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. Ciesielski, S. Lena, S. Masiero, G. P. Spada, P. Samorì**
Dynamers at the Solid–Liquid Interface: Controlling the Reversible Assembly/Reassembly Process Between Two Highly Ordered Supramolecular Guanine Motifs

*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

H. Braunschweig, C.-W. Chiu, K. Radacki, T. Kupfer*
Synthesis and Structure of an Carbene-Stabilized π-Boryl Anion

S. Zhang, Y. Shao, G. Yin, Y. Lin**
Electrostatic Self-Assembly of Platinum-Around-Gold Nanocomposite 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

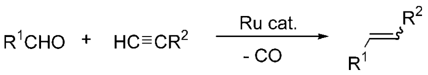
*K. Schober, E. Hartmann, H. Zhang, R. M. Gschwind**
^{1}H DOSY Spectra of Highly Enantioselective Ligands: A Fast and Simple NMR-Specroscopy Method to Optimize Catalytic Reaction Conditions

Author Profile

"My favorite subjects at school ranged from Latin to sciences, with an increasing emphasis on the latter. I chose chemistry as a career because I enjoyed the subject, its relevance to everyday life, and its versatility ..."
This and more about Pierre Braunstein can be found on page 1718.

Books

Highlights

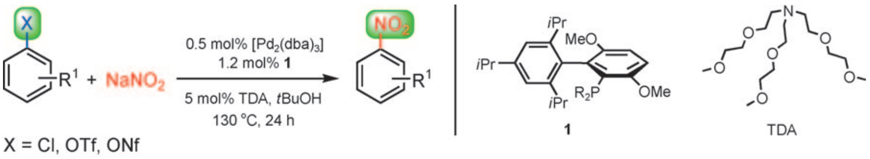


CO goes: A recent report has demonstrated that aldehydes can undergo decarbonylation and addition across alkynes to give alkenes (see scheme). The scope of the process is discussed along with an overview of other metal-catalyzed decarbonylative reactions.

Decarbonylative Coupling

Contents

ipso-Nitration



Meeting the challenge: Buchwald et al. have developed a very efficient and mild method for the *ipso*-nitration of a variety of aromatic/heteroaromatic chlorides, triflates, and nonaflates. The palladation–nitration protocol is compatible with many functional groups.

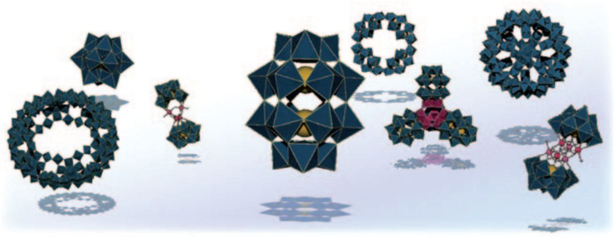
Essays

Organocatalysis

The progress of aminocatalysis has been breathtaking—but what are its roots? Why is this field only blossoming now and not earlier? This Essay takes a look back at the origins of aminocatalysis and its development over the last century, and possibly reveals some surprises.

Reviews

Polyoxometalates



The broad field between discrete metal oxo complexes and solid-state oxides is ruled by the polyoxometalates and the structures formed from them by aggregation. This Review shows which suitable building blocks are available and how they can be combined to give nano- to micrometer-scale architectures.

For the USA and Canada:
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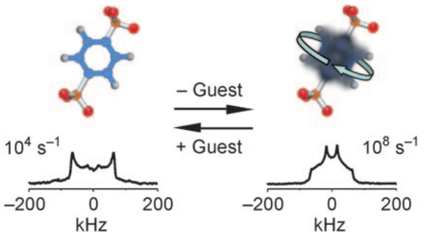
Porous Dynamical Materials

A. Comotti, S. Bracco, P. Valsesia, M. Beretta, P. Sozzani* ____ **1760 – 1764**

Fast Molecular Rotor Dynamics Modulated by Guest Inclusion in a Highly Organized Nanoporous Organosilica

Rotor speed regulation in the hybrid walls of porous *p*-phenylenesilica can be achieved by guest uptake and removal. A graduation from slow to ultrafast motional regimes ($k = 10^4$–$10^8\ s^{-1}$) can be experienced by the molecular rotors depending on guest nature and temperature, as detected by solid-state spin-echo ^2H NMR spectroscopy (see picture).

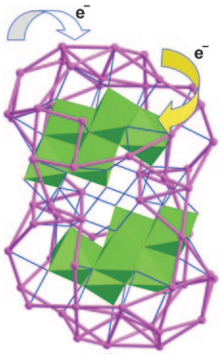


Cluster Compounds

J. Qiao, K. Shi, Q.-M. Wang* **1765 – 1767**

A Giant Silver Alkynyl Cage with Sixty Silver(I) Ions Clustered around Polyoxometalate Templates

In a nutshell: A nanosized core/shell cluster has been synthesized by reaction of AgC≡C*t*Bu with AgOTf in the presence of a polyoxometalate (POM) template under solvothermal conditions. The peanutlike structure (see picture) consists of two $Mo_6O_{22}^{8-}$ nuts (green) and an Ag_{60} shell (purple). Electrochemical studies revealed that the silver shell acts like an electronic relay, while the POM cores function as a redox buffer to stabilize the cluster.



$(Mo_6O_{22}^{8-})_2@Ag_{60}$

Polymerization

J. Wei, W. Zhang, L. R. Sita* **1768 – 1772**

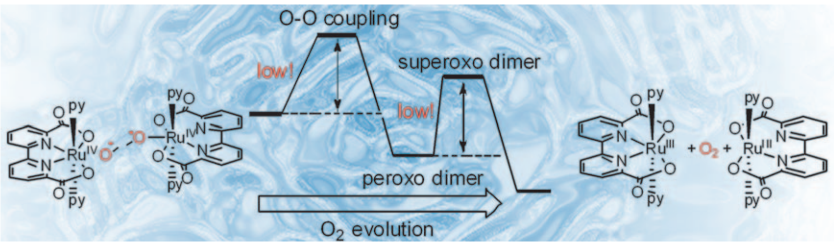
Aufbaureaktion Redux: Scalable Production of Precision Hydrocarbons from AlR_3 (R = Et or *i*Bu) by Dialkyl Zinc Mediated Ternary Living Coordinative Chain-Transfer Polymerization

Metal ménage à trois: Rapid and reversible chain transfer under living conditions between an active transition-metal propagating species, AlR_3 as a primary surrogate, and a catalytic amount of ZnR_2 as a secondary surrogate and chain-transfer mediator provides a cost-effective, scalable process for the production of precision hydrocarbons.

O_2 Evolution

J. Nyhlén, L. Duan, B. Åkermark, L. Sun, T. Privalov* ____ **1773 – 1777**

Evolution of O_2 in a Seven-Coordinate Ru^{IV} Dimer Complex with a $[HOHOH]^-$ Bridge: A Computational Study



The missing link? DFT calculations demonstrate that a binuclear mechanism of O_2 evolution involving seven-coordinate ruthenium species, which operates through the direct coupling of oxygen radicals and does not require crossing of prohibitively high potential-energy barriers, is plausible (see scheme).

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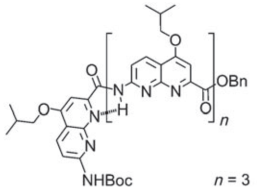
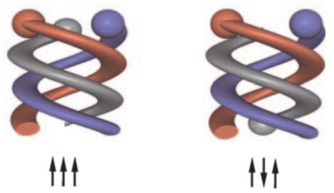
Helical Structures

Y. Ferrand, A. M. Kendhale, J. Garric,
B. Kauffmann, I. Huc* ______ 1778 – 1781

Parallel and Antiparallel Triple Helices of Naphthyridine Oligoamides



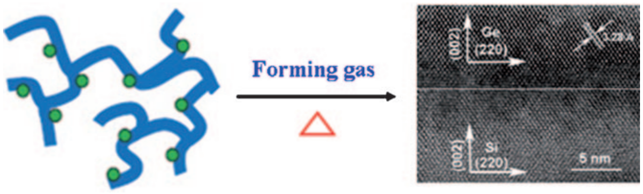


Three, no less and no more, is the number of naphthyridine oligoamide strands that intertwine to form a unique and robust triple helix architecture. The formation of either a parallel or antiparallel arrangement of the helical strands is governed by factors such as the polarity of the solvent (see picture).

Epitaxial Films

G. Zou,* H. Luo, F. Ronning, B. Q. Sun,*
T. M. McCleskey, A. K. Burrell, E. Bauer,
Q. X. Jia* ______ 1782 – 1785

Facile Chemical Solution Deposition of High-Mobility Epitaxial Germanium Films on Silicon

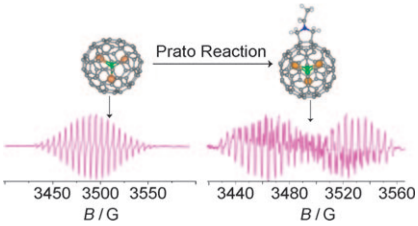


Getting a move on: A facile chemical solution deposition method is used for the first time for the epitaxial growth of germanium on an silicon substrate. The germanium films show Hall mobility values as high as 1700 cm^2 V^{-1} s^{-1} for a carrier concentration of 3.45×10^{19} cm^{-3} at room temperature.

Endofullerenes

T.-S. Wang, J.-Y. Wu, W. Xu, J.-F. Xiang,
X. Lu, B. Li, L. Jiang, C.-Y. Shu,*
C.-R. Wang* ______ 1786 – 1789

Spin Divergence Induced by Exohedral Modification: ESR Study of $Sc_3C_2@C_{80}$ Fulleropyrrolidine

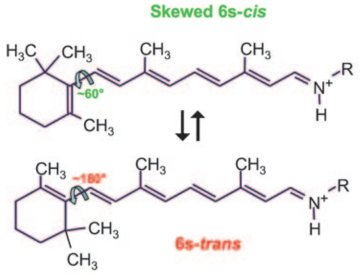


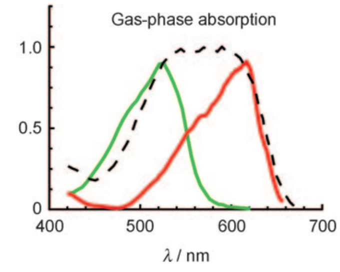
The paramagnetic properties of the endohedral fullerene $Sc_3C_2@C_{80}$ are adjustable by exohedral modification by the Prato reaction (see picture). Analysis of spin densities and endocluster dynamics reveal unique paramagnetic properties of the $Sc_3C_2@C_{80}$ fulleropyrrolidine and provide general insight into the addend-dependent paramagnetic behavior of endohedral fullerenes.

Retinal Chromophores

J. Rajput, D. B. Rahbek, L. H. Andersen,*
A. Hirshfeld, M. Sheves,* P. Altoè,
G. Orlandi, M. Garavelli* ______ 1790 – 1793

Probing and Modeling the Absorption of Retinal Protein Chromophores in Vacuo





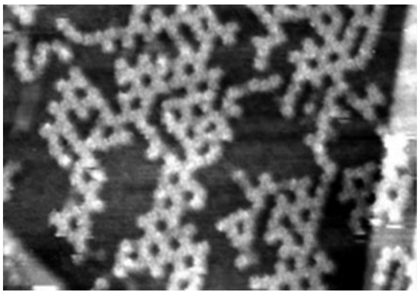
Seeing the light: A joint experimental and theoretical approach delivers the free gas-phase high-resolution absorption spectrum of the chromophore conformations implicated in the spectroscopy of retinal proteins (see scheme). Notably, many retinal pigments absorb close to the gas-phase value.

Molecular Assemblies

A. J. Pollard, E. W. Perkins, N. A. Smith, A. Saywell, G. Goretzki, A. G. Phillips, S. P. Argent, H. Sachdev, F. Müller, S. Hüfner, S. Gsell, M. Fischer, M. Schreck, J. Osterwalder, T. Greber, S. Berner, N. R. Champness,* P. H. Beton* ______ **1794 – 1799**

Supramolecular Assemblies Formed on an Epitaxial Graphene Superstructure

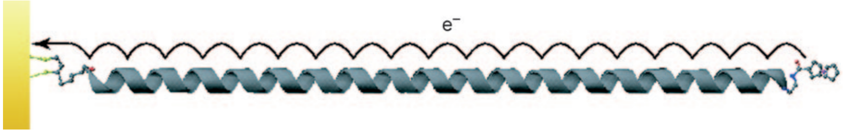
Quite comparable: A graphene monolayer is used as a substrate for the growth of two-dimensional hydrogen-bonded supramolecular structures (see STM image). The formation of these extended structures arises from a commensurability between their dimensions and a moiré pattern formed by the graphene.



Electron Transfer

Y. Arikuma, H. Nakayama, T. Morita, S. Kimura* ______ **1800 – 1804**

Electron Hopping over 100 Å Along an α Helix



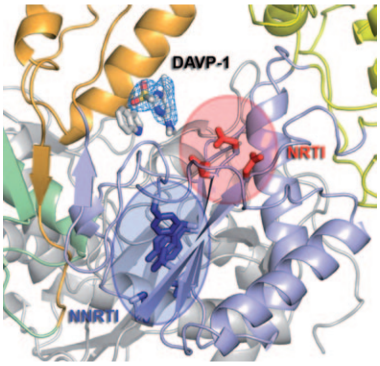
Take the stepping stones: Electrons are exchanged between both termini of α-helical peptide self-assembled monolayers (SAMs) on gold by a hopping mechanism with the amide groups as hopping sites (see picture). The rate constant of 0.45 s^{-1} for the 64-mer peptide is significantly high for electron transfer through dielectric organic materials.

Structural Biology

S. Freisz, G. Bec, M. Radi, P. Wolff, E. Crespan, L. Angeli, P. Dumas, G. Maga, M. Botta,* E. Ennifar* ______ **1805 – 1808**

Crystal Structure of HIV-1 Reverse Transcriptase Bound to a Non-Nucleoside Inhibitor with a Novel Mechanism of Action

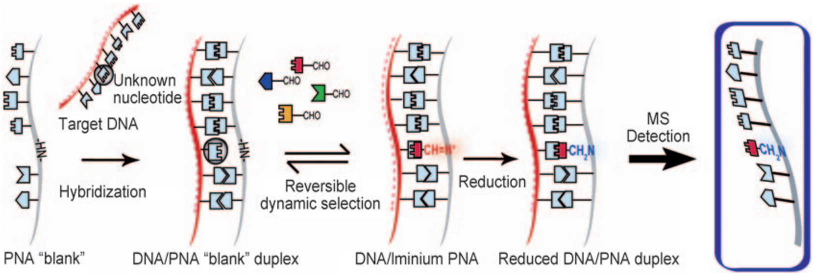
Seeing the sites: Unlike classical non-nucleoside HIV-1 reverse transcriptase (RT) inhibitors (NNRTI; active site in blue), DAVP-1 is a non-nucleoside RT inhibitor that competes with the nucleotide substrate (NcRTI). The X-ray structure of DAVP-1 bound to the unligated RT shows a new inhibitor binding site close to the polymerase active site. (Nucleoside analogue RT inhibitor (NRTI) binding site is shown in red.)



DNA Analysis

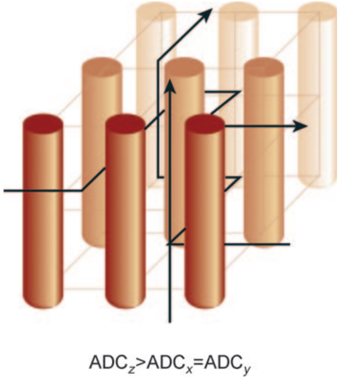
F. R. Bowler, J. J. Diaz-Mochon,* M. D. Swift, M. Bradley* ______ **1809 – 1812**

DNA Analysis by Dynamic Chemistry



Finding flaws: An enzyme-free method of DNA analysis raises the possibility of analyzing single-nucleotide polymorphism, indel, and abasic sites using mass spectrometry as a readout tool. The methodology is suitable for the dual analysis of heterozygous samples.

Added directionality: Exogenous nanotubular materials can be used to induce and perturb selectively the anisotropic diffusion of water molecules in the surrounding medium in a manner detectable by magnetic resonance imaging (see scheme; ADC: apparent translational diffusion coefficient). Nanotubes may be suitable contrast agents in studies of the microstructural basis of tissue anisotropy and its pathological implications.



Magnetic Resonance Imaging

V. Negri, A. Cerpa, P. López-Larrubia,
L. Nieto-Charques, S. Cerdán,
P. Ballesteros* ———— **1813 – 1815**

Nanotubular Paramagnetic Probes as Contrast Agents for Magnetic Resonance Imaging Based on the Diffusion Tensor

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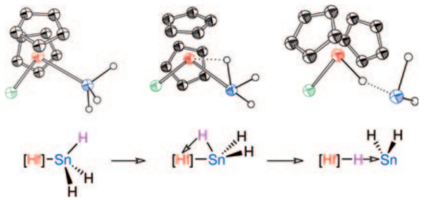

Sn two-step: Dehydrocoupling of stannanes by the d^0 complex [Cp_2(Cl)HfH] preferentially occurs by two successive reactions (see scheme): σ-bond metathesis to form [Cp_2(Cl)Hf(SnH_3)] and subsequent stannylene transfer into the Cp_2(Cl)Hf–SnH_3 bond. [Cp_2(Cl)Hf(SnH_3)] readily isomerizes to a species possessing a reactive stannylene unit, [Cp_2(Cl)Hf(μ-H)SnH_2], thus making the stannylene-transfer reaction energetically feasible.

Masked Stannylenes

J. Guihaumé, C. Raynaud,*
O. Eisenstein,* L. Perrin, L. Maron,
T. D. Tilley* ———— **1816 – 1819**

Facile Interconversion of [Cp_2(Cl)Hf(SnH_3)] and [Cp_2(Cl)Hf(μ-H)SnH_2]: DFT Investigations of Hafnocene Stannyl Complexes as Masked Stannylenes

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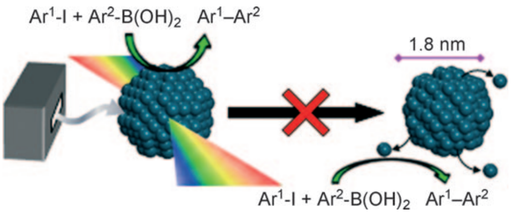

No need to get away: X-ray absorption spectroscopy of catalytically active palladium nanoparticles during a Suzuki–Miyaura cross-coupling reaction revealed that the nanoparticles were stable under the reaction conditions, and that cross-coupling involved the direct participation of surface palladium defect sites in the catalytic cycle (see picture). Selective chemical and structural poisons provided further evidence for a heterogeneous active site.

Heterogeneous Catalysis

P. J. Ellis, I. J. S. Fairlamb,*
S. F. J. Hackett, K. Wilson,
A. F. Lee* ———— **1820 – 1824**

Evidence for the Surface-Catalyzed Suzuki–Miyaura Reaction over Palladium Nanoparticles: An Operando XAS Study

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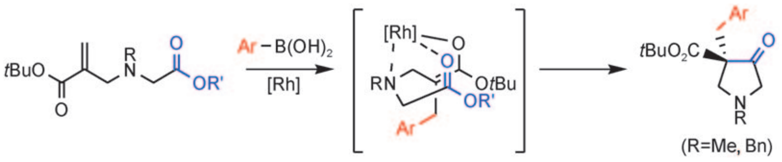


A new trick for an old dog: A Dieckmann-type cyclization was used to synthesize the title compounds with up to 96% *ee* (see scheme; Bn = benzyl). The presence of a β coordinating functionality in the substrate induces a competition between cyclization and elimination pathways that is influenced by the nature of the chiral ligand. A mechanistic rationale is proposed to account for these observations.

Asymmetric Catalysis

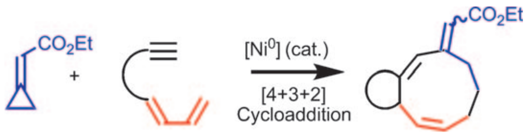
J. D. Hargrave, J. C. Allen, G. Kociok-Köhn,
G. Bish, C. G. Frost* ———— **1825 – 1829**

Catalytic Enantioselective Dieckmann-Type Annulation: Synthesis of Pyrrolidines with Quaternary Stereogenic Centers

Cycloaddition Reactions

S. Saito,* K. Maeda, R. Yamasaki,
T. Kitamura, M. Nakagawa, K. Kato,
I. Azumaya, H. Masu ——— **1830–1833**

Synthesis of Nine-Membered Carbocycles by the [4+3+2] Cycloaddition Reaction of Ethyl Cyclopropylideneacetate and Dienynes

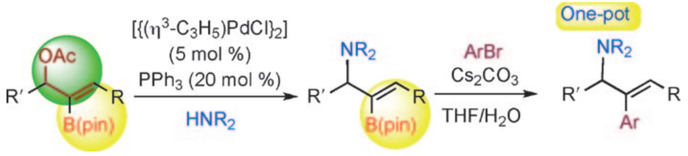


Various dienynes reacted efficiently with ethyl cyclopropylideneacetate in the presence of $[Ni(cod)_2]/PPh_3$, and cyclononadienes were synthesized in a selective manner. Dienynes tethered with aromatic rings were very good substrates, and the corresponding tricyclic compounds were isolated in high yields. The reaction provides a new route for the synthesis of nine-membered carbocycles (see scheme).

Chemoselectivity

M. M. Hussain, P. J. Walsh* **1834–1837**

Allylic Substitution versus Suzuki Cross-Coupling: Capitalizing on Chemoselectivity with Bifunctional Substrates

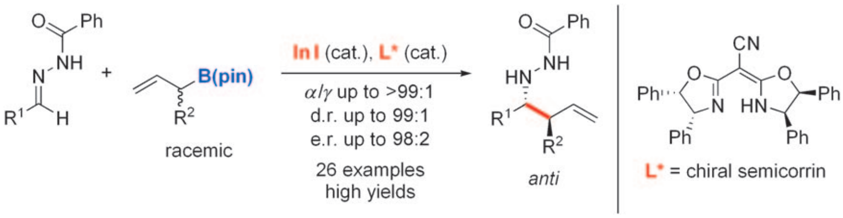


One catalyst, two reactions—a tale of chemoselectivity: Given the choice between an allylic acetate and a vinylboronate ester, palladium preferentially reacts with the allylic acetate to give the allylic substitution product. In the presence of an aryl bromide and base, Suzuki cross-coupling subsequently ensues to afford allylic amines (see scheme; pin = pinacol, THF = tetrahydrofuran).

Asymmetric Catalysis

A. Chakrabarti, H. Konishi, M. Yamaguchi,
U. Schneider, S. Kobayashi* **1838–1841**

Indium(I)-Catalyzed Asymmetric Allylation, Crotylation, and α-Chloroallylation of Hydrazones with Rare Constitutional and High Configurational Selectivities



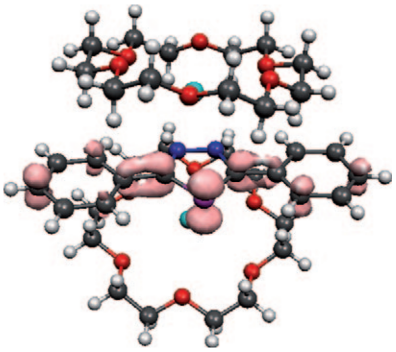
The hydra-zone: The first example of asymmetric In^I catalysis had been developed. InI combined with a chiral semicorrin ligand (L*) is an effective catalyst for enantioselective allylation, crotylation, and α-chloroallylation of hydrazones. In the two latter cases, C–C bond formations proceeded with high selectivity where both reactive aliphatic C–Cl and aromatic O–H bonds were tolerated.

Radicals

C.-F. Pi, Y. Wang, W. Zheng,* L. Wan,
H. Wu, L.-H. Weng, L.-M. Wu, Q.-S. Li,
P. von R. Schleyer* ——— **1842–1845**

A Persistent Dipotassium 1,2,4-Diazaphospholide Radical Complex: Synthesis, X-Ray Structure, and Bonding

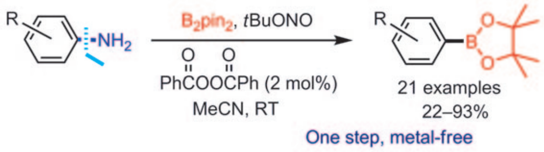
Staying power: A persistent 1,2,4-diazaphospholide dianion radical complex (see picture; N blue, P purple, K teal, O red) with a triple-decker conformation was prepared by one-electron reduction of 1,2,4-diazaphospholide anion with potassium in the presence of [18]crown-6. Computations suggested that the unpaired electron in the $[3,5\text{-}Ph_2dp]^{\bullet 2-}$ radical anion is delocalized (spin density: pink) to all three rings of the 1,2,4-diazaphospholide and the phosphorus atom.



Boronic Acids

F. Mo, Y. Jiang, D. Qiu, Y. Zhang, J. Wang* — **1846 – 1849**

Direct Conversion of Arylamines to Pinacol Boronates: A Metal-Free Borylation Process

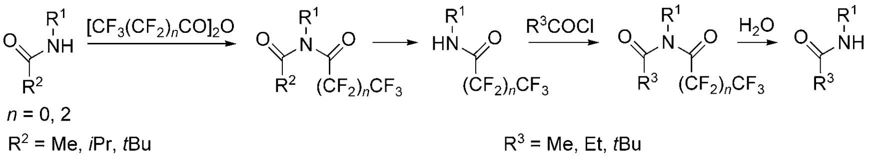


Leave the metal out: Arylboronates are produced in moderate to good yields by direct borylation of readily available aryl amines (see scheme). The reaction can be carried out under air at room temperature and transition-metal catalysis is not required. The boronate products can be used without purification in Suzuki–Miyaura cross-coupling reactions.

Transacylation

P. Rota,* P. Allevi, R. Colombo, M. L. Costa, M. Anastasia — **1850 – 1853**

General and Chemoselective N-Transacylation of Secondary Amides by Means of Perfluorinated Anhydrides

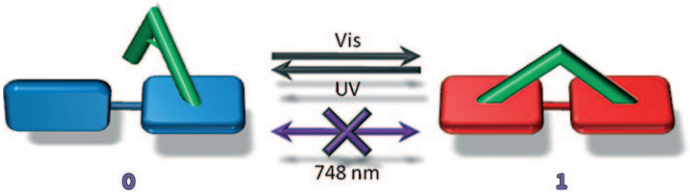


A direct route: The N-transacylation of secondary amides to their perfluorinated analogues with the possibility of subsequent conversion into a normal amide is reported (see scheme). This reaction occurs in the presence of a variety of functional groups that are labile to the hydrolysis conditions required by classical N-transacylation.

Molecular Devices

J. Kärnbratt, M. Hammarson, S. Li, H. L. Anderson, B. Albinsson, J. Andréasson* — **1854 – 1857**

Photochromic Supramolecular Memory With Nondestructive Readout

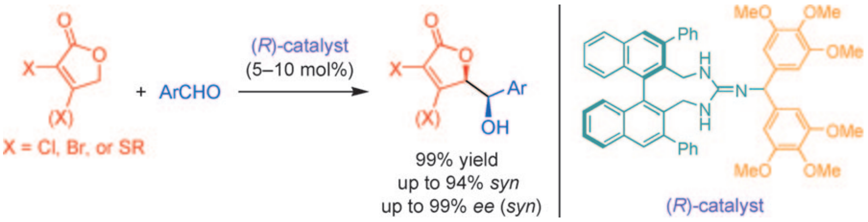


Looking without touching: The light-controlled isomerization of a complex containing a pyridine-appended dithienylethene (DTE; green) and a porphyrin dimer induces dramatic structural and spectral changes (see picture). These changes are monitored in a region outside the photochromically active absorption bands of DTE, therefore allowing a nondestructive readout so that the process functions as a molecular optically controlled memory.

Organocatalysis

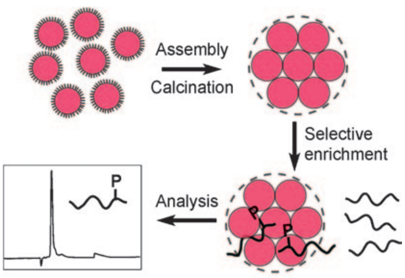
H. Ube, N. Shimada, M. Terada* — **1858 – 1861**

Asymmetric Direct Vinylogous Aldol Reaction of Furanone Derivatives Catalyzed by an Axially Chiral Guanidine Base



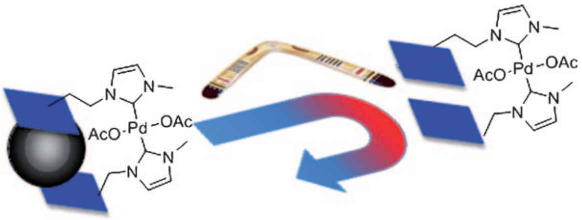
Ace of Base: The first highly enantioselective direct vinylogous aldol reaction of dihalogenated or α-thio-substituted furanones with aldehydes utilizes an axially chiral guanidine base catalyst. The method provides facile access to enantioenriched γ-substituted butenolides.

Mesoporous Materials



Mesoporous traps: The title clusters were fabricated through self-assembly of nanocrystals in emulsion droplets and subsequent protective calcination. The specific affinity offered by the metal oxide and the size-exclusion mechanism enabled by the mesoporous structure enable the use of these clusters for efficient enrichment of intact phosphorylated proteins from complex biological samples (see picture).

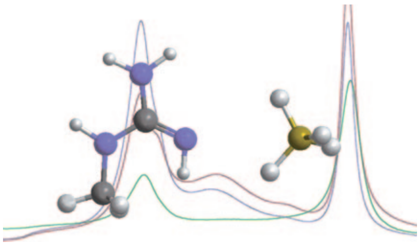
Homogeneous Catalysis



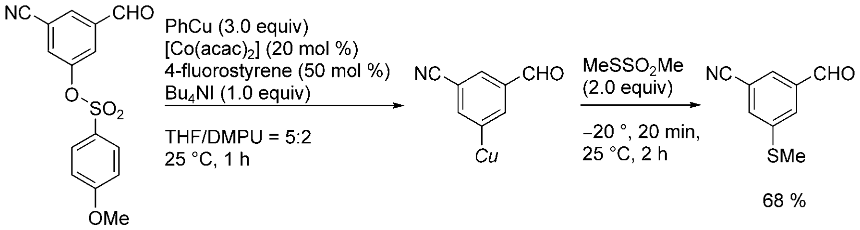
Boomerang catalysis: A catalyst catch–release system is established by the non-covalent attachment of a Pd N-heterocyclic carbene complex to graphene-coated magnetic Co nanoparticles. The immobilization by pyrene tags (see scheme; blue) is reversible at elevated temperatures, releasing the homogeneous catalyst. The hydroxycarbonylation of aryl halides is performed in 16 iterative reactions with this highly active catalyst.

Hydrogen Storage

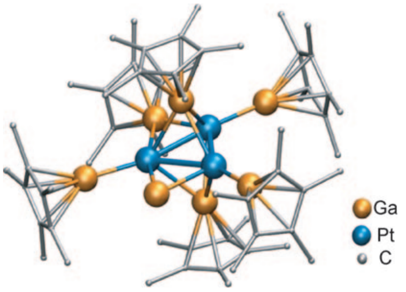
Promising: The ionic liquid methylguanidinium borohydride (see picture; blue N, yellow B, gray C, white H) is able to release 9 wt% hydrogen under thermal and catalytic conditions. The thermodynamic features and the products of the dehydrogenation are also investigated.



Organocopper Reagents



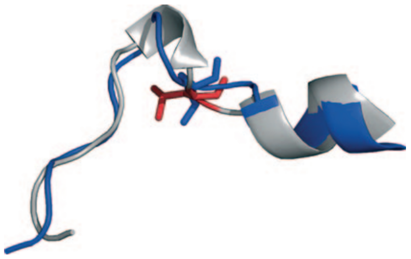
Organocopper reagents from phenols: A new cobalt-catalyzed aryl sulfonate/copper exchange reaction allows the synthesis of highly functionalized aryl copper reagents from sulfonates bearing electron-deficient substituents under mild conditions (25–45 °C, 1–6 h; see example). Sensitive functional groups, such as aldehydes, esters, and nitriles, are well-tolerated.



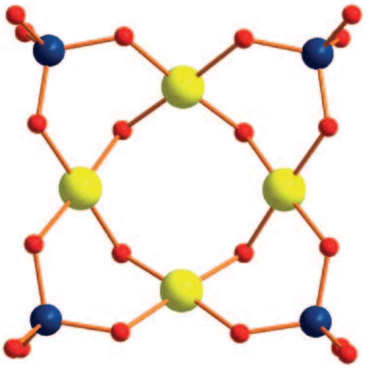
The naked and the edge: The selective oxidative cleavage of Cp* from coordinated GaCp* ligands lead to the cluster cations $[(\mu_2\text{-Ga})_2\text{Pd}_3(\text{GaCp}^*)_6]^{2+}$ and $[(\mu_2\text{-Ga})\text{Pt}_3(\text{GaCp}^*)_6]^{+}$ (see structure) which are the first examples of the edge-bridging coordination mode of "naked" Ga^+. This chemistry is a step towards a rational synthesis of metal-rich molecules as discrete models for intermetallic phases.

Group 13 Ligands

Roll out the barrel: The conformation of the N-terminal domain of a functional human voltage-dependent anion channel (hVDAC1) in lipid bilayers has been determined (see picture; overlay of NMR model (blue) and X-ray structure (red/gray)). Solid-state NMR spectroscopy reveals that the N terminus assumes a well-defined, rigid structure and that its removal induces a conformational change in the hVDAC1 β-barrel.



Membrane Proteins



More noble than ever: The first fully inorganic discrete polynuclear gold(III) oxo complex $[\text{Au}^{\text{III}}_4\text{As}^{\text{V}}_4\text{O}_{20}]^{8-}$ (see structure; Au yellow, As blue, O red) was prepared by condensation of $[\text{Au(OH)}_4]^-$ in the presence of AsO_4^{3-} ions under mild reaction conditions. The resulting polyoxoaurate exhibits a tetrameric structure with square-planar coordinated Au^{III} ions linked by oxo and arsenate bridging ligands.

Noble Metalates

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

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