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. Alcarazo, T. Stork, A. Anoop, W. Thiel, A. Fürstner**
Steering the Surprisingly Modular π-Acceptor Properties of N-Heterocyclic Carbenes: Implications for Gold Catalysis

S. Zhang, Y. Shao, G. Yin, Y. Lin**
Electrostatic Self-Assembly of Platinum-Around-Gold Nanocomposites with High Activity Towards Formic Acid Oxidation

*D. Bojer, A. Venugopal, B. Neumann, H.-G. Stammler, N. W. Mitzel**
Lewis Base Induced Reductions in Organolanthanide Chemistry

S.-H. Kim, Su Y. Lee, S.-M. Yang**
Janus Microspheres for Highly Flexible and Impregnable Water-Repelling Interfaces

*L. Frullano, C. Catana, T. Benner, A. D. Sherry, P. Caravan **
A Bimodal MR-PET Agent for Quantitative pH Imaging

*K. Schober, E. Hartmann, H. Zhang, R. M. Gschwind**
^{1}H DOSY Spectra of Highly Enantioselective Ligands: A Fast and Simple NMR-Specroscopy Method to Optimize Catalytic Reaction Conditions

*A. M. Scott, A. B. Ricks, M. T. Colvin, M. R. Wasielewski**
Comparing Spin-Selective Charge Transport through Donor-Bridge–Acceptor Molecules having Different Oligomeric Aromatic Bridges

S. Pal, Z. Deng, B. Ding, H. Yan, Y. Liu**
DNA-Origami-Directed Self-Assembly of Discrete Silver Nanoparticle Architectures

*D. Figgen, A. Koers, P. Schwerdtfeger**
NWHClI: A Small and Compact Chiral Molecule with Large Parity Violation Effects in the Vibrational Spectrum

C. Costentin, M. Robert, J. Savéant, C. Tard
Inserting a Hydrogen Bond Relay between Proton Exchanging Sites in Proton–Coupled Electron Transfers

Author Profile

"My biggest motivation is curiosity. The most significant advance in chemistry in the last hundred years has been catalysis, any catalysis …"
This and more about Alexandre Alexakis can be found on page 1914.

News

J. Weitkamp

J. Nørskov

M. Buchmeiser

Books

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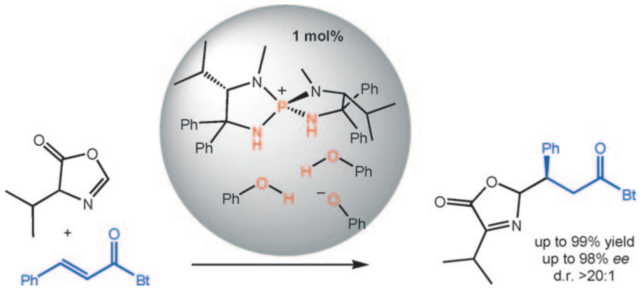
Highlights

Supramolecular Catalysis

D. Rix, J. Lacour* ———— **1918 – 1920**

Charged-Assisted Supramolecular Catalysis

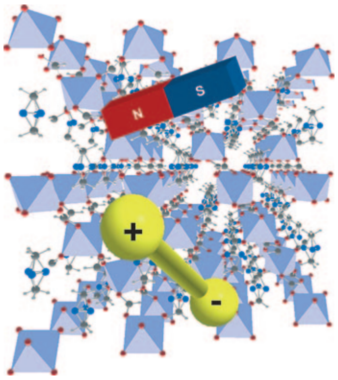


Charged up: An aminophosphonium cation, two phenols, and a phenoxide anion self-assemble in a cyclic network of intermolecular hydrogen-bonds. This charged-assisted reactive combination efficiently catalyzes the conjugate addition of azlactones to α,β-unsaturated acylbenzotriazoles.

Multiferroic MOFs

G. Rogez, N. Viart,
M. Drillon* ———— **1921 – 1923**

Multiferroic Materials: The Attractive Approach of Metal–Organic Frameworks (MOFs)



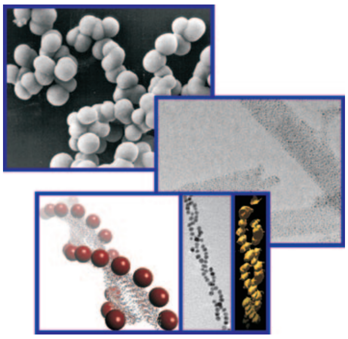
Peaceful coexistence: Metal–organic frameworks (MOFs) offer new openings in the stabilization of multiferroic materials. A series of compounds with a hydrogen-bond-triggered order–disorder transition combines both electric and magnetic order. These compounds constitute a new approach that significantly differs from other reported routes to multiferroic oxide materials.

Reviews

Inorganic Nanostructures

C.-L. Chen, N. L. Rosi* ———— **1924 – 1942**

Peptide-Based Methods for the Preparation of Nanostructured Inorganic Materials



Versatile agents: The sequence-specific recognition properties of peptides can be used to control the nucleation of inorganic nanoparticles, and their unique self-assembly properties can be used to direct the assembly of the particles. Complex peptides with both substrate recognition and self-assembly properties can be designed to simultaneously direct both nanoparticle synthesis and assembly.

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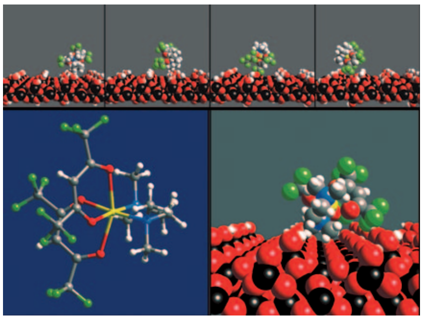
Surface Chemistry

E. Fois, G. Tabacchi,* D. Barreca, A. Gasparotto, E. Tondello **1944 – 1948**

"Hot" Surface Activation of Molecular Complexes: Insight from Modeling Studies

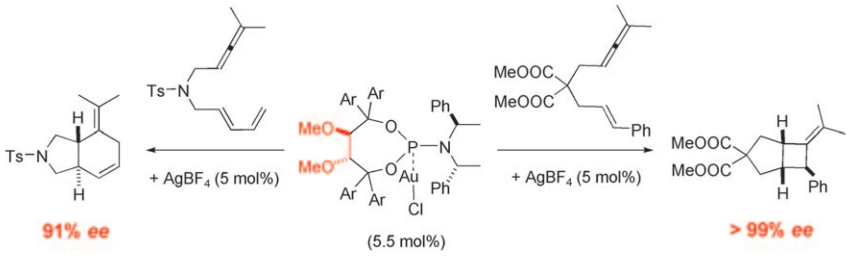


Rock-and-roll over hot floors: Theoretical modeling of the first activation stages of a Cu complex (see picture) on top of a heated surface (750 K) revealed two mobility regimes, a slow "bump-and-rock" diffusion over the surface and a fast "roll-and-go" motion accompanied by significant temperature-induced bond oscillations. This study enables a deeper insight into "hot" surface molecular activation processes.

Asymmetric Catalysis

H. Teller, S. Flügge, R. Goddard, A. Fürstner* **1949 – 1953**

Enantioselective Gold Catalysis: Opportunities Provided by Monodentate Phosphoramidite Ligands with an Acyclic TADDOL Backbone

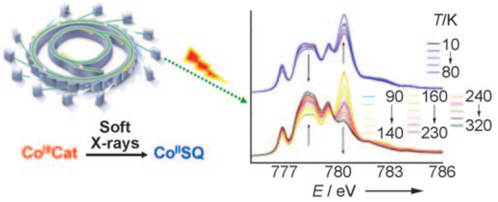


The tail makes the difference: Removing the isopropylidene acetal unit from well-known TADDOL ligands improved the performance of the derived phosphoramidite ligands in asymmetric gold catalysis (see scheme; Ts = 4-toluenesulfonyl). X-ray crystallography showed that the binding pocket has an effective threefold symmetry, with through-space interactions between the arene rings of the ligand and the gold center.

Valence Tautomerism

G. Poneti, M. Mannini, L. Sorace, P. Sainctavit, M.-A. Arrio, E. Otero, J. Criginski Cezar, A. Dei* **1954 – 1957**

Soft-X-ray-Induced Redox Isomerism in a Cobalt Dioxolene Complex



A soft touch: Interconversion of two redox isomers of a cobalt dioxolene complex (see picture; Cat: catecholato, SQ: semiquinonato) is stimulated by soft X-rays. Analysis of X-ray absorption spectroscopy (XAS) spectra shows that the soft-X-ray-induced redox isomer is the same as that obtained by optical irradiation of the sample in the near-IR region or by warming the sample.

Frontiers of Chemistry:
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at the Maison de la Chimie

(near the Eiffel Tower and Les Invalides)

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Jean-Marie Lehn
Nobel Prize 1987

Roger Y. Tsien
Nobel Prize 2008

Ada Yonath
Nobel Prize 2009

Luisa De Cola

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Posters

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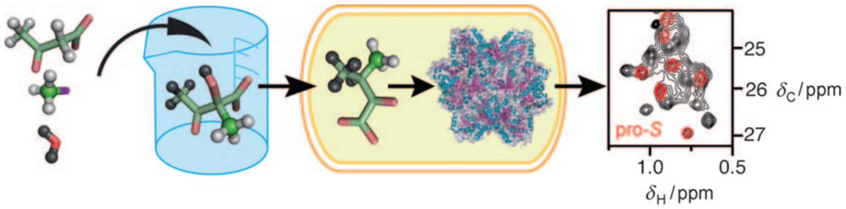
Protein Labeling

P. Gans, O. Hamelin, R. Sounier, I. Ayala,
M. A. Durá, C. D. Amero,
M. Noirclerc-Savoye, B. Franzetti,
M. J. Plevin, J. Boisbouvier* **1958 – 1962**

Stereospecific Isotopic Labeling of Methyl Groups for NMR Spectroscopic Studies of High-Molecular-Weight Proteins

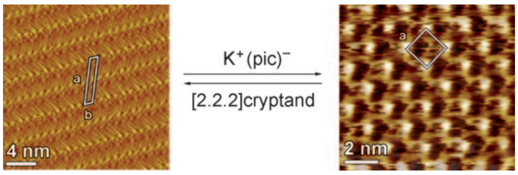


Sometimes less is more: [$^{13}C^1H_3$]methyl isotopomers can be biosynthetically incorporated specifically into the pro-*S* methyl groups of leucine and valine residues in large protein assemblies within a perdeuterated background by using an acetolactate precursor. This stereospecific labeling strategy considerably enhances NMR spectra for large protein assemblies.

Self-Assembly

A. Ciesielski, S. Lena, S. Masiero,
G. P. Spada,* P. Samorì* **1963 – 1966**

Dynamers at the Solid–Liquid Interface: Controlling the Reversible Assembly/Reassembly Process between Two Highly Ordered Supramolecular Guanine Motifs

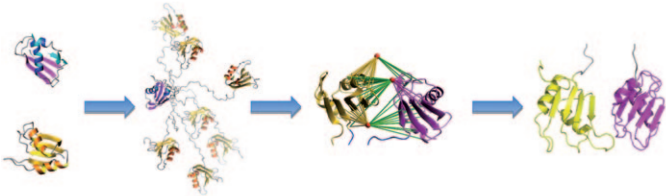


String quartet: A dynamic assembly/reassembly process in octadecyl guanine (G) monolayers was triggered by addition of [2.2.2]cryptand, potassium picrate (K$^+$(pic)$^-$), and trifluoromethanesulfonic acid. The resulting structures, which alternate between a hydrogen-bonded G ribbon and a G quartet, were monitored by STM at the solid–liquid interface on graphite (see picture).

Structural Biology

B. Simon, T. Madl, C. D. Mackereth,
M. Nilges, M. Sattler* **1967 – 1970**

An Efficient Protocol for NMR-Spectroscopy-Based Structure Determination of Protein Complexes in Solution

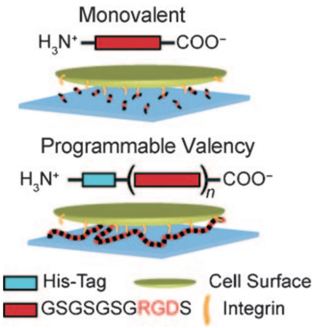


Putting the pieces together: An efficient, generally applicable approach for structural analysis of protein complexes and multidomain proteins in solution based on NMR spectroscopy is presented. Starting from available high-resolution structures of individual domains or subunits, the overall domain arrangement is calculated from NMR spectroscopy data that can be obtained for high-molecular-weight complexes.

Bioorganic Chemistry

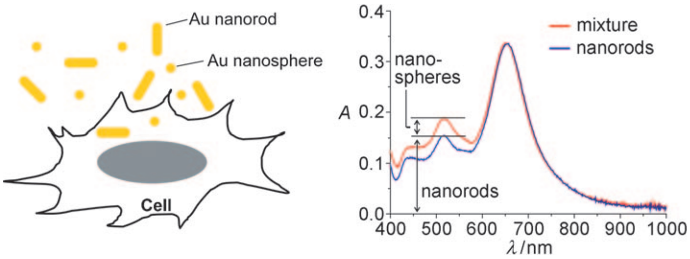
B. W. Lee, R. Schubert, Y. K. Cheung,
F. Zannier, Q. Wei, D. Sacchi,
S. K. Sia* **1971 – 1975**

Strongly Binding Cell-Adhesive Polypeptides of Programmable Valencies



Longer and stronger: Engineered multivalent polypeptides were used to increase and tune the adhesion strength of cells to surfaces. Monodisperse polypeptides containing programmable valencies of a cell-adhesion sequence were synthesized (with up to 80 repeats of the RGD sequence; see schematic illustration). The multivalent cell-adhesion polypeptides provided strong resistance to cellular delamination under shear.

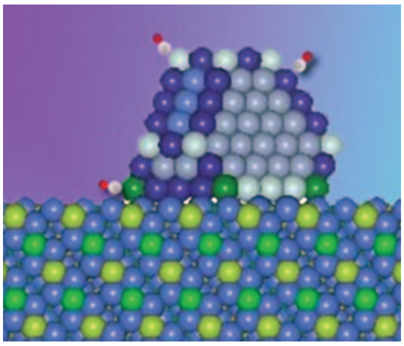
Nanoparticles



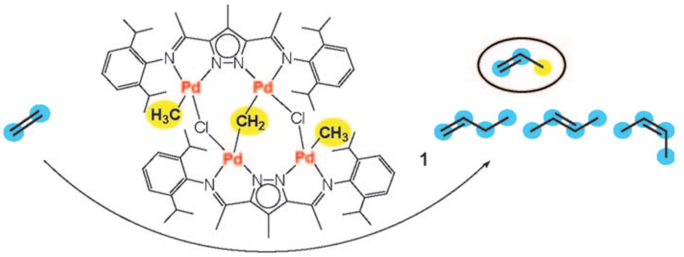
See the difference: UV/Vis spectroscopy allows differentiation of the cellular uptakes of gold nanospheres and nanorods from their mixtures by taking advantage of their distinctive optical signatures (see picture).

Surface Chemistry

A happy medium: Volumetric adsorption of carbon monoxide at 308 K and UHR-HAADF-STEM, HREM, and computer modeling techniques were compared. Experimental CO/Au ratios at saturation coverage for two supported gold catalysts were shown to fit very well the predictions of a nanostructural model that considers CO adsorption on gold sites with coordination numbers of less than eight.

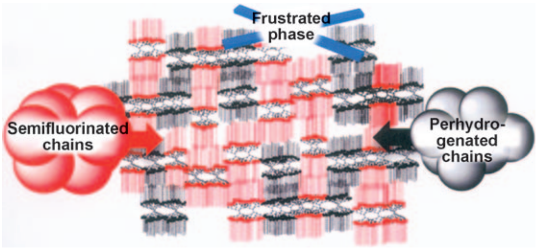


Multinuclear Complexes



Ménage à quatre: The Pd_4 complex **1** features both terminal CH_3 and bridging CH_2 groups, and it reacts with ethylene at room temperature to give mainly propene. NMR spectroscopic studies reveal several intermediates in the formation of **1** from Pd_2 building blocks.

Supramolecular Chemistry

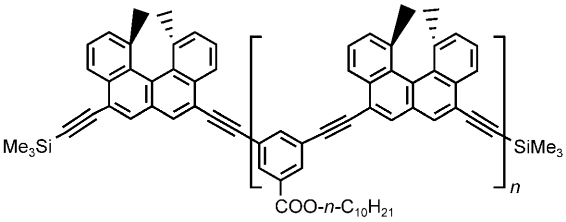


A molecular tug of war between non- and semifluorinated alkyl chains (see picture) occurs when they are forced together by ionic attachment to a poly(propylene imine) dendrimer. Unexpected mesomorphic properties appear as a consequence of the competition of both substituents to control the supramolecular organization of the molecules.

Sol–Gel Processes

R. Amemiya, M. Mizutani,
M. Yamaguchi* ____________ **1995 – 1999**

Two-Component Gel Formation by Pseudoenantiomeric Ethynylhelicene Oligomers

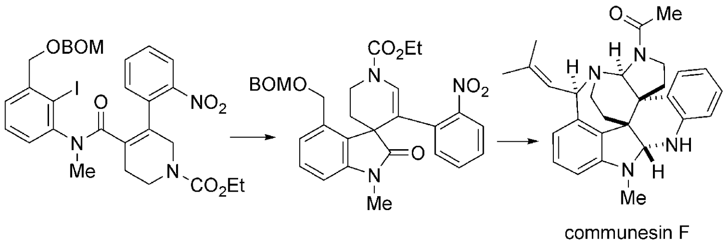


Long and winding gel: Mixtures of (*M*)- and (*P*)-ethynylhelicene oligomers (see structure) differing in the numbers of helicene units formed organogels in toluene, which exhibited better thermoreversibility in the sol–gel process than those formed from enantiomers. Various two-component gels were obtained by changing the combination of the component pseudoenantiomeric oligomers, provided that they were larger than a trimer.

Total Synthesis

P. Liu, J. H. Seo,
S. M. Weinreb* ____________ **2000 – 2003**

Total Synthesis of the Polycyclic Fungal Metabolite (±)-Communesin F

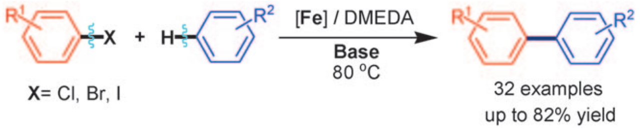


What the Heck: The heptacyclic fungal alkaloid communesin F was the target of a total synthesis featuring a rare example of an intramolecular Heck cyclization of a tetrasubstituted alkene, a reductive cyclization of an *N*-Boc aniline, a stereoselective C allylation of a lactam, and an azide reduction/*N*-Boc-δ-lactam ring opening sequence (see scheme, BOM = benzyloxymethyl).

C–H Activation

W. Liu, H. Cao, A. Lei* ______ **2004 – 2008**

Iron-Catalyzed Direct Arylation of Unactivated Arenes with Aryl Halides

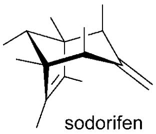


Iron tough: Various aryl halides were treated with unactivated arenes to form biaryl compounds in moderate to good yields. The reactions were carried out at relatively low temperature in the presence of a catalytic amount of $FeCl_3$, with DMEDA as the ligand and LiHMDS as the base (see scheme; DMEDA = *N*,*N*′-dimethylethane-1,2-diamine, HDMS = hexamethyldisilazanide).

Structure Elucidation

S. H. von Reuß, M. Kai, B. Piechulla,
W. Francke* ____________ **2009 – 2010**

Octamethylbicyclo[3.2.1]octadienes from the Rhizobacterium *Serratia odorifera*



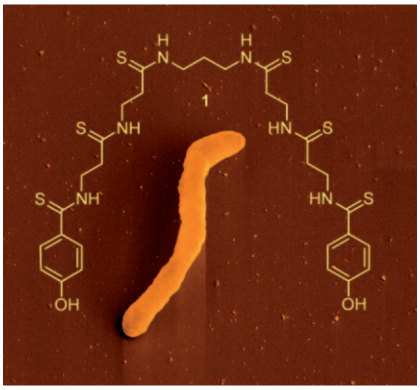
sodorifen

Volatile matters: A hydrocarbon containing 16 carbon atoms with an unprecedented framework, sodorifen (see structure), is the major volatile component released by the rhizobacterium *Serratia odorifera*. Its structure was elucidated by NMR and EIMS experiments and confirmed by synthesis.

Natural Products

T. Lincke, S. Behnken, K. Ishida, M. Roth, C. Hertweck* ______ **2011 – 2013**

Closthioamide: An Unprecedented Polythioamide Antibiotic from the Strictly Anaerobic Bacterium *Clostridium cellulolyticum*

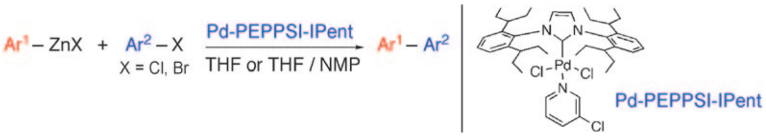


Choose sulfur in an oxygen-free world: Closthioamide (**1**) was isolated from the anaerobe *Clostridium cellulolyticum* (see SEM image) after the induction of its biosynthesis with an aqueous soil extract. An unprecedented type of symmetrical natural product in which all building blocks are connected through thioamide linkages, **1** is active against multiresistant staphylococci. It is the only known secondary metabolite from a strictly anaerobic bacterium.

Synthetic Methods

S. Çalimsiz, M. Sayah, D. Mallik, M. G. Organ* ______ **2014 – 2017**

Pd-PEPPSI-IPent: Low-Temperature Negishi Cross-Coupling for the Preparation of Highly Functionalized, Tetra-*ortho*-Substituted Biaryls



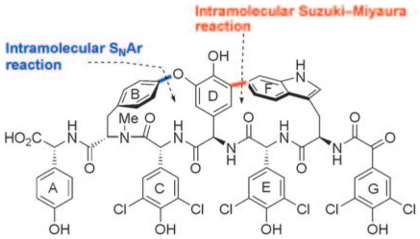
Cool couplings: Complex, hindered biaryls have been prepared at temperatures ranging from 0°C to room temperature, or with gentle heating. The Pd-PEPPSI-IPent catalyst (see scheme) nicely couples starting materials containing acidic moieties and routinely prepares biaryl derivatives where one or both rings comprising the biaryl are heterocyclic. Ar^1 = hindered aryl or heteroaryl, Ar^2 = unactivated aryl or heteroaryl.

Total Synthesis

Z. H. Wang, M. Bois-Choussy, Y. Jia, J. Zhu* ______ **2018 – 2022**

Total Synthesis of Complestatin (Chloropeptin II)

Substrate-dependent atropostereoselectivity: Cyclization of a linear DEFG tripeptide by an intramolecular Suzuki–Miyaura reaction afforded the 16-membered DEFG ring with complete atroposelectivity. Intramolecular S$_\text{N}$Ar reaction of a hexapeptide that contained a prebuilt DEFG ring afforded the bismacrocycle ABCDEFG that was converted to complestatin.

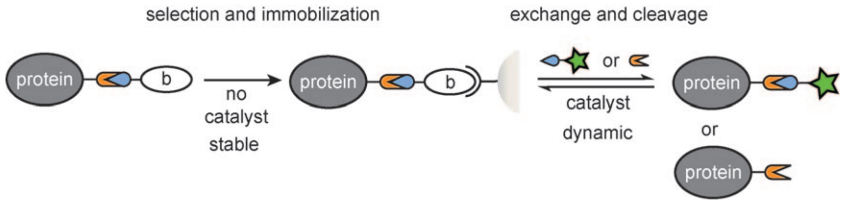


Complestatin

Cleavable Linkers

A. Dirksen, S. Yegneswaran, P. E. Dawson* ______ **2023 – 2027**

Bisaryl Hydrazones as Exchangeable Biocompatible Linkers

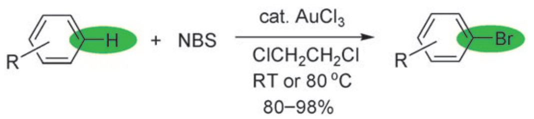


Catch and release: Stable bisaryl hydrazones undergo rapid exchange under mild conditions in the presence of a catalyst (see schematic illustration; b = biotin). This highly efficient hydrazone exchange is useful for the affinity purification of biotinylated proteins on (strept)avidin beads. The method enables the mild elution of label-exchanged or chemically functionalized proteins.

Gold Catalysis

F. Mo, J. M. Yan, D. Qiu, F. Li, Y. Zhang, J. Wang* ——— **2028 – 2032**

Gold-Catalyzed Halogenation of Aromatics by *N*-Halosuccinimides



Golden bromination: A highly efficient and mild AuCl$_3$-catalyzed bromination of aromatic rings with *N*-bromosuccinimide (NBS) has been developed. This method works with a low catalyst loading (down to 0.01 mol %) and can be combined with transition metal catalyzed transformations to deliver various aryl products.

Pheromones (1)

S. P. Chinta, S. Goller, J. Lux, S. Funke, G. Uhl,* S. Schulz* ——— **2033 – 2036**

The Sex Pheromone of the Wasp Spider *Argiope bruennichi*

Wasp spider looking for a mate: Female wasp spiders (see picture) use trimethyl methylcitrate as a volatile cue to attract males. The experiments were performed on a sunny meadow, showing for the first time that spider traps can be used to trap spiders in the field (photo: Helen Sandford).

Pheromones (2)

E. Jerhot, J. A. Stoltz, M. C. B. Andrade, S. Schulz* ——— **2037 – 2040**

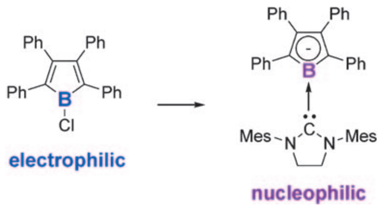
Acylated Serine Derivatives: A Unique Class of Arthropod Pheromones of the Australian Redback Spider, *Latrodectus hasselti*

Irresistible: Amino acid derivatives are very rarely used as pheromones by arthropods. The widow spider *Latrodectus hasselti* (see picture) uses a unique compound (see formula) to lure its males. The molecular configuration plays an important role in this unique chemical communication system.

Boron Heterocycles

H. Braunschweig,* C.-W. Chiu, K. Radacki, T. Kupfer ——— **2041 – 2044**

Synthesis and Structure of a Carbene-Stabilized π-Boryl Anion

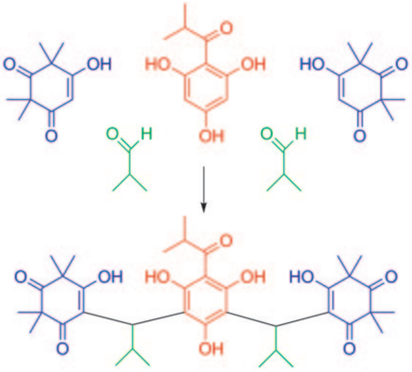


Attack with π electrons: Reduction of a chloroborole coordinated by an N-heterocyclic carbene results in the formation of a carbene-stabilized borole monoanion (see scheme; Mes = mesityl), the molecular structure of which has been determined by X-ray analysis. Computational and reactivity studies of this boracycle confirm the presence of a π-nucleophilic boron atom, which represents a rare example in the chemistry of boryl anions.

Natural Product Synthesis

H. Müller, M. Paul, D. Hartmann, V. Huch, D. Blaesius, A. Koeberle, O. Werz, J. Jauch* ________ **2045 – 2049**

Total Synthesis of Myrtucommulone A

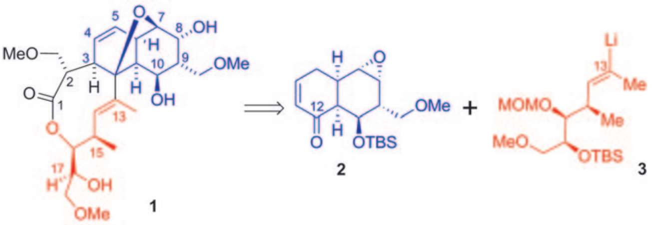


In a one-step conversion, commercially available or known compounds are connected to form myrtucommulone A, an anti-inflammatory and apoptosis-inducing substance from the common myrtle *Myrtus communis* (see scheme). This strategy can be used, as well to prepare myrtucommulone libraries.

Natural Product Synthesis

S. Marchart,* A. Gromov, J. Mulzer* ________ **2050 – 2053**

Total Synthesis of the Antibiotic Branimycin



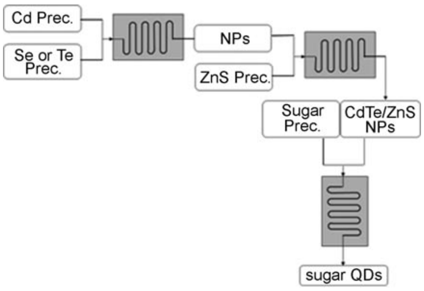
Catch 22: The first total synthesis of branimycin (**1**) has been achieved by a highly convergent approach in which the vinyl lithium derivative **3** was added to a *cis*-decalin ketone **2**. The route has 22 steps in the longest linear sequence and an overall yield of 2%. It is highly stereocontrolled, scaleable, and flexible. MOM = methoxymethyl, TBS = *tert*-butyldimethylsilyl.

Microreactors

R. Kikkeri, P. Laurino, A. Odedra, P. H. Seeberger* ________ **2054 – 2057**

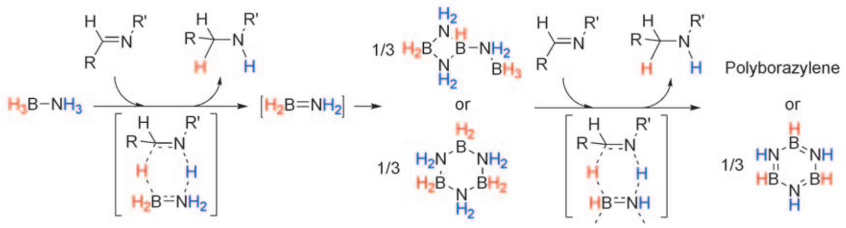
Synthesis of Carbohydrate-Functionalized Quantum Dots in Microreactors

Continuous sugar coating: A process has been developed for the mild, continuous-flow microreactor synthesis of carbohydrate-coated CdSe/ZnS and CdTe/ZnS quantum dots of narrow size distribution (see scheme; NP: nanoparticle, QD: quantum dot, Prec.: precursor). The products can be prepared efficiently and reproducibly in larger amounts. The surface of the QDs can be modified with biologically relevant molecules.



Hydrogen Transfer

Transfer Hydrogenation of Imines with Ammonia–Borane: A Concerted Double-Hydrogen-Transfer Reaction



Direct transfer hydrogenation of imines was observed with ammonia–borane, which proceeded under mild conditions without the help of a catalyst. The results of deuterium kinetic isotope effects, Hammett correlations, and DFT calculations all support a concerted double-hydrogen-transfer mechanism (see scheme).

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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Corrigendum

In this Communication reference [2c] is wrong. The correct citation is: G. A. Abakumov, G. A. Razuvaev, V. I. Nevodchikov, V. K. Cherkasov, *J. Organomet. Chem.* **1988**, *341*, 485–494.

Electromeric Rhodium Radical Complexes

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