Aspergillus niger*

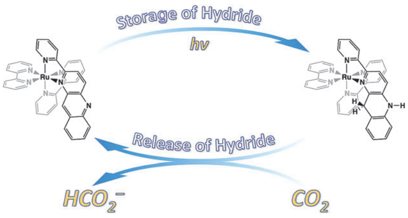


Piecing it together: *Aspergillus niger* produces kotanin (see structure) by dimerization of the monomeric, polyketide-synthase-derived (PKS) 7-demethylsiderin. A combined approach, comprising bioinformatics and gene-deletion experiments, identified the biosynthetic cluster responsible for kotanin production. Homology modeling and substrate docking provide a rationale for the regio- and stereoselective phenol coupling reaction.

Carbon Dioxide Reduction

H. Ohtsu, K. Tanaka* **9792 – 9795**

An Organic Hydride Transfer Reaction of a Ruthenium NAD Model Complex Leading to Carbon Dioxide Reduction

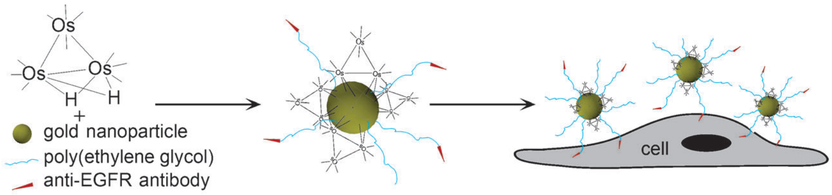


Ruthenium will fix it: CO_2 undergoes reduction to HCO_2^- when placed over a solution of a ruthenium complex bearing an NADH model ligand **1** (black in right structural formula). The organic hydride transfer is triggered by the addition of benzoate anion, which rapidly forms a complex with **1**, a complex that is a stronger reductant than **1**. A photocatalytic variant of the reaction using triethanolamine as a sacrificial reagent has also been developed.

Imaging Agents

K. V. Kong, Z. Lam, W. D. Goh,
W. K. Leong,* M. Olivo* **9796 – 9799**

Metal Carbonyl–Gold Nanoparticle Conjugates for Live-Cell SERS Imaging



Conjugates of organometallic osmium carbonyl clusters and gold nanoparticles (see picture) show a strong carbonyl signal in surface-enhanced Raman spectroscopy. The ease of bio-functionalization and the high stability and good dispersibility in aqueous solution make these conjugates excellent candidates for biomedical applications, as demonstrated by live-cell imaging with the carbonyl signals of OM-NP(PEG)-L conjugates.

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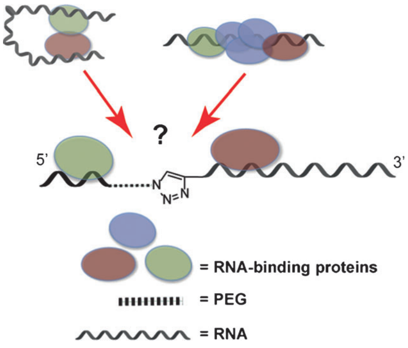
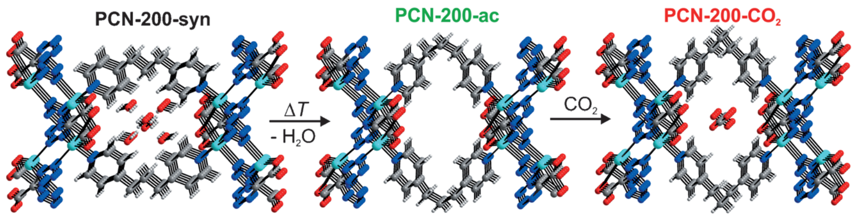
mRNA splicing

H. Lewis, A. J. Perrett, G. A. Burley,*
I. C. Eperon* **9800 – 9803**

An RNA Splicing Enhancer that Does Not Act by Looping



Out of the loop: Do the proteins bound to an enhancer site on pre-mRNA interact directly with the splice site by diffusion (looping), as is generally accepted, or does the intervening RNA play a role (see scheme)? By inserting a PEG linker between an enhancer sequence and alternative splice sites, the interaction of these two elements can be studied. Intervening RNA was essential for the enhancer activity, which rules out the looping model.



Single-molecule trap: Easy activation of the water-stable metal–organic framework PCN-200 provides a new route to low-energy selective CO_2 capture through stimuli-responsive adsorption behavior. This elastic CO_2 trapping effect was confirmed by single-component and binary gas-adsorption isotherms and crystallographic determination.

CO_2 Capture

M. Wriedt, J. P. Sculley, A. A. Yakovenko, Y. Ma, G. J. Halder, P. B. Balbuena, H.-C. Zhou* ——— **9804 – 9808**

Low-Energy Selective Capture of Carbon Dioxide by a Pre-designed Elastic Single-Molecule Trap

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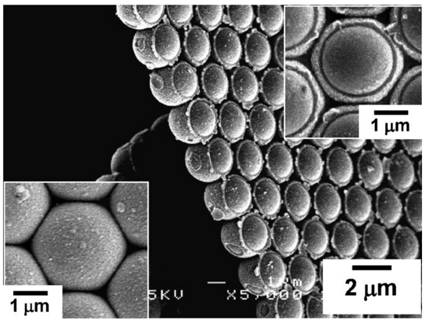
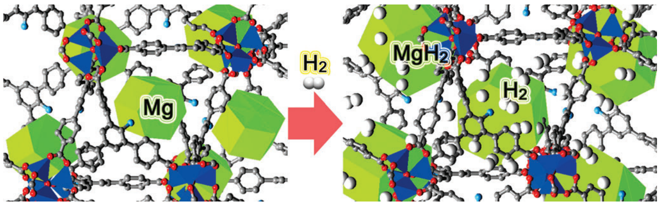


Two-faced character in a film: Soft "Janus" two-dimensional colloidal crystal films were made using polystyrene (PS) particles, on an air–water interface as a mold for a flexible polypyrrole layer. By removing the PS particles, an array of femtoliter-sized cups was produced. These two-dimensional colloidal crystal films can also be transferred onto substrates with curvature.

Flexible Materials

S. Fujii,* M. Kappl, H.-J. Butt, T. Sugimoto, Y. Nakamura ——— **9809 – 9813**

Soft Janus Colloidal Crystal Film



Hexagonal-disk-shaped magnesium nanocrystals (Mg NCs) are fabricated within a porous metal–organic framework (MOF, see picture). The Mg NCs@MOF stores hydrogen by both physi- and chemisorptions, exhibiting synergistic effects to decrease the isosteric heat of H_2 physisorption compared with that of pristine MOF, and decrease the H_2 chemisorption/desorption temperatures by 200 K compared with those of bare Mg powder.

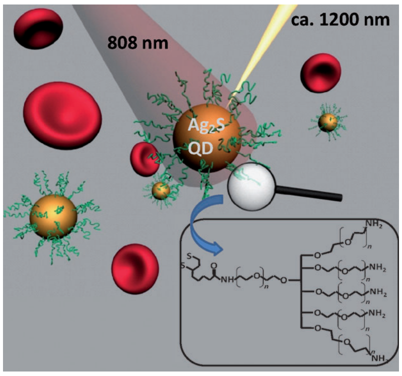
Hydrogen Storage

D.-W. Lim, J. W. Yoon, K. Y. Ryu, M. P. Suh* ——— **9814 – 9817**

Magnesium Nanocrystals Embedded in a Metal–Organic Framework: Hybrid Hydrogen Storage with Synergistic Effect on Physi- and Chemisorption

Inside Back Cover

Hits the dot: Ag_2S quantum dots (QDs) with bright near-infrared-II fluorescence emission (around 1200 nm) and six-arm branched PEG surface coating (see scheme) were synthesized for in vivo small-animal imaging. The 6PEG-Ag_2S QDs afforded a tumor uptake of approximately 10% injected dose/gram, owing to a long circulation half-life of approximately 4 h. Clearance of the injected 6PEG-Ag_2S QDs occurs mainly through the biliary pathway in mice.



Near-Infrared Imaging

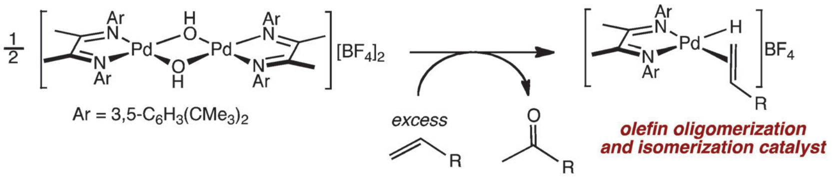
G. Hong, J. T. Robinson, Y. Zhang, S. Diao, A. L. Antaris, Q. Wang,* H. Dai* ——— **9818 – 9821**

In Vivo Fluorescence Imaging with Ag_2S Quantum Dots in the Second Near-Infrared Region

Palladium Catalysis

M. S. Winston, P. F. Oblad,
J. A. Labinger,*
J. E. Bercaw* ______ **9822 – 9824**

Activator-Free Olefin Oligomerization and Isomerization Reactions Catalyzed by an Air- and Water-Tolerant Wacker Oxidation Intermediate

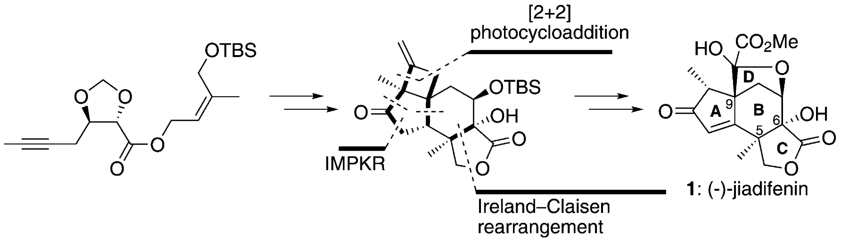


A bench-stable, hydroxy-bridged α-diimine-Pd dimer can self-activate to an olefin oligomerization and isomerization catalyst in the presence of substrate (see scheme). A cationic Pd-hydride is generated principally through a Wacker oxidation of olefin to ketone, and with C_{4+} olefins, lesser amounts of allylic C-H activation, β-H transfer, and release of diene products are observed.

Natural Product Synthesis

Y. Yang, X. Fu, J. Chen,
H. Zhai* ______ **9825 – 9828**

Total Synthesis of (−)-Jiadifenin

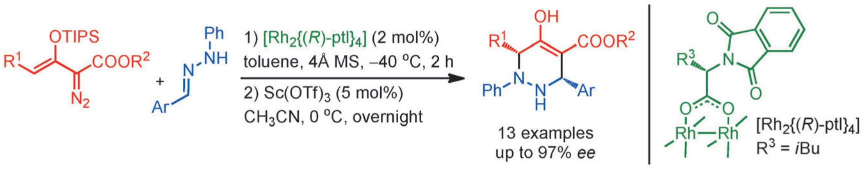


As easy as ABCD: (−)-Jiadifenin was synthesized in eighteen reaction steps from 1-[(*E*)-(4′-bromo-2′-butenyl)oxy]-4-methoxybenzene. Key features of this synthesis include: 1) Ireland–Claisen rearrangement to produce the two contiguous quaternary centers at C5 and C6 simultaneously, 2) intramolecular Pauson–Khand reaction (IMPKR) to concurrently construct the A and B rings, and 3) [2+2] photo-cycloaddition to generate the all-carbon quaternary center at C9.

Cascade Catalysis

X. Xu, P. Y. Zavalij,
M. P. Doyle* ______ **9829 – 9833**

Synthesis of Tetrahydropyridazines by a Metal–Carbene-Directed Enantioselective Vinylogous N−H Insertion/Lewis Acid-Catalyzed Diastereoselective Mannich Addition

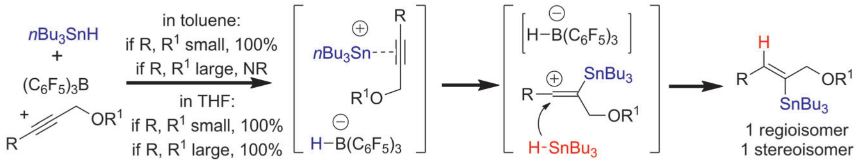


A versatile cascade of reactions, triggered by Rh^{II}-catalyzed diazo decomposition followed by a vinylogous N−H insertion/Lewis acid catalyzed Mannich addition, that produces highly substituted 1,2,3,6-tetrahydropyridazines in up to 97% *ee* with high yield and diastereocontrol has been developed.

Hydrostannylation

M. S. Oderinde,
M. G. Organ* ______ **9834 – 9837**

Studies on the Mechanism of $B(C_6F_5)_3$-Catalyzed Hydrostannylation of Propargylic Alcohol Derivatives

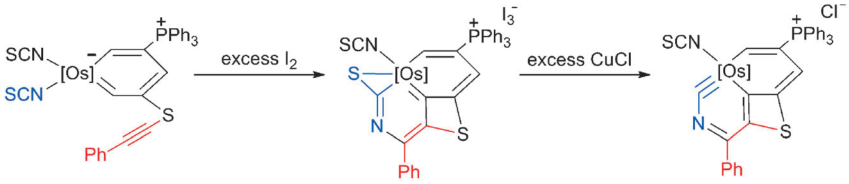


Sleight of hydride: $B(C_6F_5)_3$ catalyzes the hydrostannylation of propargylic alcohols in a regio- and stereoselective manner (see scheme). This Lewis acid first abstracts a hydride from the stannane, thus forming a borohydride/stannyl cation pair, the stability of which depends on solvent and ligands. Deuterium-labeling experiments showed that the source that delivers a hydride to the alkenyl cation is not the borohydride but rather a second molecule of stannane.

Metallacycles

T. Wang, H. Zhang, F. Han, R. Lin, Z. Lin,*
H. Xia* ——— **9838–9841**

Synthesis and Characterization of a Metallapyridyne Complex

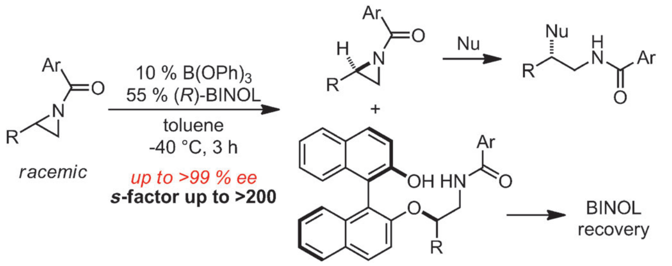


Building bridges: The first *m*-metallapyridine and the first metallapyridyne were synthesized under mild reaction conditions (see scheme). The two complexes are metal-bridged polycyclic metallabenzenoid aromatics, in which the transition-metal center is shared by both six-membered rings. The synthetic method permits the use of metallabenzene as a starting material to access higher π-electron metallaaromatics.

Enantioselective Synthesis

J. Cockrell, C. Wilhelmsen, H. Rubin, A. Martin, J. B. Morgan* ——— **9842–9845**

Enantioselective Synthesis and Stereoselective Ring Opening of *N*-Acylaziridines

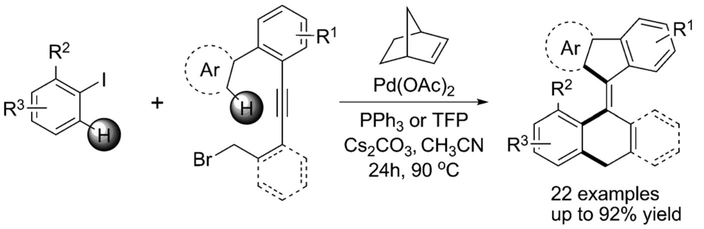


Kinetic resolution of *N*-acylaziridines by nucleophilic ring opening was achieved with (*R*)-BINOL as the chiral modifier under boron-catalyzed conditions (see scheme; Ar = 3,5-dinitrophenyl). The consumed enantiomer of aziridine can be further converted to an enantioenriched 1,2-chloroamide with recovery of (*R*)-BINOL.

Domino Reactions

H. Liu, M. El-Salfiti, M. Lautens* ——— **9846–9850**

Expeditious Synthesis of Tetrasubstituted Helical Alkenes by a Cascade of Palladium-Catalyzed C–H Activations

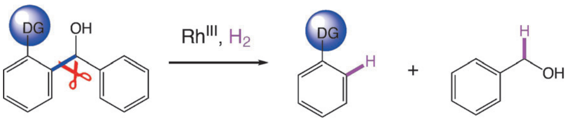


Twisted molecules: A modular approach for the synthesis of tetrasubstituted helical alkenes by a palladium-catalyzed norbornene-mediated domino reaction is presented. This intermolecular domino process allows the formation of three C–C bonds in one operation through a C–H activation/carbopalladation/C–H activation sequence.

Synthetic Methods

K. Chen, H. Li, Z.-Q. Lei, Y. Li, W.-H. Ye, Li.-S. Zhang, J. Sun, Z.-J. Shi* ——— **9851–9855**

Reductive Cleavage of the C_{sp^2}–C_{sp^3} Bond of Secondary Benzyl Alcohols: Rhodium Catalysis Directed by N-Containing Groups



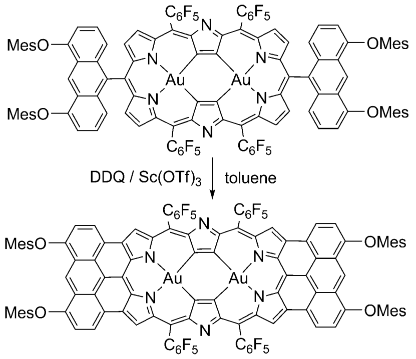
Cutting loose: 1,1-Biarylmethanol substrates undergo reductive cleavage of the C–C bond in the presence of a cationic Rh^{III} catalyst and H_2 (see scheme; DG = directing group). Various functional groups are tolerated in the reaction system. Preliminary studies indicate that a five-membered rhodacycle intermediate, which then converts into a Rh^{III} hydride species for the reduction, is involved in the catalytic cycle.

Porphyrinoids

K. Naoda, H. Mori, N. Aratani, B. S. Lee, D. Kim,* A. Osuka* ________ **9856 – 9859**

Hexaphyrin Fused to Two Anthracenes

Inside Cover

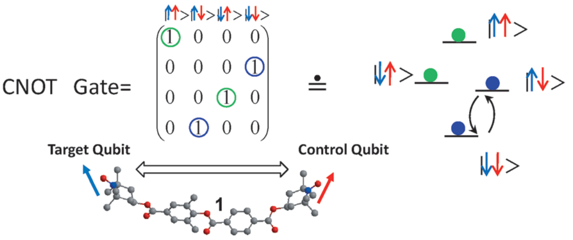


Gold standard: A bis(Au^{III}) complex containing the title compound was prepared and characterized (see scheme; DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, Tf = trifluoromethanesulfonyl). Owing to the effective conjugative network over the flat and elongated rectangular molecular frame, this complex displays a remarkably red-shifted and sharp Q-band-like band at 1467 nm, multiple reversible redox potentials, and a large TPA cross-section value.

Quantum Computer

S. Nakazawa,* S. Nishida, T. Ise, T. Yoshino, N. Mori, R. D. Rahimi, K. Sato,* Y. Morita,* K. Toyota, D. Shiomi, M. Kitagawa, H. Hara, P. Carl, P. Höfer, T. Takui* ________ **9860 – 9864**

A Synthetic Two-Spin Quantum Bit: *g*-Engineered Exchange-Coupled Biradical Designed for Controlled-NOT Gate Operations



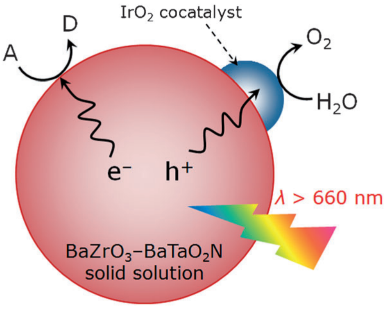
A quantum gate: A system of two coupled electron spins that is useful for simple quantum computing operations has been prepared by synthesis of a biradical **1** and co-crystallization with an isomorphous host molecule. The two weakly exchange-coupled quantum bits (target qubit blue and control qubit red) span four electron spin states. The electron spin transition is denoted by two black arrows.

Photocatalysis

K. Maeda,* K. Domen* ____ **9865 – 9869**

Water Oxidation Using a Particulate $BaZrO_3$-$BaTaO_2N$ Solid-Solution Photocatalyst That Operates under a Wide Range of Visible Light

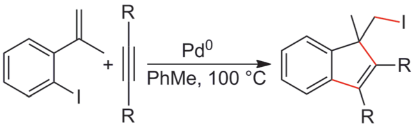
Tripping the light fantastic: Despite small band gap energies (1.7–1.8 eV), $BaZrO_3$-$BaTaO_2N$ solid solutions (Zr/Ta $\leq$ 0.1) are capable of photocatalyzing both water oxidation and reduction even under irradiation above 660 nm. Solar water splitting to form H_2 and O_2 was also demonstrated using a photoelectrochemical cell consisting of a $BaZrO_3$–$BaTaO_2N$ solid solution as an anode and a Pt wire cathode.



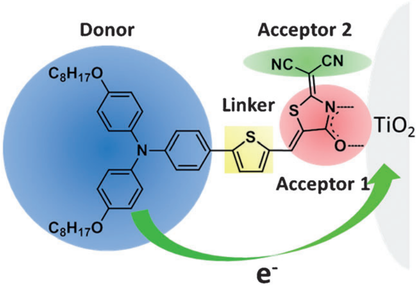
Carbohalogenation

X.-D. Jia, D. A. Petrone, M. Lautens* ________ **9870 – 9872**

A Conjunctive Carboiodination: Indenes by a Double Carbopalladation–Reductive Elimination Domino Process



Something gained, nothing lost: A Pd^0-catalyzed domino intermolecular/intramolecular process terminated by carbohalogenation is reported. In this reaction, two new C–C bonds, one new C–I bond and one five-membered ring are formed in a single step, and all of the atoms in the starting materials are incorporated into the product (see scheme).

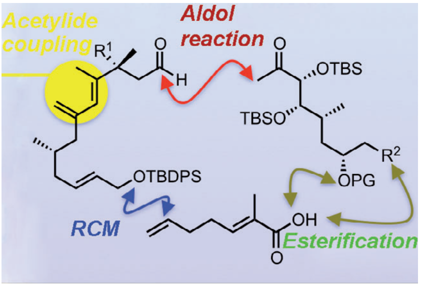


The electron acceptor 2-(1,1-dicyanomethylene) rhodanine is a promising alternative to cyanoacrylic acid as an anchoring group for organic dyes. For example, the RD-II-based dye-sensitized solar cell has an overall conversion efficiency of 7.11 % and long-term stability.

Organic Solar Cells

J. Mao, N. He, Z. Ning, Q. Zhang, F. Guo,
L. Chen, W. Wu, J. Hua,*
H. Tian* ________ **9873 – 9876**

Stable Dyes Containing Double Acceptors without COOH as Anchors for Highly Efficient Dye-Sensitized Solar Cells

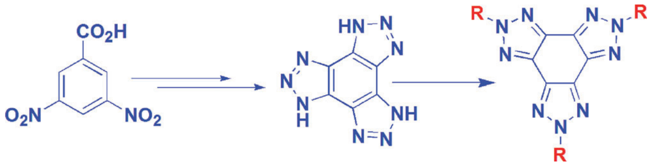


Not one, not two, but three: Total syntheses of amphidinolides B, G, and H, which exhibit strong, nanogram-scale cytotoxicity against various tumor cell lines, have been executed. The synthetic strategy relied on implementation of a diene construction protocol and a diastereoselective aldol process. The 26- and 27-membered macrocyclic lactone rings were efficiently constructed by using ring-closing metathesis (RCM).

Natural Products

A. Hara, R. Morimoto, Y. Iwasaki,
T. Saitoh, Y. Ishikawa,
S. Nishiyama* ________ **9877 – 9880**

Total Syntheses of Amphidinolides B, G, and H

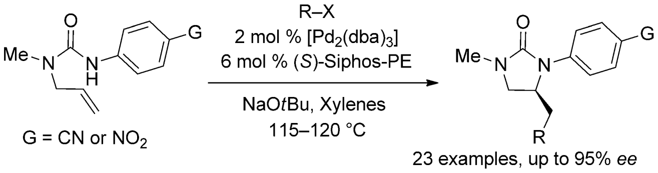


High-performance explosives: Tris(triazolo)benzene was synthesized and converted to its trinitro and trichloro derivatives (see scheme; R = NO_2, Cl). The heats of formation of this “high-nitrogen” compounds were calculated and combined with experimentally determined densities to determine detonation pressures and velocities. They exhibit high density, good thermal stability, high heats of formation, and moderate to good detonation properties.

Energetic Materials

V. Thottempudi, F. Forohor, D. A. Parrish,
J. M. Shreeve* ________ **9881 – 9885**

Tris(triazolo)benzene and Its Derivatives: High-Density Energetic Materials



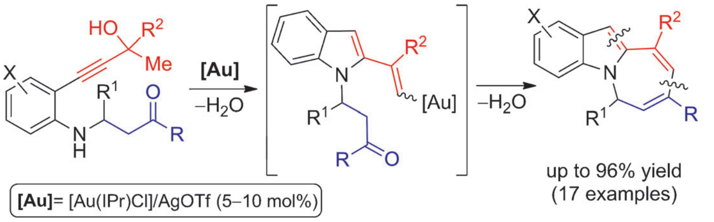
Positive water effect: A catalyst composed of $[Pd_2(dba)_3]$ (dba = dibenzylideneacetone) and (*S*)-Siphos-PE is effective for the enantioselective coupling of *N*-allyl ureas with aryl bromides to afford 4-substituted imidazolidin-2-ones. Added water leads to significantly improved enantioselectivities with electron-poor aryl halide substrates. It is suggested that the C–C bond-forming reductive elimination is the enantiodetermining step in these reactions.

Asymmetric Catalysis

B. A. Hopkins, J. P. Wolfe* _ **9886 – 9890**

Synthesis of Enantiomerically Enriched Imidazolidin-2-Ones through Asymmetric Palladium-Catalyzed Alkene Carboamination Reactions

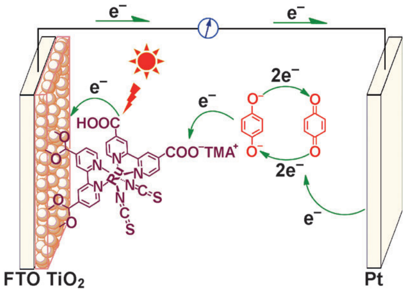
Gold Catalysis



Indoles from scratch: A gold(I)/N-heterocyclic carbene complex (IPr = 1,3-di-(isopropylphenyl)imidazol-2-ylidene) was found to be particularly effective as a catalyst, enabling the one-pot synthesis of tricyclic azepinoindoles by an unprecedented cascade reaction. Readily available substrates, high chemoselectivity, good yields, and water as the only stoichiometric by-product are some of the main advantages of this method.

Solar Cells

A hybrid electrolyte involving tetramethylammonium (TMA) hydroquinone/benzoquinone redox couple is formulated. This electrolyte is more transparent than the traditional I^-/I_3^- electrolyte and has negligible absorption in the visible region. Dye-sensitized solar cells using the hybrid electrolyte show higher light-to-electricity conversion efficiency. FTO = fluorine-doped tin oxide.



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50 Years Ago . . .

Angewandte Chemie International Edition was first published in 1962, the mother journal first in 1888. In this monthly flashback, we feature some of the articles that appeared 50 years ago. This look back can open our eyes, stimulate discussion, or even raise a smile.

Women in chemistry was a central topic of the International Year of Chemistry in 2011, and Issue 4/2011 was even dedicated entirely to this topic. 50 years ago, reports from female chemists were more rare, but still appeared in *Angewandte Chemie*: Margot Becke-Goehring and H. P. Latscha described the synthesis of the alkylated disulfur(IV) nitride $[(CH_3)_2S{-}N{=}S(CH_3)_2]Cl$. This compound was produced in 60% yield from the reaction of trithiazyl chloride with dimethyl sulfoxide. Becke-Goehring, who was the mentor of the late Rolf Appel (see recent Obituary), was Rector of the University of Heidelberg and later Director of the Gmelin Institute for Inorganic Chemistry, which was responsible for publishing the *Gmelin Handbook of Inorganic Chemistry*.

The synthesis of anionic heterosiloxanes was reported by Hubert Schmidbaur and Max Schmidt. They described how equimolar mixtures of $[\{(CH_3)_3SiO\}_3X]_2$ (X = Al or Ga) and $MOSi(CH_3)_3$ (M = Li, Na, or K) reacted in CCl_4 to produce $M[X\{OSi(CH_3)_3\}_4]$. Schmidbaur was later Chairman of the Editorial Board of *Angewandte Chemie* and an Essay by him on coordination chemistry at carbon is in press.

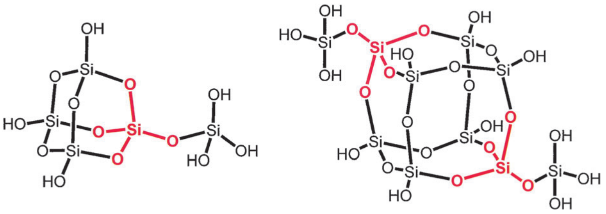
The increasing popularity of organometallic chemistry was reflected in two Communications. Hans Bock discussed the synthesis of nickel(0) dialkylcyanamide carbonyls, which were formed by the reaction of dialkylcyanamides with an excess of $Ni(CO)_4$. These compounds, which exist as orange crystals, comprise two nickel centers that are bridged by two carbonyl groups. Ernst Bayer et al. reported the synthesis of a ferrole dicarboxylic acid dimethyl ester tricarbonyl compound. Ferrole is a five-membered heterocycle that contains iron as the heteroatom and is formed by the elimination reaction of 1,4-dichlorobutadiene derivatives.

Read more in Issue 10/1962

Silicates

C. T. G. Knight, R. J. Balec,
S. D. Kinrade* ______ **9900 – 9903**

Aqueous Alkali-Metal Silicate Anions Containing Fully Condensed Four-Coordinate Sites

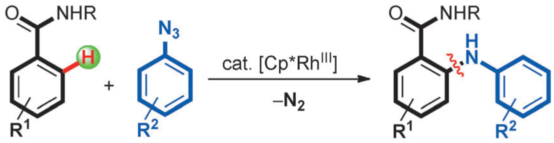


Conspicuous absence: ^{29}Si NMR studies show that highly condensed, four-coordinate Si-containing anions are common in concentrated alkali-metal silicate solutions, but reveal no evidence for the existence of specialized zeolite building units. The results add to the mounting evidence that silicate polymerization simply proceeds through stepwise condensation of monosilicate tetrahedra.

C–H Activation

J. Ryu, K. Shin, S. H. Park, J. Y. Kim,
S. Chang* ______ **9904 – 9908**

Rhodium-Catalyzed Direct C–H Amination of Benzamides with Aryl Azides: A Synthetic Route to Diarylamines

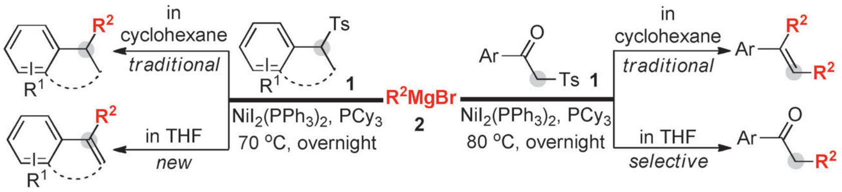


No muss, no fuss: A rhodium-catalyzed direct intermolecular C–H amination of benzamides and ketoximes using aryl azides as the amine source has been developed. The reaction exhibits a broad substrate scope with excellent functional-group tolerance, requires no external oxidants, releases N_2 as the only by-product, and produces diarylamines in high yields.

Cross-Coupling

J.-C. Wu, L.-B. Gong, Y. Xia, R.-J. Song,
Y.-X. Xie, J.-H. Li* ______ **9909 – 9913**

Nickel-Catalyzed Kumada Reaction of Tosylalkanes with Grignard Reagents to Produce Alkenes and Modified Arylketones

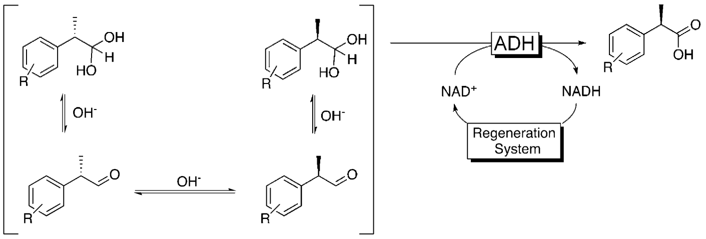


Open a new door: The first example of alkene synthesis from alkyl electrophiles with Grignard reagents using the Kumada cross-coupling reaction strategy is reported. This method opens a new door for the Kumada cross-coupling reaction, allowing alkenes to be prepared from the reaction of tosylalkanes with Grignard reagents.

Enzyme Catalysis

P. Könst, H. Merkens, S. Kara, S. Kochius,
A. Vogel, R. Zuhse, D. Holtmann,
I. W. C. E. Arends,
F. Hollmann* ______ **9914 – 9917**

Enantioselective Oxidation of Aldehydes Catalyzed by Alcohol Dehydrogenase

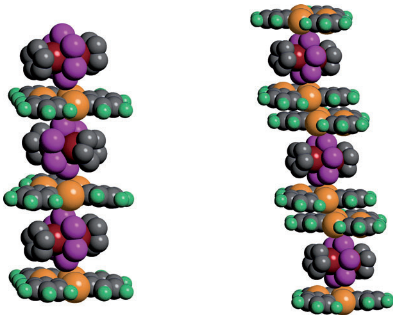


Teaching old dogs new tricks: Alcohol dehydrogenases (ADHs) may be established redox biocatalysts but they still are good for a few surprises. ADHs can be used to oxidize aldehydes, and this was demonstrated by the oxidative dynamic kinetic resolution of profens. In the presence of a suitable cofactor regeneration system, this reaction can occur with high selectivity.

Weak Interactions

M. Fleischmann, C. Heindl, M. Seidl, G. Balázs, A. V. Virovets, E. V. Peresypkina, M. Tsunoda, F. P. Gabbaï, M. Scheer* ______ **9918 – 9921**

Discrete and Extended Supersandwich Structures Based on Weak Interactions between Phosphorus and Mercury

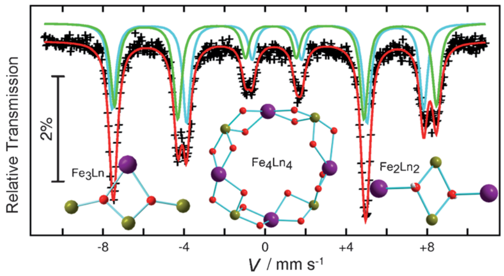


Supersized mercury: Adducts with polymeric (left) or discrete supersandwich structures (right) form from mixtures of the trinuclear mercury complex [(o-$C_6F_4Hg)_3$] (**A**) with the triple-decker complex [$(CpMo)_2(\mu\text{-}\eta^6{:}\eta^6\text{-}P_6)$] (**B**) in the solid state. This arrangement arises from P⋯Hg interactions between opposing atoms of the P_6 units and the Hg_3 units (see picture; P purple, Hg orange, F green, Mo red, C gray).

Lanthanide Anisotropy

V. Mereacre* ______ **9922 – 9925**

Differentiation of Highly Anisotropic Tb^{III} and Dy^{III} with ^{57}Fe Mössbauer Spectroscopy

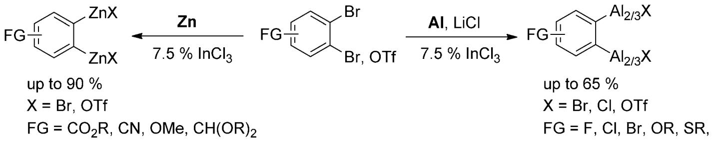


Using ^{57}Fe Mössbauer spectroscopy, three examples of coordination compounds with different topologies containing Fe^{III} and Ln^{III} ions (Dy^{III} and Tb^{III}; see diagram; insets: clusters cores) were analyzed. In the same crystal field environment, Dy and Tb ions show different degrees of anisotropy, which can be qualitatively detected using an indirect method.

1,2-Dimetallic Compounds

T. D. Blümke, T. Klatt, K. Koszinowski, P. Knochel* ______ **9926 – 9930**

$InCl_3$-Catalyzed Synthesis of 1,2-Dimetallic Compounds by Direct Insertion of Aluminum or Zinc Powder



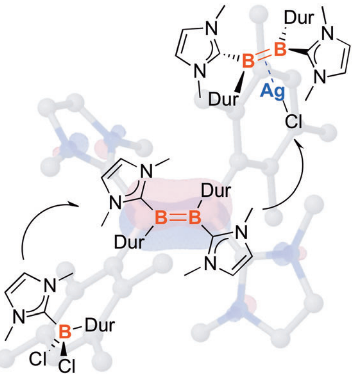
In-sertion of metal: Catalytic amounts of $InCl_3$ allow the insertion of aluminum and zinc into aromatic 1,2-dibromides or 1,2-bromotriflates (see scheme). These 1,2-dimetallic species can undergo Cu or Pd-catalyzed acylations, allylations, or cross-couplings.

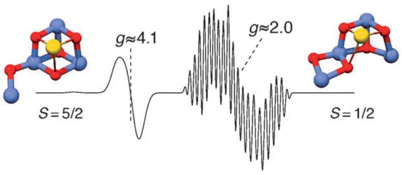
Diborenes

P. Bissinger, H. Braunschweig,* A. Damme, T. Kupfer, A. Vargas ______ **9931 – 9934**

Base-Stabilized Diborenes: Selective Generation and η^2 Side-on Coordination to Silver(I)

(B)olefin complexes: Reductive coupling of designed monoborane precursors (see scheme; Dur = 2,3,5,6-tetramethylphenyl) gives convenient access to N-heterocyclic carbene stabilized diborenes. The presence of B=B multiple bonds in the dark red diborenes is shown experimentally and theoretically. Reaction with AgCl afforded a Ag^I species with an unprecedented, olefin-like η^2 coordination mode.





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