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. Staubitz, A. Presa, I. Manners**
Iridium-Catalyzed Dehydrocoupling of Primary Amine–Borane Adducts: A Route to High Molecular Weight Polyaminoboranes, Boron–Nitrogen Analogues of Polyolefins

S. Gerlich, M. Gring, H. Ulbricht, K. Hornberger, J. Tüxen, M. Mayor,* M. Arndt**
Matter-Wave Metrology as a Complementary Tool for Mass Spectrometry

V. L. Blair, L. M. Carrella, W. Clegg, B. Conway, R. W. Harrington, L. M. Hogg, J. Klett, R. E. Mulvey, E. Rentschler, L. Russo*
Tuning the Basicity of Synergic Bimetallic Reagents: Switching the Regioselectivity of Direct Dimetalation of Toluene from 2,5- to 3,5-Positions

*J.-J. Li, T.-S. Mei, J.-Q. Yu**
Synthesis of Indolines and Tetrahydroisoquinolines from Arylethylamines by Palladium(II)-Catalyzed C–H Activation Reactions

*S. G. Srivatsan, N. J. Greco, Y. Tor**
Highly Emissive Fluorescent Nucleoside Signals the Activity of Toxic Ribosome-Inactivating Proteins

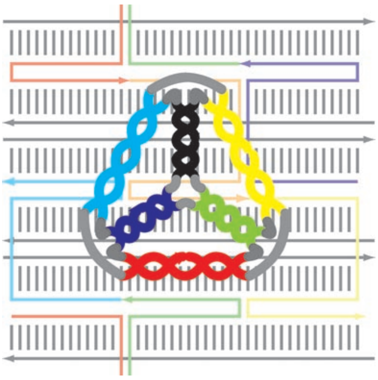
M. Mascal, E. B. Nikitin*
Direct, High-Yield Conversion of Cellulose into Biofuel

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

Books

Highlights

DNA Nanotechnology



Recent advances in DNA nanotechnology have resulted in improved supramolecular architectures and novel assembly strategies such as DNA origami and hierarchical assembly. This has now led to the experimental demonstration of a variety of rigid nanoscale three-dimensional objects entirely self-assembled from DNA molecules.

Oxidation of Water

$$4\,[\mathrm{Ru(bpy)_3}]^{3+} + 2\,\mathrm{H_2O} \longrightarrow 4\,[\mathrm{Ru(bpy)_3}]^{2+} + \mathrm{O_2} + 4\,\mathrm{H^+}$$

$$\text{catalyst} = [\{\mathrm{Ru_4O_4(OH)_2(H_2O)_4}\}(\mathrm{SiW_{10}O_{36}})_2]^{10-}$$

Water damage: A problem in the catalytic oxidation of water has until now been the stability of the catalyst because of oxidative degradation of the organic ligands. A solution to this problem has been found in the form of a highly active and stable purely inorganic catalyst (see scheme; bpy = 2,2′-bipyridine).

Correspondence

Uranium Compounds

C. Villiers, P. Thuéry,
M. Ephritikhine* ________ **5892 – 5893**

The First *cis*-Dioxido Uranyl Compound under Scrutiny

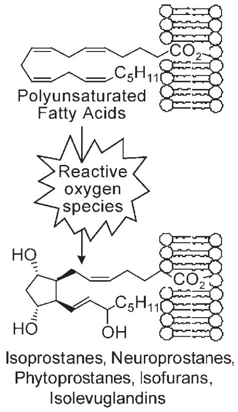
The identity of a *cis*-dioxido uranyl compound recently reported by P. B. Duval et al., is questioned on the basis of the structural characterization of three other compounds obtained using the reported reactants.

Reviews

Cyclic Lipids

U. Jahn,* J.-M. Galano,*
T. Durand* ________ **5894 – 5955**

Beyond Prostaglandins—Chemistry and Biology of Cyclic Oxygenated Metabolites Formed by Free-Radical Pathways from Polyunsaturated Fatty Acids

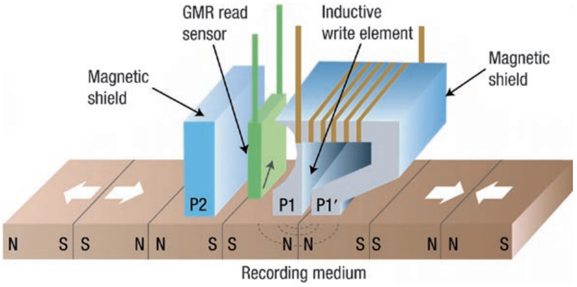


Oxidative stress and fatty acids: Polyunsaturated fatty acids form diverse cyclic metabolites, namely isoprostanes, neuroprostanes, or phytoprostanes, in vivo by free-radical pathways triggered by reactive oxygen species. Their structural variety, modes of formation, biological activities, and diagnostic applications of these fatty acids as well as synthetic routes are summarized.

Spintronics

A. Fert* ________ **5956 – 5967**

Origin, Development, and Future of Spintronics (Nobel Lecture)



Going for a spin: The discovery of giant magnetoresistance (GMR) opened up a new area of technology—spintronics—which, in contrast to conventional electronics, uses not only the charge, but also the spin of the electron. Applications of GMR have revolutionized hard-disk technology (see picture). Albert Fert, Nobel laureate in Physics 2007, describes firsthand the discovery of GMR and the development of spintronics.

For the USA and Canada:
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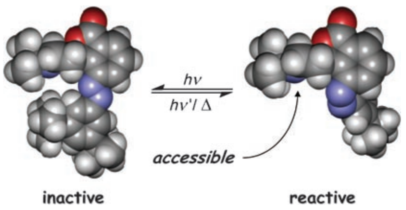
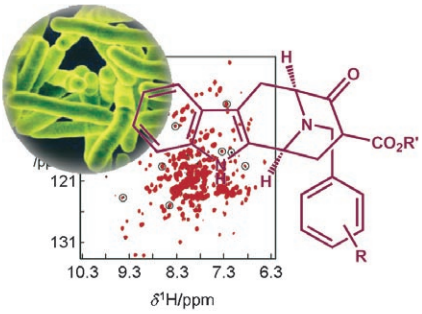


Smart bases: By using a photochromic azobenzene-derived blocking group, a piperidine base can be switched between a sterically shielded, inactive form and an accessible, reactive form (see picture; C dark gray, H light gray, O red, N blue). Thus, light can be used for the reversible external modulation of ground-state basicity and hence activity in general base catalysis.

Photochemistry

M. V. Peters, R. S. Stoll, A. Kühn, S. Hecht* ______ **5968 – 5972**

Photoswitching of Basicity



A biologically relevant collection: The synthesis of a macroline-derived compound collection (see general structural formula) on the basis of the criterion of biological relevance yielded an unprecedented class of inhibitors of the title mycobacterial enzyme, which is a potential target for the development of new antimycobacterial drug candidates.

Enzyme Inhibitors

A. Nören-Müller, W. Wilk, K. Saxena, H. Schwalbe, M. Kaiser,* H. Waldmann* ______ **5973 – 5977**

Discovery of a New Class of Inhibitors of *Mycobacterium tuberculosis* Protein Tyrosine Phosphatase B by Biology-Oriented Synthesis

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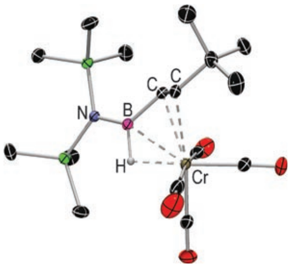
Borylene insertion: Irradiation of the terminal borylene complex $[(OC)_5Cr{=}BN(SiMe_3)_2]$ at room temperature in the presence of 3,3-dimethyl-1-butene leads to insertion of the aminoborylene moiety into the olefinic C–H bond and formation of a vinylborane complex (see structure).



B–H Agostic Interactions

H. Braunschweig,* R. D. Dewhurst, T. Herbst, K. Radacki ______ **5978 – 5980**

Reactivity of a Terminal Chromium Borylene Complex towards Olefins: Insertion of a Borylene into a C–H Bond

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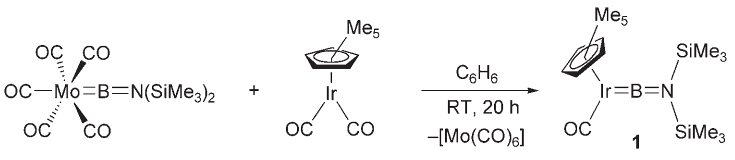
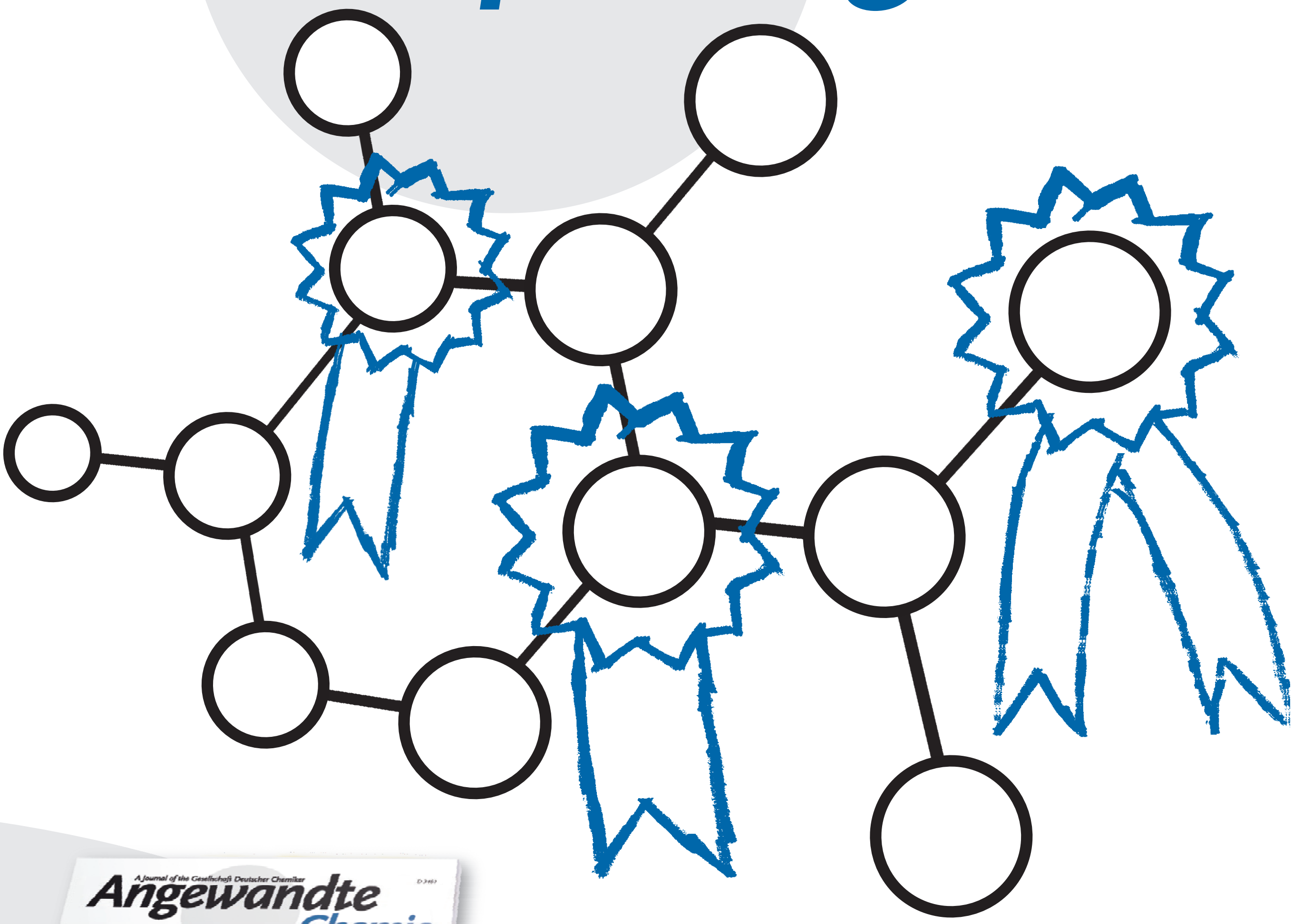


Borylene transfer reactions to $[(\eta^5\text{-}C_5R_5)M(CO)_2]$ (M = Rh, R = H; M = Ir, R = Me) using $[(OC)_5Mo{=}BN(SiMe_3)_2]$ as a borylene source proceed at room temperature and generate terminal rhodium and iridium borylene complexes (see scheme). Iridium complex **1** was characterized by X-ray crystallography.

Borylene Complexes

H. Braunschweig,* M. Forster, T. Kupfer, F. Seeler ______ **5981 – 5983**

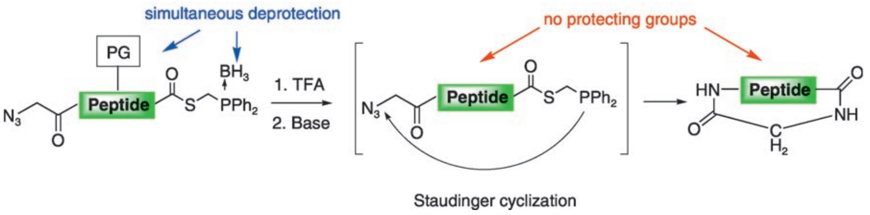
Borylene Transfer under Thermal Conditions for the Synthesis of Rhodium and Iridium Borylene Complexes



Staudinger Ligation

R. Kleineweischede,
C. P. R. Hackenberger* **5984 – 5988**

Chemoselective Peptide Cyclization by Traceless Staudinger Ligation



Two birds with one stone! An intramolecular traceless Staudinger ligation was employed to synthesize cyclic peptides. The final amide bond formation was induced by deprotection of the azidopeptide phosphinothioesters. Treatment with trifluoroacetic acid (TFA) results in the simultaneous removal of the borane along with the protecting groups on the peptide side chains, and chemoselective amide bond cyclization ensues.

Isotopically Labeled Formaldehyde

J. M. Hooker,* M. Schönberger,
H. Schieferstein,
J. S. Fowler **5989 – 5992**

A Simple, Rapid Method for the Preparation of [^{11}C]Formaldehyde

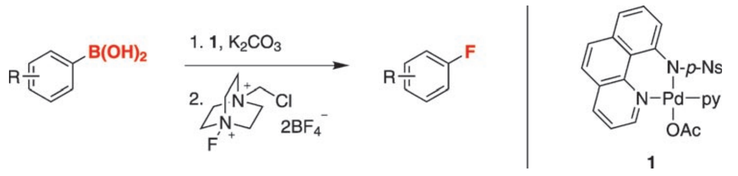
$$^{11}CH_3I \xrightarrow[70\,^{\circ}C,\ 2\ min]{TMAO,\ DMF} \boxed{^{11}CH_2O}$$

A PET project: A powerful reagent for the synthesis of positron-emitting imaging molecules—[^{11}C]formaldehyde—is accessible from [^{11}C]methyl iodide and trimethylamine *N*-oxide (TMAO) in high yields and under mild conditions. Easy access to [^{11}C]formaldehyde expands the scope of the carbon-11 toolbox and will lead to new reaction methodology and imaging compounds.

Fluorination

T. Furuya, H. M. Kaiser,
T. Ritter* **5993 – 5996**

Palladium-Mediated Fluorination of Arylboronic Acids

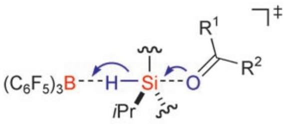


Saving the best for last: Novel palladium complexes allow mild, two-step fluorination of aryl boronic acids (see scheme). The reaction is regiospecific, functional-group tolerant, has a broad substrate scope, and is ideally suited for the introduction of fluorine substituents at a late stage for aryl fluoride synthesis.

Reaction Mechanisms

S. Rendler, M. Oestreich* **5997 – 6000**

Conclusive Evidence for an S_N2-Si Mechanism in the $B(C_6F_5)_3$-Catalyzed Hydrosilylation of Carbonyl Compounds: Implications for the Related Hydrogenation



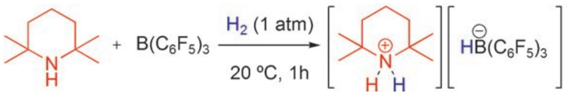
concerted S_N2-Si mechanism

Just ask silicon: An experimentally straightforward yet effective Walden-type analysis showcases the usefulness of silanes with a stereogenic silicon center as stereochemical probes. The $B(C_6F_5)_3$-catalyzed hydrosilylation and likely the related hydrogenation proceed through linear B-H-Si-O transition states, as verified by flawless inversion of the absolute configuration at silicon (see scheme).

H_2 Activation

V. Sumerin, F. Schulz, M. Nieger,
M. Leskelä, T. Repo,*
B. Rieger* ______ **6001 – 6003**

Facile Heterolytic H_2 Activation by Amines and $B(C_6F_5)_3$

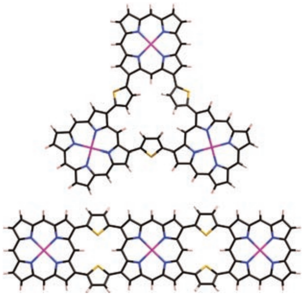


Divide and conquer: Metal-free systems consisting of amines and $B(C_6F_5)_3$ cleave H_2 heterolytically at ambient pressure and often at room temperature. The efficient reduction of benzaldehyde by the product shown in the scheme highlights the potential of such systems for application in hydrogenation reactions.

Macrocyclic Porphyrins

J. Song, S. Y. Jang, S. Yamaguchi, J. Sankar,
S. Hiroto, N. Aratani, J. Y. Shin,
S. Easwaramoorthi, K. S. Kim, D. Kim,*
H. Shinokubo,* A. Osuka* _ **6004 – 6007**

2,5-Thienylene-Bridged Triangular and Linear Porphyrin Trimers



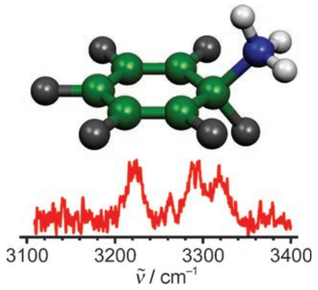
A question of shape: Palladium-catalyzed cross-coupling of borylporphyrins has led to the synthesis of a β-to-β thienylene-bridged porphyrin dimer and two types of trimer (see picture; gray C; white H, pink Ni, yellow S, blue N). The ladderlike trimer exhibits a very large two-photon absorption cross-section (17300 GM) at 800 nm, while that of the triangular trimer is moderate in comparison (8600 GM).

Reaction Intermediates

H. Hasegawa, K. Mizuse, M. Hachiya,
Y. Matsuda, N. Mikami,
A. Fujii* ______ **6008 – 6010**

Observation of an Isolated Intermediate of the Nucleophilic Aromatic Substition Reaction by Infrared Spectroscopy

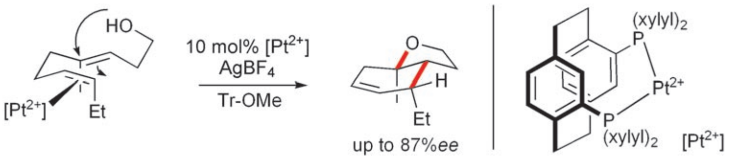
Caught in the act: The σ complex formed as an intermediate in a nucleophilic aromatic substitution has been observed experimentally. Efficient direct ionization of C_6F_6 by coherent vacuum ultraviolet light was employed to effect the formation of $C_6F_5NH_2^+$ from $C_6F_6^+/NH_3$. Comparison of the IR spectrum of $(C_6F_6\text{-}NH_3)^+$ with that predicted from DFT calculations showed that the cluster cation forms a stable σ complex (see picture).



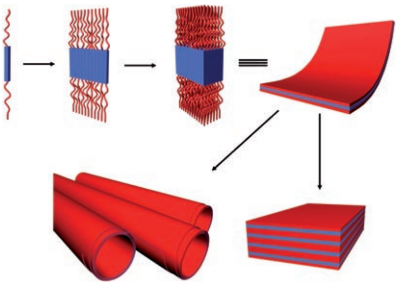
Asymmetric Catalysis

C. A. Mullen, A. N. Campbell,
M. R. Gagné* ______ **6011 – 6014**

Asymmetric Oxidative Cation/Olefin Cyclization of Polyenes: Evidence for Reversible Cascade Cyclization



Platinum and silver work together: Activation of [(xylyl-phanephos)$PtCl_2$] by silver generates an electrophilic catalyst that can enantioselectively, diastereoselectively, and regioselectively promote the stereospecific oxidative cyclization of polyene-ols (see scheme; Tr = trityl). Mechanistic experiments indicate that the stereochemistry-determining step is not the initial cyclization step, but rather a subsequent step in the reaction.



Roll up! Roll up! The self-assembly of *para*-terphenylen-1,4″-ylenebis(dodecanamide) in THF results in either multiwalled, rolled-up, open-ended organic nanotubes or layered sheets (see picture) depending on the conditions used. The nanotubes can co-assemble with fullerene to produce quasi-cable-like structures with C_{60} nanowires inside the nanotubes.

Nanotube Self-Assembly

Y. Chen, B. Zhu, F. Zhang, Y. Han, Z. Bo* ——— **6015–6018**

Hierarchical Supramolecular Self-Assembly of Nanotubes and Layered Sheets

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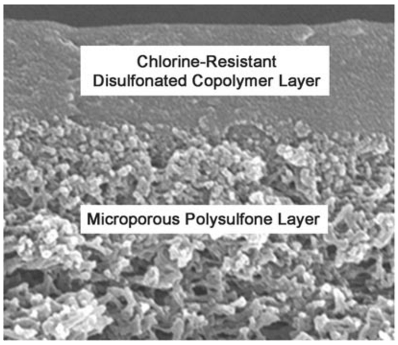


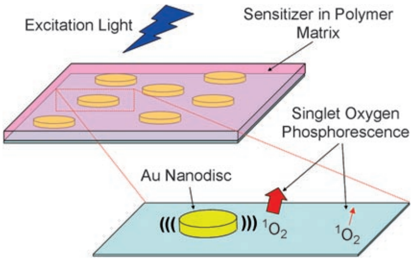
Get the salt out: Conventional polyamide desalination membranes suffer from low chlorine tolerance, leading to short membrane life. Using newly synthesized sulfonated copolymers prepared by direct copolymerization of disulfonated monomer, chlorine-tolerant desalination membranes (see picture) showing high flux and high salt rejection were developed.

Desalination Membranes

H. B. Park,* B. D. Freeman,* Z.-B. Zhang, M. Sankir, J. E. McGrath ——— **6019–6024**

Highly Chlorine-Tolerant Polymers for Desalination

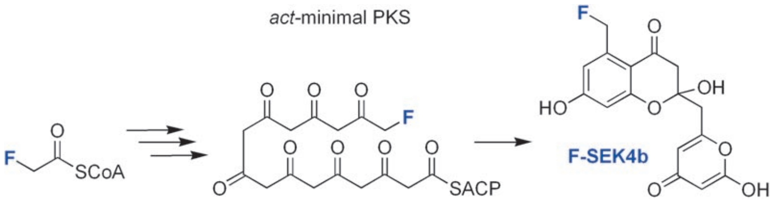
Giving singlet oxygen emission a boost: With the aid of specifically designed gold nanodiscs, one of nature's most improbable transitions, singlet oxygen radiative decay, can be significantly enhanced by interaction with localized surface plasmons.



Phosphorescent Enhancement

R. Toftegaard, J. Arnbjerg, K. Daasbjerg, P. R. Ogilby,* A. Dmitriev, D. S. Sutherland, L. Poulsen **6025–6027**

Metal-Enhanced 1270 nm Singlet Oxygen Phosphorescence



Fluorine, changing course: Challenging the actinorhodin minimal polyketide synthase (*act*-minimal PKS) with fluoroacetyl-CoA as a starter unit yielded a fluorinated octaketide intermediate that led to the selective formation of fluoro-SEK4b (see scheme); no fluoro-SEK4 was formed (not shown).

Enzymology

H. Hong,* D. Spiteller, J. B. Spencer ——— **6028–6032**

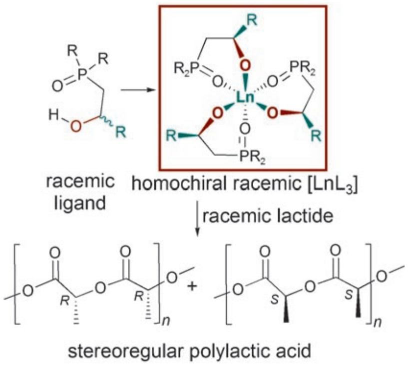
Incorporation of Fluoroacetate into an Aromatic Polyketide and Its Influence on the Mode of Cyclization

Stereoselective Polymerization

P. L. Arnold,* J.-C. Buffet, R. P. Blaudeck, S. Sujecki, A. J. Blake, C. Wilson ________ **6033 – 6036**

C_3-Symmetric Lanthanide Tris(alkoxide) Complexes Formed by Preferential Complexation and Their Stereoselective Polymerization of *rac*-Lactide

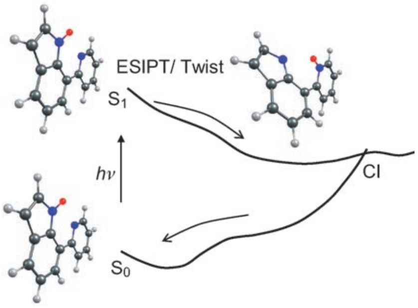
Restoring order: Y^{III}, Eu^{III}, and Er^{III} tris(ligand) complexes of a new chiral alkoxide ligand, tBu$_2$P(O)CH$_2$CH(tBu)OH (HL), preferentially form as C_3-symmetric diastereomers. Thus racemic HL affords (*RRR*)- and (*SSS*)-[LnL$_3$] complexes, which are active catalysts for the stereoselective polymerization of *rac*-lactide to afford highly isotactic polylactic acid.



Photoinduced Proton Transfer

Y. Nosenko, G. Wiosna-Sałyga, M. Kunitski, I. Petkova, A. Singh, W. J. Buma,* R. P. Thummel,* B. Brutschy,* J. Waluk* ____ **6037 – 6040**

Proton transfer with a twist? Femtosecond Dynamics of 7-(2-pyridyl)-indole in Condensed Phase and in Supersonic Jets



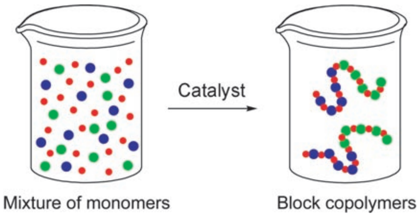
Twist-assisted proton transfer: Excited-state intramolecular proton transfer (ESIPT) in 7-(2-pyridyl)indole proceeds in a barrierless fashion and is coupled with mutual twisting of the pyridine and indole moieties. As a result, the reaction is slower in a condensed phase than in the supersonic jet-isolated molecule (1 ps vs. about 300 fs). Ultrafast radiationless deactivation of the phototautomer occurs via a conical intersection (CI).

Diblock Copolymers

R. C. Jeske, J. M. Rowley, G. W. Coates* ________ **6041 – 6044**

Pre-Rate-Determining Selectivity in the Terpolymerization of Epoxides, Cyclic Anhydrides, and CO$_2$: A One-Step Route to Diblock Copolymers

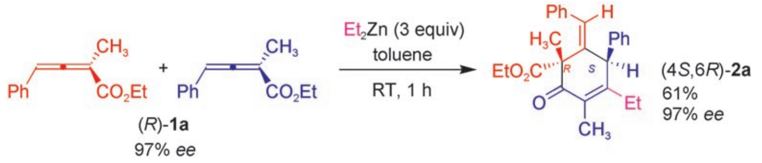
Catching a second wind: In kinetic resolution polymerization, one monomer is consumed faster than the other, which creates diblock copolymers that only slowly approach 100% conversion and contain tapering. In the title reaction, the opposite is true: the first block forms cleanly, followed by a second block that has an even higher rate of polymerization. This unique reaction allows for the programmed self-assembly of diblock polymers that display little tapering.



Domino Reactions

Z. Lu, G. Chai, S. Ma* ____ **6045 – 6048**

Highly Regio- and Stereoselective Double Michael Addition–Cyclization of 2,3-Allenoates with Organozinc Compounds: Efficient Synthesis of 5-Benzylidenecyclohex-2-enones

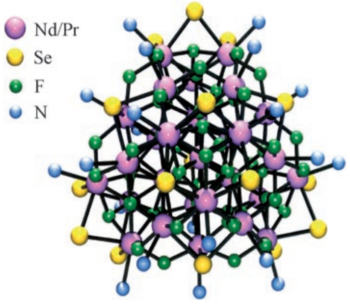


Highly substituted α,β-unsaturated cyclohexenones, a key structural motif in many natural products, were prepared in the title reaction (see scheme). High diastereoselectivity was observed with respect to the two stereogenic centers at the 4- and 6-positions. When optically active starting materials were used, the desired products were formed without evident racemization. A rationale for the observed stereoselectivity is proposed.

Lanthanoid Fluoride Nanoclusters

M. Romanelli, G. A. Kumar, T. J. Emge, R. E. Riman, J. G. Brennan* **6049 – 6051**

Intense Near-IR Emission from Nanoscale Lanthanoid Fluoride Clusters



Fluoride clusters of lanthanoids can be prepared in organic solvents by metathetical reactions of Ln(SePh)$_3$ with NH$_4$F. The first products of these reactions, [(py)$_{24}$Ln$_{28}$F$_{68}$(SePh)$_{16}$] (Ln = Pr, Nd; py = pyridine; see structure), are currently the largest discrete lanthanoid clusters ever isolated. Emission experiments on the neodymium compound reveal a near-IR quantum efficiency of 41 %.

Plasma Chemistry

A. Wang,* M. Qin, J. Guan, L. Wang, H. Guo, X. Li, Y. Wang, R. Prins, Y. Hu **6052 – 6054**

The Synthesis of Metal Phosphides: Reduction of Oxide Precursors in a Hydrogen Plasma

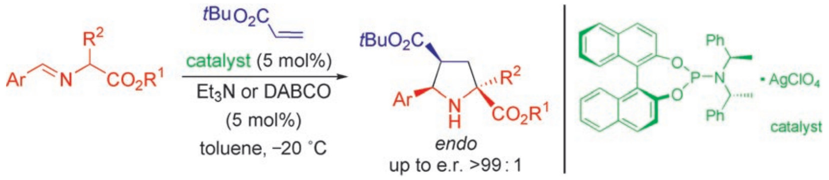
$$4\ \mathrm{NiO\ (s)} + \mathrm{P_2O_5\ (s)} + 9\ \mathrm{H_2\ (g)} \underset{\text{[very fast]}}{\overset{\text{[slow]}}{\rightleftharpoons}} 2\ \mathrm{Ni_2P\ (s)} + 9\ \mathrm{H_2O\ (g)}$$

A NiPpy phosphide synthesis: Nickel phosphides such as Ni$_2$P and Ni$_3$P are synthesized stoichiometrically from oxide precursors in a nonthermal hydrogen plasma at atmospheric pressure and low temperature in 60 min (see scheme). This energy- and time-efficient approach can also be applied to the synthesis of other metal phosphides such as GaP, InP, MoP, and WP.

Asymmetric Catalysis

C. Nájera,* M. d. G. Retamosa, J. M. Sansano* **6055 – 6058**

Catalytic Enantioselective 1,3-Dipolar Cycloaddition Reactions of Azomethine Ylides and Alkenes by Using Phosphoramidite–Silver(I) Complexes



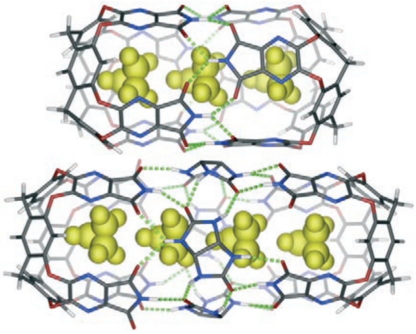
Silver catalysts: A novel chiral phosphoramidite–silver perchlorate complex has been used for the synthesis of highly substituted pyrolidine rings. This method is valuable for the synthesis of biologically active α-substituted prolines by using hindered dipoles generated from α-substituted α amino acids (see scheme; DABCO = 1,4-diazabicyclo[2.2.2]octane).

Host–Guest Systems

D. Ajami, J. Rebek, Jr.* **6059 – 6061**

Gas Behavior in Self-Assembled Capsules

Gas encapsulation: Several cyclopropane or butane molecules are reversibly bound in self-assembled, hydrogen-bonded capsules under ambient conditions (see picture). A stable arrangement results when approximately 40% of the space is occupied. The gas pressures in these complexes have been calculated, and are shown to deviate from ideal gas behavior as a result of CH–π interactions with the capsule walls.

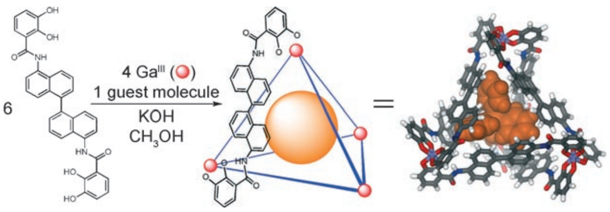


Contents

Supramolecular Chemistry

S. M. Biros, R. M. Yeh,
K. N. Raymond* **6062 – 6064**

Design and Formation of a Large Tetrahedral Cluster Using 1,1′-Binaphthyl Ligands

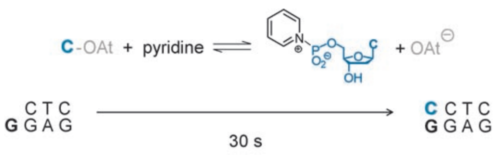


Greater than 700 Å^3 is the calculated interior volume of a novel [Ga$_4$L$_6$] cluster constructed with a derivatized 1,1′-binaphthyl ligand. Due to the size of the cavity, a guest molecule of suitable size and shape is employed to template the supramolecular assembly (see scheme).

Primer Extension

M. Röthlingshöfer, E. Kervio, T. Lommel,
U. Plutowski, A. Hochgesand,
C. Richert* **6065 – 6068**

Chemical Primer Extension in Seconds

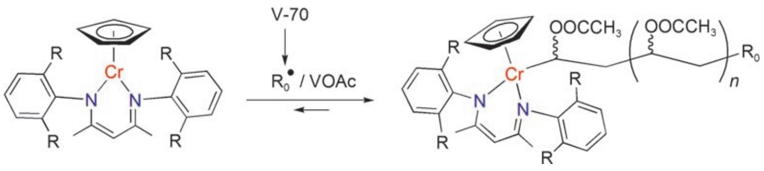


Rapid extention: Catalysis by pyridine accelerates template-directed chemical primer extension to $t_{1/2} < 1$ min for all four nucleotides (A/C/G/T). For C and G, greater than 99% conversion is observed after 30 s (see picture). These sequence-selective reactions open up new avenues for the interrogation of DNA sequences and chemical replication.

Chromium Complexes

Y. Champouret, U. Baisch, R. Poli,*
L. Tang, J. L. Conway,
K. M. Smith* **6069 – 6072**

Homolytic Bond Strengths and Formation Rates in Half-Sandwich Chromium Alkyl Complexes: Relevance for Controlled Radical Polymerization



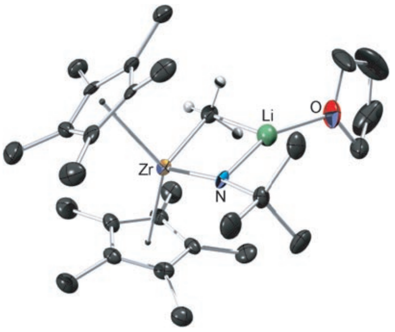
Radicals in check: The steric properties of the aryl substituents in chromium β-ketiminato complexes can be tuned to achieve reversible radical trapping of a growing poly(vinyl acetate) radical chain (see scheme; V-70 = radical initiator, VOAc = vinyl acetate).

Zirconium Complexes

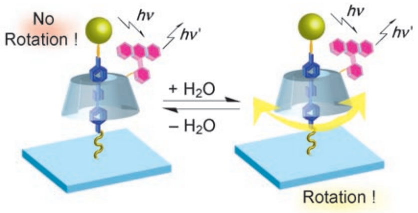
M. Chiu, H. M. Hoyt, F. E. Michael,
R. G. Bergman,*
H. van Halbeek **6073 – 6076**

Synthesis, Structural Characterization, and Quantitative Basicity Studies of Lithium Zirconimidate Complexes

Lithium zirconimidate complexes (see structure) were isolated by deprotonation of zirconium methyl amide complexes or by addition of methyllithium across imidozirconium complexes. Quantitative studies on the acidity of these conjugate bases of zirconium amide complexes showed that both the kinetics and thermodynamics of proton exchange are influenced by the ancillary ligands on the zirconium center.

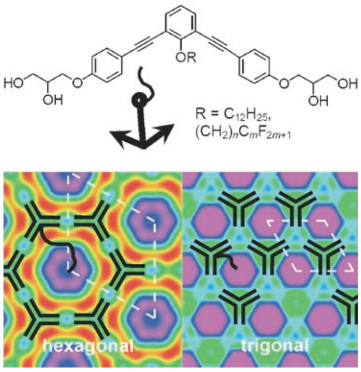


Hula hoop: The rotary movement of a chromophore-modified α-cyclodextrin (α-CD) was studied in a rotaxane structure attached to a glass substrate. The rotary movement of the α-CD was demonstrated by defocused wide-field imaging with total internal reflection fluorescence microscopy. The motion of the α-CD is suspended in the dry state, whereas a fast rotary movement/rotary vibration is observed in the wet state.



Single Molecular Motors

Anchored in hexagons: The molecules shown display two new complex liquid-crystalline phases formed by arrays of hexagonal cylinders, each hexagon comprising either three or six molecules. The phase type can be selected by choosing the right size ratio between the π-conjugated aromatic core (the anchor) and the flexible chain. One of the phases is the first columnar liquid crystal with trigonal symmetry.



Liquid crystals

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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