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:

*A. Asati, S. Santra, C. Kaittanis, S. Nath, J M. Perez**
Oxidase Activity of Polymer-Coated Cerium Oxide Nanoparticles Multivalent Choline Dendrimers as Potent Inhibitors of Pneumococcal Cell Wall Hydrolysis

*J.-Q. Wang, S. Stegmaier, T. F. Fässler**
$[Co@Ge_{10}]^{3-}$: An Intermetalloid Cluster with an Archimedean Pentagonal Prismatic Structure

A. Mukherjee, M. Martinho, E. L. Bominaar, E. Münck, L. Que Jr.**
Shape-Selective Interception by Hydrocarbons of the O_2-Derived Oxidant of a Biomimetic Nonheme Iron Complex

A. Katranidis, D. Atta, R. Schlesinger, K. H. Nierhaus, T. Choli-Papadopoulou, I. Gregor, M. Gerrits, G. Büldt, J. Fitter**
Fast Biosynthesis of Green Fluorescent Protein Molecules—A Single-Molecule Fluorescence Study

L. Xu, C. E. Doubleday, K. N. Houk**
Dynamics of 1,3-Dipolar Cycloadditions of Diazonium Betaines with Acetylene and Ethylene: Bending Vibrations Facilitate Reaction

*C. Chandler, P. Galzerano, A. Michrowska, B. List**
The Proline-Catalyzed Double Mannich Reaction of Acetaldehyde with *N*-Boc imines

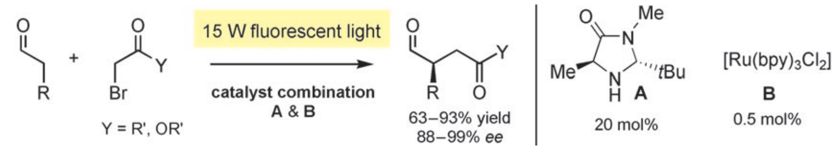
*P. Antoni, Y. Hed, A. Nordberg, D. Nyström, H. von Holst, A. Hult, M. Malkoch**
Bifunctional Dendrimers: From Robust Synthesis and Accelerated One-Pot Postfunctionalization Strategy to Potential Applications

Author Profile

Books

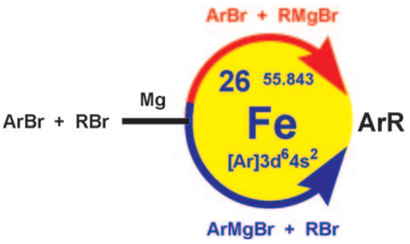
Highlights

Asymmetric Organocatalysis



Following the light: Photoredox catalysis along with aminocatalysis have proved to be the right combination for one of the most challenging asymmetric transformation in organic synthesis: the direct intermolecular α-alkylation of aldehydes.

Domino Reactions

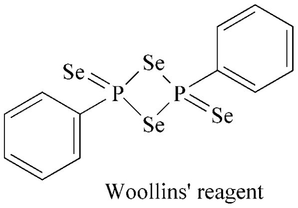


Sleeping beauty? Is the scientific community about to kiss awake iron catalysis, a topic that has been dormant for decades? A recent study on a user-friendly direct cross-coupling reaction of alkyl and aryl halides constitutes an important step toward this end through the integration of two different iron-catalyzed elementary steps into a practical one-pot procedure.

Contents

Minireviews

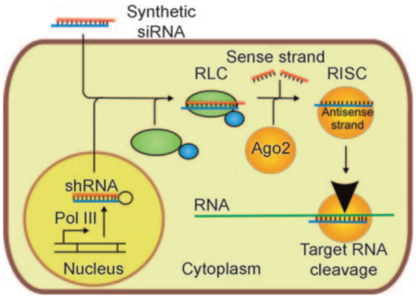
Synthetic Methods



Lawesson reagent for selenium fans: Phosphorus selenium heterocycles and, in particular, $[PhPSe_2]_2$ (known as Woollins' reagent) are proving valuable in the synthesis of new heterocycles and for the insertion of selenium into organic substrates. Incorporation of phosphorus and selenium atoms into the products leads to a surprising variety of structures.

Reviews

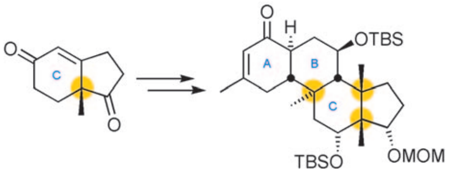
Molecular Medicine



An efficient mechanism for the sequence-specific inhibition of gene expression is RNA interference. In this process, double-stranded RNA molecules induce cleavage of a selected target RNA (see picture). This technique has in recent years developed into a standard method of molecular biology. Successful applications in animal models have already led to the initiation of RNAi-based clinical trials as a new therapeutic option.

Communications

Natural Products Synthesis (1)



Throw your hat in the ring: A highly diastereoselective synthesis of the ABC rings of (−)-norzoanthamine has been achieved starting from the (−)-Hajos–Parrish ketone (see scheme). Three asymmetric quaternary carbon centers on the C ring were constructed by a 1,4-addition, and an intramolecular Diels–Alder reaction provided a *trans*-decalin scaffold on the AB rings.

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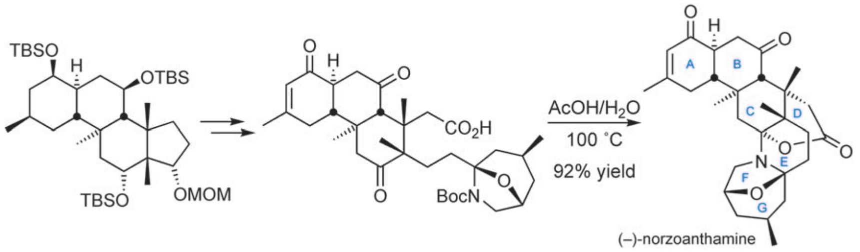


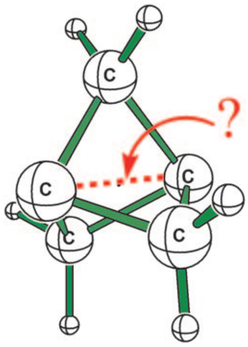
No bones about it: (–)-Norzoanthamine, a promising candidate for an anti-osteoporotic drug, was the target of a total synthesis (see scheme). The final bisaminal formation with AcOH/H_2O gave the DEFG ring, while the cyclization precursor was prepared by installing the remaining bisaminal unit after oxidative cleavage of the cyclopentanol moiety.

Natural Products Synthesis (2)

D. Yamashita, Y. Murata, N. Hikage,
K.-i. Takao, A. Nakazaki,
S. Kobayashi* ———— **1404 – 1406**

Total Synthesis of (–)-Norzoanthamine

Bonded or not bonded? An ab initio valence bond study of [1.1.1]propellane shows that the two bridgehead carbons are linked by a strong and direct σ bond that is neither classically covalent nor classically ionic, but rather a charge-shift bond, in which the covalent–ionic resonance energy plays the major role. As such, the central bond of [1.1.1]propellane closely resembles the single bond of difluorine.



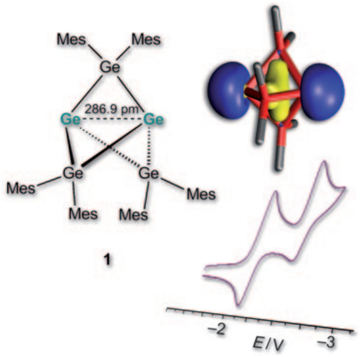
Bond Theory

W. Wu,* J. Gu, J. Song, S. Shaik,*
P. C. Hiberty* ———— **1407 – 1410**

The Inverted Bond in [1.1.1]Propellane is a Charge-Shift Bond

---

Ge, whiz! A detailed study of the synthesis, structure, redox chemistry, and bonding properties of pentagerma[1.1.1]propellane (**1**, see picture) examines fundamental aspects of the interactions between the bridgehead germanium atoms. DFT and CASSCF calculations unravel the biradicaloid characteristics of **1**, and preliminary reactivity studies indicate that **1** features some radical-type behavior.



Metallapropellanes

D. Nied, W. Klopper,*
F. Breher* ———— **1411 – 1416**

Pentagerma[1.1.1]propellane: A Combined Experimental and Quantum Chemical Study on the Nature of the Interactions between the Bridgehead Atoms

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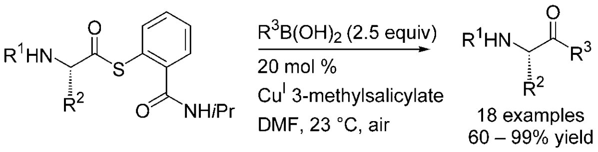
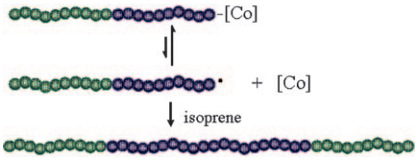


A copper-catalyzed transformation of peptidic thiol esters and boronic acids gives peptidyl ketones and takes place in DMF or DMF/H_2O at room temperature in air (see scheme). This aerobic reaction only occurs at a thiol ester group capable of coordinating to Cu through its appendage on the sulfur center and is not hampered by racemization of the reactants or products.

Synthetic Methods

L. S. Liebeskind,* H. Yang,
H. Li ———— **1417 – 1421**

A Copper-Catalyzed, pH-Neutral Construction of High-Enantiopurity Peptidyl Ketones from Peptidic *S*-Acylthiosalicylamides in Air at Room Temperature

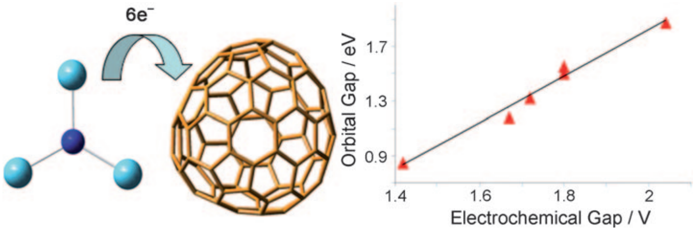


Tackling blocks: The isoprene-assisted radical coupling (I-ARC) of polymers prepared by cobalt-mediated radical polymerization (see picture) is the first efficient radical coupling method that is not restricted to short chains. When applied to AB diblock copolymers, I-ARC constitutes a straightforward approach to the preparation of novel symmetrical ABA triblock copolymers.

Radical Coupling

A. Debuigne, C. Jérôme,
C. Detrembleur* ________ **1422 – 1424**

Isoprene-Assisted Radical Coupling of (Co)polymers Prepared by Cobalt-Mediated Radical Polymerization



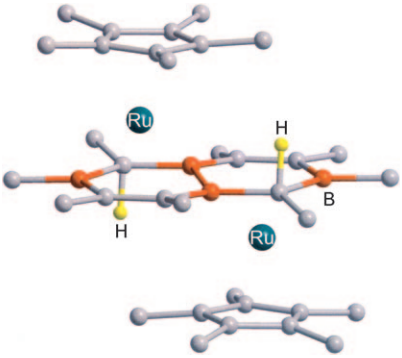
Size doesn't matter: Metallic nitride endohedral fullerenes (MNEFs) exhibit redox properties that are not dependent on the size of the carbon cage, but on its electronic properties. These findings support the ionic model of MNEFs.

Metallofullerenes

M. N. Chaur, R. Valencia,
A. Rodríguez-Fortea, J. M. Poblet,*
L. Echegoyen* ________ **1425 – 1428**

Trimetallic Nitride Endohedral Fullerenes: Experimental and Theoretical Evidence for the $M_3N^{6+}@C_{2n}^{6-}$ model

Colliding double deckers: Addition of zinc to a reaction mixture of $[\{Cp^*RuCl\}_4]$/pentamethyl-2,3-dihydro-1,3-diborole ($C_3B_2Me_5H$) in THF leads to three known double- and triple-decker complexes of $[C_3B_2Me_5]^-$, and unexpectedly to the slipped triple-decker (see picture) with two fused diborole rings. The *endo* C—H bonds of two MeC—H groups donate two additional electrons to achieve the stable 34 VE configuration.

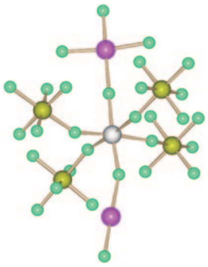


Metallocene Fusion

E. V. Mutseneck, H. Wadepohl, M. Enders,
A. R. Kudinov,* W. Siebert* **1429 – 1431**

Fusion of a 1,3-Diboraruthenocene to Form a Slipped μ-Hexahydrotetraboranaphthalene Triple-Decker Complex with Two Axial C—H Bonds

Noble molecule: $[Mg(XeF_2)(XeF_4)](AsF_6)_2$ is the first coordination compound in which XeF_4 acts as a ligand to a metal center. It is also the first known compound, in which XeF_2 and XeF_4 are simultaneously coordinated to the same metal center (see structure; purple Xe, green F, gray Mg, yellow As).



Noble Gas Compounds

G. Tavčar,* B. Žemva ________ **1432 – 1434**

XeF_4 as a Ligand for a Metal Ion

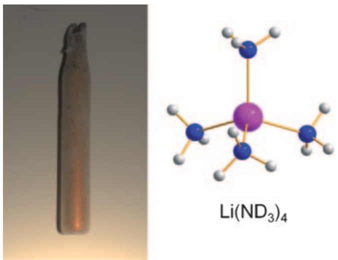
Contents

Expanded Metals

R. M. Ibberson,* A. J. Fowkes,
M. J. Rosseinsky, W. I. F. David,
P. P. Edwards ________ **1435 – 1438**

Structure and Phase Behavior of the Expanded-Metal Compound $^7Li(ND_3)_4$

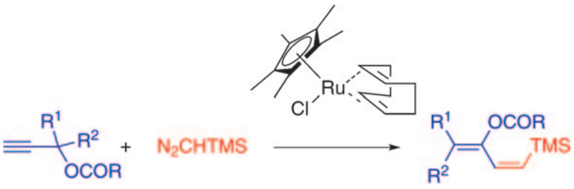
Metal lite: High-resolution neutron powder diffraction data reveals that the body-centered cubic crystal structure of lithium(0)tetraamine transforms to a simple cubic structure below 22 K. The detailed structure determinations will allow new insights into the coupled structural and electronic properties of the lightest metal.



Synthetic Methods

C. Vovard-Le Bray, S. Dérien,
P. H. Dixneuf* ________ **1439 – 1442**

Ruthenium-Catalyzed Synthesis of Functionalized Dienes from Propargylic Esters: Formal Cross-Coupling of Two Carbenes

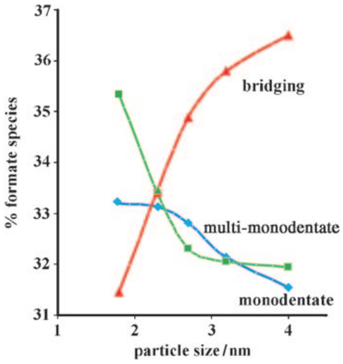


Cross-coupling carbenes: The coupling of a propargylic ester with a diazoalkane in the presence of [RuCl(cod)Cp*] catalyst leads to the formation of functionalized conjugated dienes with high stereoselectivity. The reaction involves the cross-coupling of a vinylcarbene fragment, arising from a ruthenium-catalyzed propargylic ester rearrangement, with a diazoalkane carbene.

Nanoparticles

K. Tedsree, A. T. S. Kong,
S. C. Tsang* ________ **1443 – 1446**

Formate as a Surface Probe for Ruthenium Nanoparticles in Solution ^{13}C NMR Spectroscopy

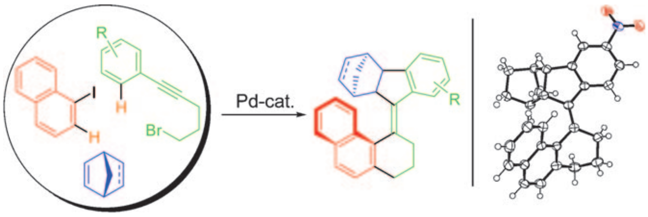


Formic acid adsorption on ruthenium nanoparticles of different sizes allows differentiation of differently bound formate species by solution ^{13}C NMR spectroscopy (see picture). The chemical shifts are comparable to those of organometallic analogues, thus indicating that formate can act as a probe to distinguish surface features of metallic nanoparticles in solution with good quantification and resolution.

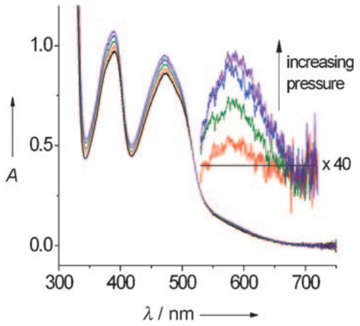
C–H Functionalization

K. M. Gericke, D. I. Chai, N. Bieler,
M. Lautens* ________ **1447 – 1451**

The Norbornene Shuttle: Multicomponent Domino Synthesis of Tetrasubstituted Helical Alkenes through Multiple C–H Functionalization



Shall we dance? Within the proposed mechanism for the palladium-catalyzed title reaction, the strained alkene norbornene (or norbornadiene) enters and exits the catalytic cycle in a catalytic “square dance”, acting as both a promoter and a coupling partner in the formation of four carbon–carbon bonds, two of them by challenging C–H activation processes.



Putting the squeeze on: Hydrostatic pressure causes a shortening of the charge-transfer bond in the binary complex of morphinone reductase and $NADH_4$ (see diagram). Molecular dynamics simulations suggest that pressure reduces the average reaction barrier width by restricting the conformational space available to the flavin mononucleotide and NADH within the active site. The apparent rate of catalysis increases with pressure.

Enzyme Catalysis

S. Hay, C. R. Pudney, T. A. McGrory,
J. Pang, M. J. Sutcliffe,*
N. S. Scrutton* ______ **1452 – 1454**

Barrier Compression Enhances an Enzymatic Hydrogen-Transfer Reaction

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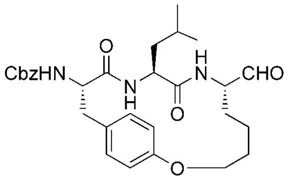

1

The design and elaboration of a series of macrocyclic templates that exhibit a propensity to adopt a β-strand-like peptide-backbone conformation led to potent and selective inhibitors of calpain 2. Macrocycle **1** retarded calcium-induced opacification in an ovine-lens culture assay and is a lead compound for the development of a drug for cataract treatment. Cbz = carbobenzyloxy.

Drug Design

A. D. Abell,* M. A. Jones, J. M. Coxon,
J. D. Morton, S. G. Aitken, S. B. McNabb,
H. Y.-Y. Lee, J. M. Mehrtens,
N. A. Alexander, B. G. Stuart, A. T. Neffe,
R. Bickerstaffe ______ **1455 – 1458**

Molecular Modeling, Synthesis, and Biological Evaluation of Macrocyclic Calpain Inhibitors

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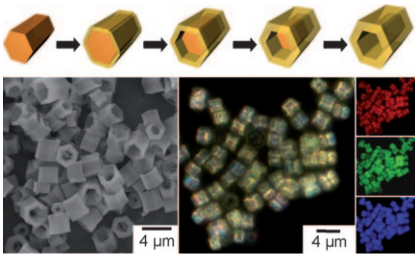

This template will self-destruct: A unique particle-growth mechanism involves growth of new coordination polymers on the surface of initially formed hexagonal blocks and concomitant dissolution of the blocks to form hexagonal tubes (see scheme and scanning electron, optical, and fluorescence microscopy images). Calcination of the tubes yields ZnO particles of the same shape.

Template Synthesis

S. Jung, W. Cho, H. J. Lee,
M. Oh* ______ **1459 – 1462**

Self-Template-Directed Formation of Coordination-Polymer Hexagonal Tubes and Rings, and their Calcination to ZnO Rings

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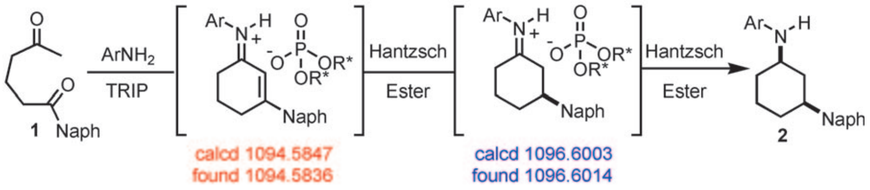


Chemical scrabble: Mechanistic studies of complex organocatalytic cascade reactions are challenging owing to the presence of many species involved. Electrospray ionization mass spectrometry provides details about a one-pot quadruple organocatalytic cascade reaction, and allows detailed characterization of the reaction and its key intermediates.

Mass Spectrometry

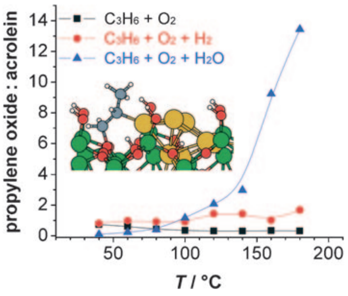
W. Schrader,* P. P. Handayani, J. Zhou,
B. List* ______ **1463 – 1466**

Characterization of Key Intermediates in a Complex Organocatalytic Cascade Reaction Using Mass Spectrometry

Heterogeneous Catalysis

S. Lee, L. M. Molina,* M. J. López,
J. A. Alonso, B. Hammer, B. Lee, S. Seifert,
R. E. Winans, J. W. Elam, M. J. Pellin,
S. Vajda ______ **1467 – 1471**

Selective Propene Epoxidation on Immobilized Au_{6-10} Clusters: The Effect of Hydrogen and Water on Activity and Selectivity



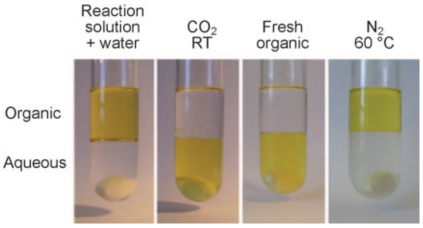
Epoxidation made easy: Subnanometer gold clusters immobilized on amorphous alumina result in a highly active and selective catalyst for propene epoxidation. The highest selectivity is found for gas mixtures involving oxygen and water, thus avoiding the use of hydrogen. Ab initio DFT calculations are used to identify key reaction intermediates and reaction pathways. The results confirm the high catalyst activity owing to the formation of propene oxide metallacycles. Al green, Au yellow, O red, and C gray.

Homogeneous Catalysis

S. L. Desset,
D. J. Cole-Hamilton* ______ **1472 – 1474**

Carbon Dioxide Induced Phase Switching for Homogeneous-Catalyst Recycling

SwitchPhos: Rhodium complexes formed from PPh_3 ligands functionalized with weakly basic amidine groups are highly active catalysts for the hydroformylation of alkenes. On bubbling with CO_2 in the presence of water, the yellow rhodium complexes move into the water phase, whereas bubbling with N_2 at 60 °C causes them to switch back into the organic phase. The catalysts can be used for reactions in water or an organic phase.

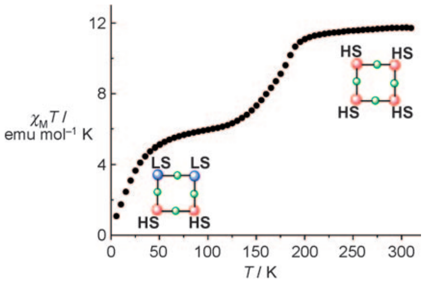


Spin Crossover

D. Wu, O. Sato,* Y. Einaga,
C. Duan ______ **1475 – 1478**

A Spin-Crossover Cluster of Iron(II) Exhibiting a Mixed-Spin Structure and Synergy between Spin Transition and Magnetic Interaction

How low can you go? An Fe^{II}_4 square was prepared by self-assembly and exhibits both thermally induced and photoinduced spin crossover from a system with four high-spin (HS) centers to one with two high-spin and two low-spin (LS) centers. The spin-crossover sites are located on the same side of the square, and the spin transition and magnetic interactions (see picture) are synergistically coupled.

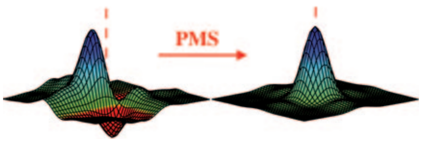


NMR Spectroscopy

Y. Wu, A. Ghosh,
T. Szyperski* ______ **1479 – 1483**

Clean Absorption-Mode NMR Data Acquisition

A new acquisition: Based on “phase-shifted mirrored sampling” (PMS) of indirect evolution periods of multidimensional experiments, new acquisition schemes eliminate, without application of a phase correction, dispersive signal components that exacerbate peak identification and shift peak maxima. The resulting enhanced resolution is of particular value for systems with high chemical shift degeneracy.

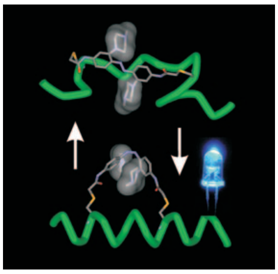


Photoswitches

O. Sadovski, A. A. Beharry, F. Zhang,
G. A. Woolley* ———— **1484 – 1486**

Spectral Tuning of Azobenzene Photoswitches for Biological Applications

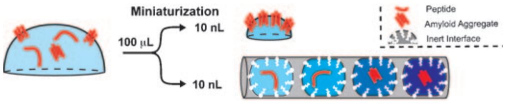
Longer switching wavelengths and good photochemical yields and stabilities of the *cis* isomers in reducing aqueous environments are achieved by introducing 2,2′-aminoalkyl substituents into 4,4′-diamido-substituted azobenzenes. The products are thus suitable for photocontrol of biomolecular structures in intracellular environments, such as switching between two peptide configurations (see picture).



Microfluidics

M. Meier, J. Kennedy-Darling, S. H. Choi,
E. M. Norstrom, S. S. Sisodia,
R. F. Ismagilov* ———— **1487 – 1489**

Plug-Based Microfluidics with Defined Surface Chemistry to Miniaturize and Control Aggregation of Amyloidogenic Peptides

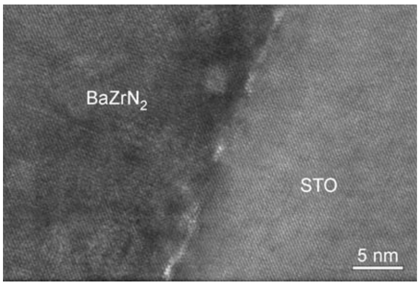


Small with control: For miniaturization of protein aggregation experiments the interfacial chemistry must be controlled to avoid protein aggregation caused by interfacial adsorption. Plug-based microfluidics with defined surface chemistry (see schematic picture) can then be used to perform hundreds of aggregation experiments with volume-limited samples, such as cerebrospinal fluid from mice.

Ternary Nitrides

H. M. Luo,* H. Wang, Z. Bi, G. F. Zou,
T. M. McCleskey, A. K. Burrell, E. Bauer,
M. E. Hawley, Y. Wang,
Q. X. Jia* ———— **1490 – 1493**

Highly Conductive Films of Layered Ternary Transition-Metal Nitrides

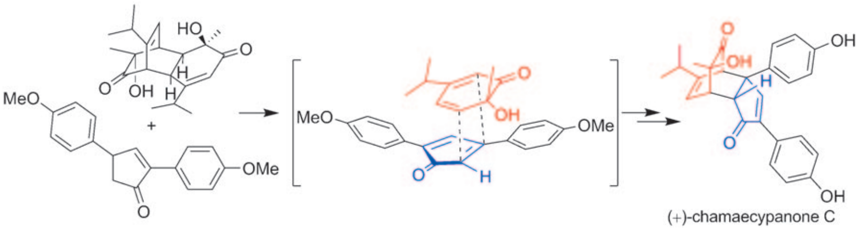


Film studies: Epitaxial films of $BaZrN_2$ (see TEM image) and $BaHfN_2$ are grown by polymer-assisted deposition on $SrTiO_3$ (STO) substrates. The films are phase-pure, allowing the intrinsic physical properties of the ternary nitrides to be studied. From 5 to 300 K, the films exhibit metallic-like resistivity–temperature behavior, with large residual resistivity ratios.

Natural Product Synthesis

S. Dong, E. Hamel, R. Bai, D. G. Covell,
J. A. Beutler, J. A. Porco, Jr.* **1494 – 1497**

Enantioselective Synthesis of (+)-Chamaecypanone C: A Novel Microtubule Inhibitor

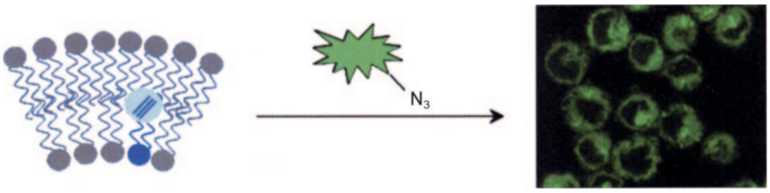


A bicycle built for tubulin: The total synthesis of (+)-chamaecypanone C has been achieved by using a tandem retro-Diels–Alder/Diels–Alder cascade reaction (see scheme). Initial biological studies demonstrate that (+)-chamaecypanone C is an inhibitor of tubulin assembly and binds at the colchicine site.

Live-Cell Imaging

A. B. Neef, C. Schultz* ____ **1498 – 1500**

Selective Fluorescence Labeling of Lipids in Living Cells

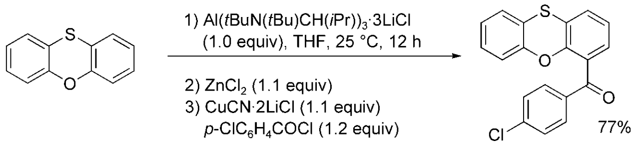


Click chemistry in vivo: Three phosphatidic acid derivatives with alkyne groups in their fatty acid chains were synthesized and incorporated into mammalian cell membranes. Copper(I)-catalyzed and strain-promoted azide–alkyne cycloaddition reactions were used for their visualization (see schematic representation and fluorescence microscopic image).

Directed Alumination

S. H. Wunderlich,
P. Knochel* ____ **1501 – 1504**

Aluminum Bases for the Highly Chemoselective Preparation of Aryl and Heteroaryl Aluminum Compounds



Selective C—H activation with a series of neutral aluminum trisamide bases led to a wide range of polyfunctional aryl and heteroaryl aluminum reagents. Ester and cyano groups are stable under the reaction conditions for this direct alumination, and donor oxygen substituents are efficient directing groups. High metalation regioselectivities were observed with O,S and N,S heterocycles (see example).

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).

Service

Corrigenda

Cross-Coupling of Aryl/Alkenyl Pivalates with Organozinc Reagents through Nickel-Catalyzed C–O Bond Activation under Mild Reaction Conditions

B.-J. Li, Y.-Z. Li, X.-Y. Lu, J. Liu, B.-T. Guan, Z.-J. Shi* ______ **10124–10127**

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Reversible "Chiral Memory" in Ruthenium Tris(phenanthroline)–Anionic Porphyrin Complexes

R. Randazzo, A. Mammana, A. D'Urso, R. Lauceri, R. Purrello* ______ **9879–9882**

Angew. Chem. Int. Ed. **2008**, *47*

DOI 10.1002/anie.200803619

In this communication all the CD signals of the lamda isomer have been inadvertently swapped with those of the delta isomer and vice versa. The authors apologize for these errors and wish to note that none of the interpretations in the paper are affected by this change.

Asymmetric Alkaloid Synthesis: A One-Pot Organocatalytic Reaction to Quinolizidine Derivatives

J. Franzén,* A. Fisher ______ **787–791**

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

DOI 10.1002/anie.200805130

During the preparation of this Communication we failed to reference a relevant article by Córdova and co-workers, which should be included in reference [11]. It should also be noticed that in this article an enantioselective organocatalytic synthesis of 5-hydroxyproline derivatives from 2-amidomalonates and α,β-unsaturated aldehydes is described. The authors apologize for this oversight.

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[11] a) S. Brandau, A. Landa, J. Franzén, M. Marigo, K. A. Jørgensen, *Angew. Chem.* **2006**, *118*, 4411; *Angew. Chem. Int. Ed.* **2006**, *45*, 4305; b) A. Carlone, S. Cabrera, M. Marigo, K. A. Jørgensen, *Angew. Chem.* **2007**, *119*, 1119; *Angew. Chem. Int. Ed.* **2007**, *46*, 1101; c) M. Marigo, S. Bertelsen, A. Landa, K. A. Jørgensen, *J. Am. Chem. Soc.* **2006**, *128*, 5475; d) A. Carlone, M. Marigo, C. North, A. Landa, K. A. Jørgensen, *Chem. Commun.* **2006**, 4928; e) L. Zu, H. Xie, H. Li, J. Wang, X. Yu, W. Wang, *Chem. Eur. J.* **2008**, *14*, 6333; f) R. Rios, I. Ibrahem, J. Vesely, H. Sundén, A. Córdova, *Tetrahedron Lett.* **2007**, *48*, 8695.