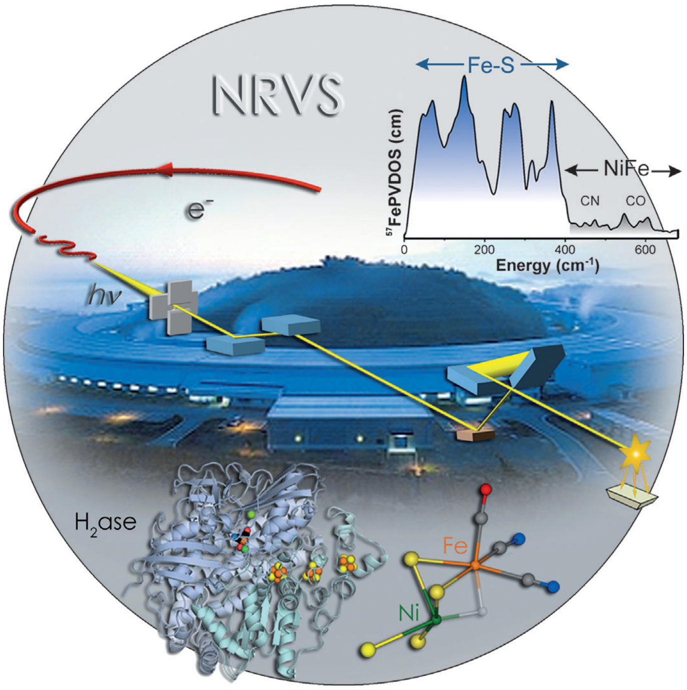
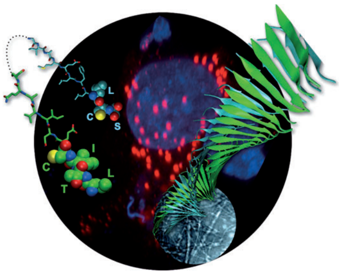
The active site ...

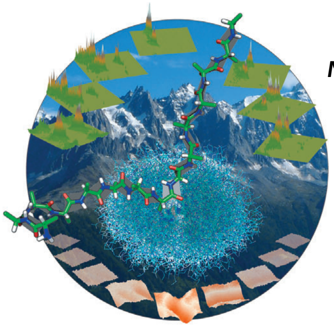


… of [NiFe] hydrogenase is an excellent catalyst for hydrogen conversion with an intriguing ability to recover from exposure to dioxygen. In their Communication on page 724 ff., W. Lubitz, S. P. Cramer, and co-workers use the synchrotron technique of nuclear resonance vibrational spectroscopy to identify normal modes associated with active-site Fe−CN and Fe−CO motion.

Huntingtin Protein

H. A. Lashuel and co-workers show in their Communication on page 562 ff. that an N-terminal domain in the huntingtin protein is highly prone to aggregation. The consequences for toxicity are discussed.





NMR Spectroscopy

An approach for predicting residual dipolar couplings from disordered protein chains is reported by M. Blackledge et al. in their Communication on page 687 ff.

Bimetallic Nanocrystals

In their Communication on page 645 ff., A. W. Xu et al. describe the synthesis of highly branched star-shaped bimetallic nanocrystals and their application as catalysts for the oxidation of ethanol.

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Service

Author Profile

"My favorite food is Thai (red) curry.
The most exciting thing about my research is working with bright, dynamic, and motivated researchers …"
This and more about Frank Caruso can be found on page 496.

News

G. M. Whitesides

R. Zellner

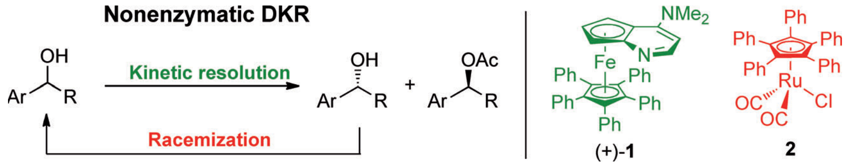
F. Diederich

R. S. Langer

Books

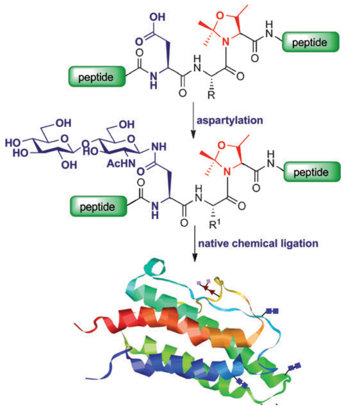
Highlights

Dynamic Kinetic Resolution



“Ruth” helps iron! A novel method for the non-enzymatic dynamic kinetic resolution (DKR) of secondary aryl alcohols by the use of the planar chiral ferrocene derivative (+)-**1** in combination with the ruthenium racemization catalyst **2** yields acetylated alcohols in high enantioselectivity and yield. This development opens opportunities for new developments in the field of non-enzymatic dynamic kinetic resolution.

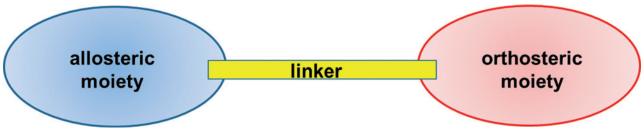
Glycoproteins



A convergent and operationally simple method for the preparation of N-linked glycopeptides (see picture) was highlighted in the preparation of three glycopeptide fragments of erythropoietin. These fragments were assembled by ligation chemistry in the first total synthesis of erythropoietin bearing four glycans. This methodology should find far-reaching applications in the synthesis of a whole range of glycoproteins for biological study.

Minireviews

Receptor Ligands



Balance of power: The simultaneous binding of a ligand to two binding sites of a receptor can leads to high selectivity as an agonist and/or antagonist and may induce pathway-specific signaling. This concept offers access to GPCR modulators with an unprecedented receptor-subtype and signaling selectivity profile and, as a consequence, to drugs with fewer side effects (GPCR = G protein coupled receptor).

For the USA and Canada:
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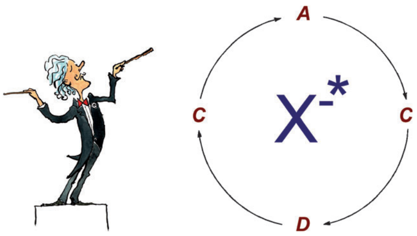
Reviews

ACDC

M. Mahlau, B. List* ______ **518 – 533**

Asymmetric Counteranion-Directed Catalysis: Concept, Definition, and Applications

Opposites attract: This simple realization is the basis for asymmetric counteranion-directed catalysis (ACDC). All reactions proceeding via cationic intermediates are accompanied by a counteranion. Inducing high enantioselectivities in these reactions merely by ion pairing with an enantiomerically pure counteranion has been achieved for the first time during recent years.

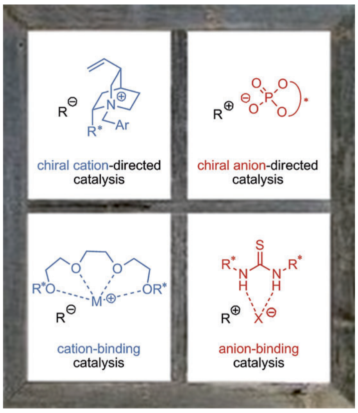


Asymmetric Catalysis

K. Brak, E. N. Jacobsen* ______ **534 – 561**

Asymmetric Ion-Pairing Catalysis

Framing the field, this review provides an overview of four ion-pairing strategies that have emerged for asymmetric catalysis of transformations proceeding through charged intermediates or reagents (see picture). Particular emphasis is placed on the mechanistic features that enable high asymmetric induction in these systems.



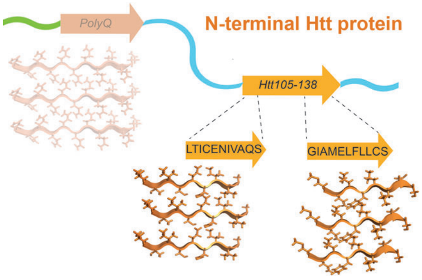
Communications

Protein Models

Z. M. Wang, H. A. Lashuel* ______ **562 – 567**

Discovery of a Novel Aggregation Domain in the Huntingtin Protein: Implications for the Mechanisms of Htt Aggregation and Toxicity

Aggravating aggregation: An N-terminal domain that is in close proximity to the polyQ domain in the huntingtin protein, htt105–138, is shown to be highly aggregation prone (see scheme). Potential cross-talk between this domain and the polyQ region may play a central role in regulating the aggregation and toxicity of Htt-N-terminal fragments.

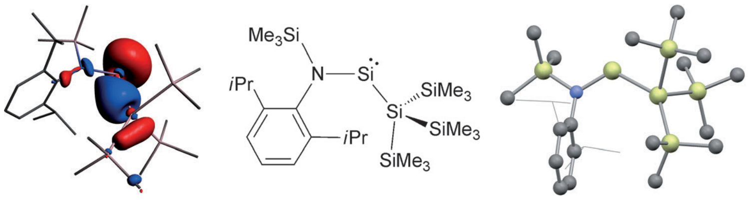


Frontispiece

Silicon Chemistry

A. V. Protchenko, A. D. Schwarz,
M. P. Blake, C. Jones,* N. Kaltsoyannis,*
P. Mountford,* S. Aldridge* ______ **568 – 571**

A Generic One-Pot Route to Acyclic Two-Coordinate Silylenes from Silicon(IV) Precursors: Synthesis and Structural Characterization of a Silylsilylene



Si in sight: A one-pot, single-step synthesis of an acyclic silylsilylene, Si{Si(SiMe$_3$)$_3$}{N(SiMe$_3$)Dipp} (Dipp = 2,6-iPr$_2$C$_6$H$_3$), from a silicon(IV) starting material is reported, together with evidence for a mechanism involving alkali metal silylenoid intermediates.

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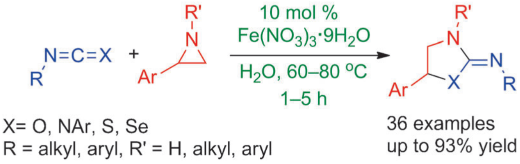
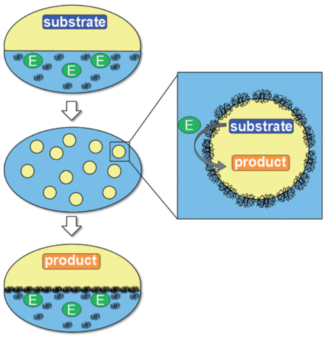
Synthetic Methods



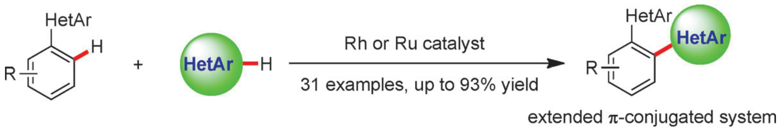
In suspension: The reaction of aziridines with heterocumulenes in the presence of $Fe(NO_3)_3 \cdot 9H_2O$ in aqueous suspension provides access to functionalized five-membered heterocycles in good to high yields. This protocol has a wide substrate scope, is simple, and uses a nontoxic and cheap catalyst.

Biotechnology



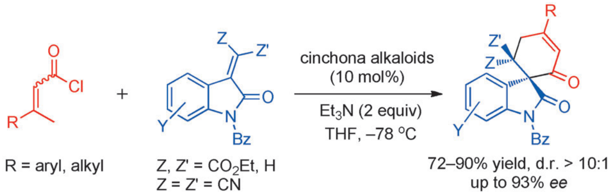
Emulsions stabilized by stimuli-responsive microgels were used to perform enzyme catalysis. Many substrates are poorly water-soluble, while enzymes naturally require aqueous environments, thus resulting in a two-phase aqueous–organic system. Smart microgels allow an enzyme-catalyzed reaction to be performed in an emulsion that can be broken under controlled conditions to separate the reaction product and to recycle the enzyme (E) and the microgel.

C–H Activation



Doubling up: A chemo- and regioselective oxidative cross-coupling between various N-heteroarene-containing arenes and heteroarenes has been carried out by rhodium- or ruthenium-catalyzed twofold C–H activation, to deliver an array of highly functionalized π-conjugated systems.

Carbocycles

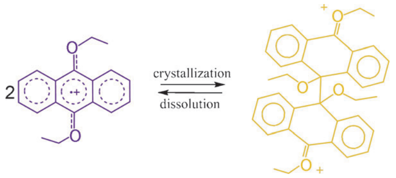


Cinchona alkaloids were used as Lewis base catalysts in the title reaction. The [4+2] cyclization of α,β-unsaturated acyl chlorides with electron-deficient alkenes derived from oxindole gave the corresponding spirocarbocyclic oxindoles.

Radicals

X. Chen, X. Wang, Z. Zhou, Y. Li, Y. Sui, J. Ma, X. Wang,* P. P. Power* **589 – 592**

Reversible σ-Dimerizations of Persistent Organic Radical Cations

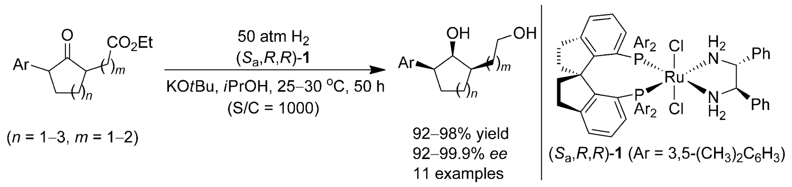


A class of well-defined reversible σ-dimerizations of 9,10-dialkoxyanthracene radical cations are presented. Yellow crystals of the σ-dimerized dication dissociate to purple solutions of monomeric radical cations in solution (see scheme). The identity and stability of radical cations were unequivocally confirmed, providing evidence for reversible σ-dimerizations of persistent radical cations of aromatic systems.

Asymmetric Synthesis

C. Liu, J.-H. Xie,* Y.-L. Li, J.-Q. Chen, Q.-L. Zhou* **593 – 596**

Asymmetric Hydrogenation of α,α′-Disubstituted Cycloketones through Dynamic Kinetic Resolution: An Efficient Construction of Chiral Diols with Three Contiguous Stereocenters

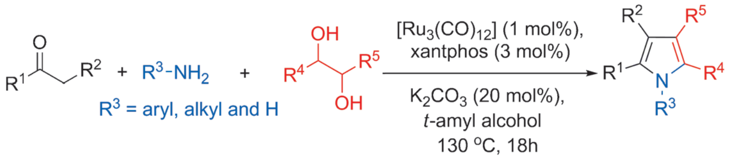


Chiral diols with three contiguous stereocenters were synthesized by a highly enantioselective ruthenium-catalyzed asymmetric hydrogenation of racemic α,α′-disubstituted cycloketones involving dynamic kinetic resolution. This new catalytic asymmetric method provides a concise route to the alkaloid (+)-γ-lycorane.

Heterocycles

M. Zhang, H. Neumann, M. Beller* **597 – 601**

Selective Ruthenium-Catalyzed Three-Component Synthesis of Pyrroles

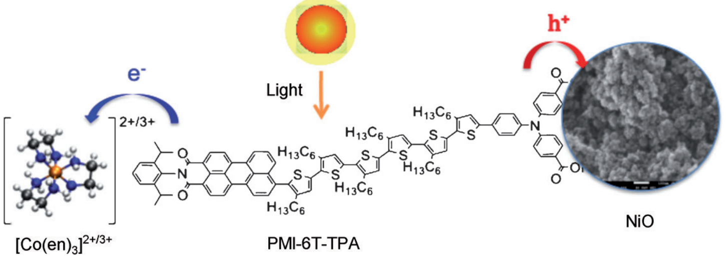


It's a snap: A novel catalytic three-component coupling reaction using simple and easily available substrates leads to a wide range of substituted pyrroles with high regioselectively (see scheme; Xantphos = 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene).

Solar cells

S. Powar, T. Daeneke, M. T. Ma, D. Fu, N. W. Duffy, G. Götz, M. Weidelener, A. Mishra, P. Bäuerle, L. Spiccia,* U. Bach* **602 – 605**

Highly Efficient p-Type Dye-Sensitized Solar Cells based on Tris(1,2-diaminoethane)Cobalt(II)/(III) Electrolytes

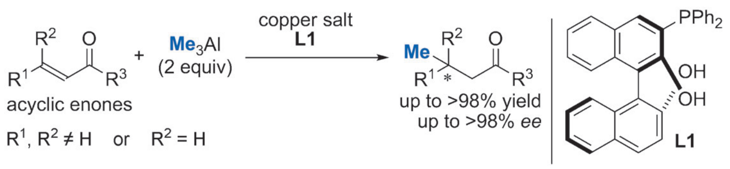


Co-produced: Using $[Co(en)_3]^{2+/3+}$ based-electrolytes in p-type dye-sensitized solar cells (p-DSCs) gives record energy conversion efficiencies of 1.3 % and open-circuit voltages up to 709 mV under simulated sun light. The increase in photovoltage is due to the more negative redox potential of $[Co(en)_3]^{2+/3+}$ compared to established mediators.

Synthetic Methods

K. Endo,* D. Hamada, S. Yakeishi, T. Shibata* **606 – 610**

Effect of Multinuclear Copper/Aluminum Complexes in Highly Asymmetric Conjugate Addition of Trimethylaluminum to Acyclic Enones

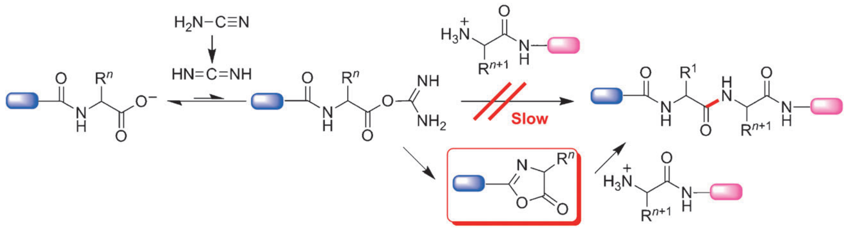


Al and friends: Asymmetric conjugate addition of Me_3Al to β,β-disubstituted α,β-unsaturated ketones in the presence copper and **L1** leads to a highly efficient construction of an all-carbon-substituted chiral quaternary center. This result is the first example of an asymmetric conjugate addition of Me_3Al to acyclic enones to give a chiral quaternary carbon center with excellent yield and enantioselectivity under mild reaction conditions.

Amino Acids

G. Danger,* A. Michaut, M. Bucchi, L. Boiteau, J. Canal, R. Plasson, R. Pascal* **611 – 614**

5(4*H*)-Oxazolones as Intermediates in the Carbodiimide- and Cyanamide-Promoted Peptide Activations in Aqueous Solution

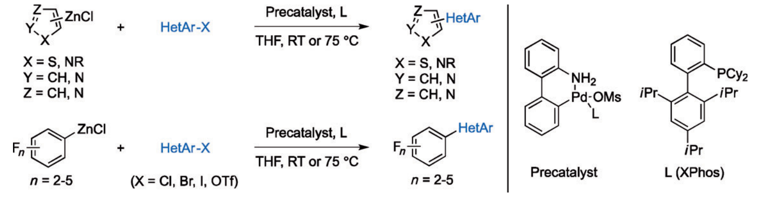


The early days: Although considered a species to be avoided in peptide chemistry, the intermediacy of 5(4*H*)-oxazolones is demonstrated to be essential for the formation of peptides through cyanamide and carbodiimide activation in aqueous solution (see scheme).

Cross-Coupling

Y. Yang, N. J. Oldenhuis, S. L. Buchwald* **615 – 619**

Mild and General Conditions for Negishi Cross-Coupling Enabled by the Use of Palladacycle Precatalysts

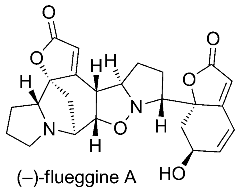


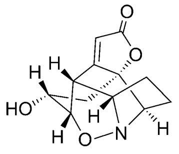
A wide range of biaryls were synthesized by palladium-catalyzed Negishi cross-couplings at ambient temperature or with low catalyst loading. This protocol features the use of a recently reported aminobiphenyl palladacycle precatalyst to generate the catalytically active $XPhosPd^0$ species. Significantly, a wide range of challenging heterocyclic and polyfluorinated aromatic substrates can be employed to give products in excellent yields.

Natural Products

H. Wei, C. Qiao, G. Liu, Z. Yang,* C.-C. Li* **620 – 624**

Stereoselective Total Syntheses of (−)-Flueggine A and (+)-Virosaine B


(−)-flueggine A

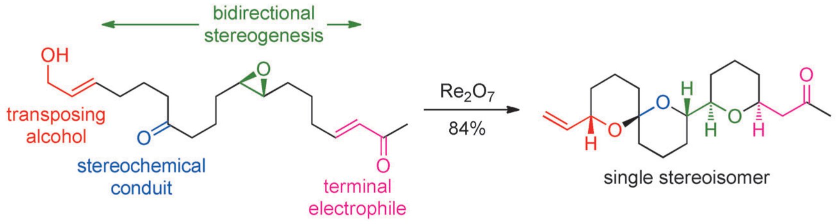

(+)-virosaine B

Convergent approach: The total syntheses of (−)-flueggine A and (+)-virosaine B (see scheme) have been accomplished in a concise and convergent manner. Key steps in these approaches were relay ring-closing metathesis reactions for rapid construction of the key intermediates, and 1,3-dipolar cycloaddition reactions for the formation of the natural products.

Cascade Reactions

Y. Xie, P. E. Floreancig* ______ **625 – 628**

Cascade Approach to Stereoselective Polycyclic Ether Formation: Epoxides as Trapping Agents in the Transposition of Allylic Alcohols

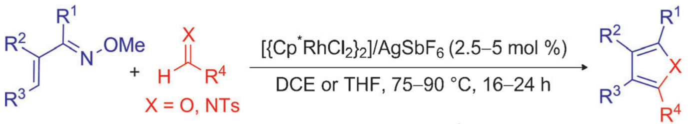


Complexity from simplicity: Polycyclic ethers are synthesized by cascade reactions involving the use of epoxides as electrophilic traps in the transposition of allylic alcohols. Stereogenic centers are created by functionalizing prochiral sites under thermodynamic control, and remote stereoinduction can be achieved through the use of ketones as conduits.

Annulation

Y. Lian, T. Huber, K. D. Hesp, R. G. Bergman, J. A. Ellman* _ **629 – 633**

Rhodium(III)-Catalyzed Alkenyl C–H Bond Functionalization: Convergent Synthesis of Furans and Pyrroles



22 examples for X = O (R^4 = CO_2Et, aryl, alkyl)
6 examples for X = NTs (R^4 = CO_2Et)

Ring in the new: A new annulation for the efficient synthesis of substituted furans and pyrroles is reported. The Rh^{III}-catalyzed reaction of O-methyl α,β-unsaturated oximes with aldehydes and N-tosyl imines affords secondary alcohol and amine intermediates, respectively. Cyclization and aromatization occurs under the reaction conditions to provide access to biologically relevant furans and pyrroles in good yields. Cp* = C_5Me_5, DCE = 1,2-dichloroethane, THF = tetrahydrofuran.

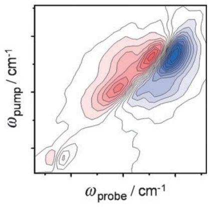
VIP

Surface-Enhanced Spectroscopy

P. M. Donaldson, P. Hamm* _ **634 – 638**

Gold Nanoparticle Capping Layers: Structure, Dynamics, and Surface Enhancement Measured Using 2D-IR Spectroscopy

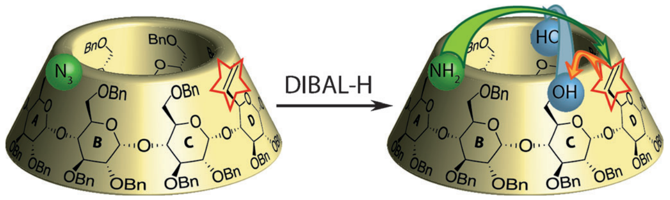
Surface analysis: Two-dimensional infrared spectroscopy (2D-IR) was used to probe amide and carboxylate functional groups in the vicinity of gold nanoparticles and their aggregates. The data presented shows that the unique ability of 2D-IR spectroscopy to characterize broadening mechanisms and cross peaks offers new insights into gold nanoparticle capping layer structure and dynamics (see picture).



Cyclodextrin Functionalization

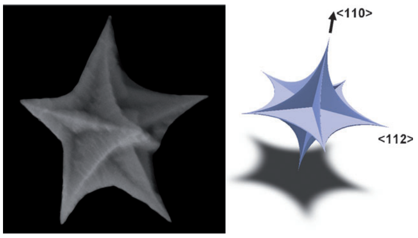
E. Zaborova, M. Guitet, G. Prencipe, Y. Blériot, M. Ménand, M. Sollogoub* ______ **639 – 644**

An “Against the Rules” Double Bank Shot with Diisobutylaluminum Hydride To Allow Triple Functionalization of α-Cyclodextrin



Frustration leads to overreaction: When diametrically opposed regioselective debenzylation is frustrated, an unexpected double debenzylation reaction affords original tetrafunctionalized cyclodextrins in a controlled and efficient manner. A rationale of the reaction is proposed based on a kinetic study.

Superstar: Branched concave Au/Pd bimetallic nanocrystals (see picture) were synthesized in high yield by seed-mediated co-reduction of Au and Pd metal precursors in an aqueous solution at room temperature. The branches are concave and have high-index facets on their surfaces. These nanocrystals show superior electrocatalytic activity for the oxidation of ethanol and highly efficient SERS enhancement.



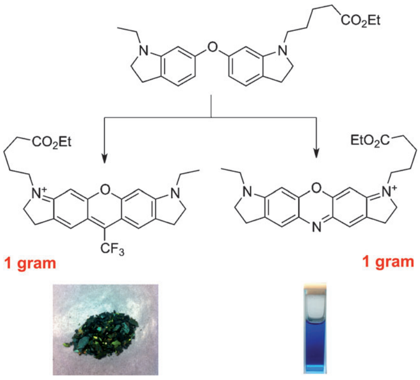
Bimetallic Nanocrystals

L. F. Zhang, S. L. Zhong,
A. W. Xu* **645 – 649**

Highly Branched Concave Au/Pd Bimetallic Nanocrystals with Superior Electrocatalytic Activity and Highly Efficient SERS Enhancement

Back Cover

Common ground: Copper-catalyzed coupling reactions can be used for the high-yielding preparation of widely used oxazine and xanthene fluorophores from a common diaryl ether intermediate on a gram-scale (see scheme). This general approach may facilitate the future development of novel fluorophores and probes with unique properties.



Fluorescent Dyes

A. V. Anzalone, T. Y. Wang, Z. Chen,
V. W. Cornish* **650 – 654**

A Common Diaryl Ether Intermediate for the Gram-Scale Synthesis of Oxazine and Xanthene Fluorophores

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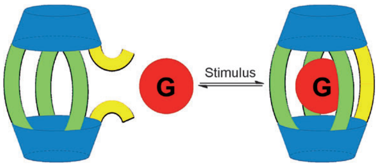

Guests in a gated community: Introduction of two anthracene groups into a linker in a hemicarcerand creates a new type of photochemically controlled gated hemicarcerand. The reversible opening and closing of the "gate" of the host is controlled photochemically. The encapsulation and release of the guest molecules such as 1,4-dimethoxybenzene is controlled by irradiation with light of different wavelengths.

Host–Guest Chemistry

H. Wang, F. Liu, R. C. Helgeson,
K. N. Houk* **655 – 659**

Reversible Photochemically Gated Transformation of a Hemicarcerand to a Carcerand

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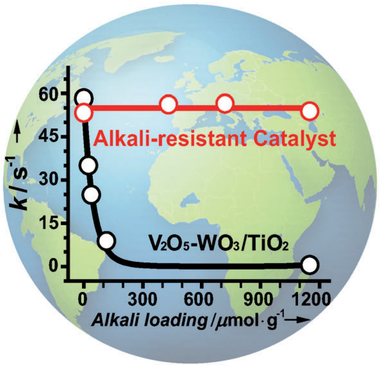


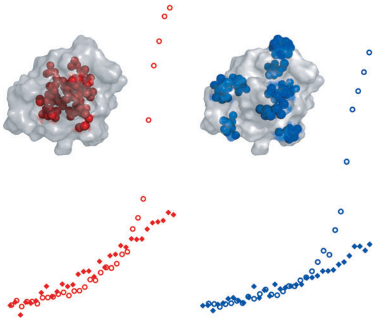
Banish the villains to their own realm: Biomass has gained widespread attention as a renewable energy source. However, commercial catalysts used in power plants (co-)fuelled by biomass are deactivated by the alkali-rich flue gas (see graph, black line). In contrast, one of two types of active sites in a promising alkali-resistant hollandite catalyst traps alkali-metal ions to free up the catalytically active sites for the reduction of NO by NH_3.

Alkali-Resistant Catalysts

Z. Huang, X. Gu, W. Wen, P. Hu,
M. Makkee, H. Lin, F. Kapteijn,
X. Tang* **660 – 664**

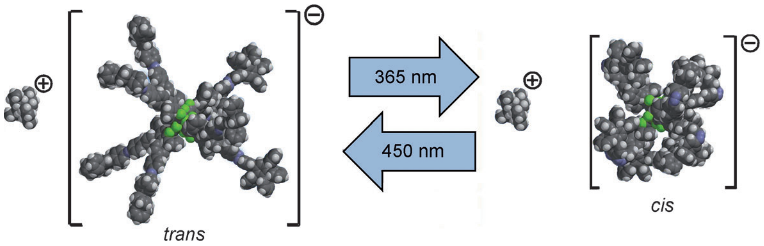
A "Smart" Hollandite DeNO$_x$ Catalyst: Self-Protection against Alkali Poisoning

Protein Dynamics



By specifically labeling leucine/valine methyl groups and lysine side chains "inside" and "outside" dynamics of proteins on the nanosecond timescale are compared using neutron scattering (see picture). Surprisingly, both groups display similar dynamics as a function of temperature, and the buried hydrophobic core is sensitive to hydration and undergoes a dynamical transition.

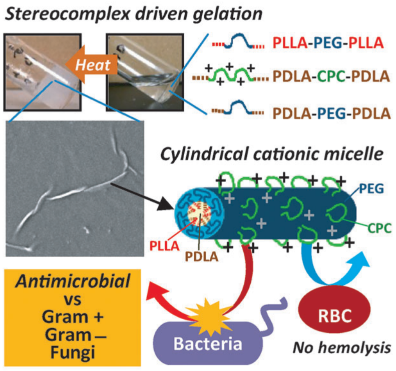
Dendrimers



Light switch: A dendronized salt exhibiting photoswitchable conductivity was designed and synthesized. The salt consists of tetrabutylammonium cations and large, rigidly dendronized borate anions, each bearing eight photoresponsive azobenzene moieties. The conductivity of solutions of this salt can be reversibly switched by irradiation, owing to light-induced changes in the overall size of the dendronized anion and the density of its polyphenylene shell.

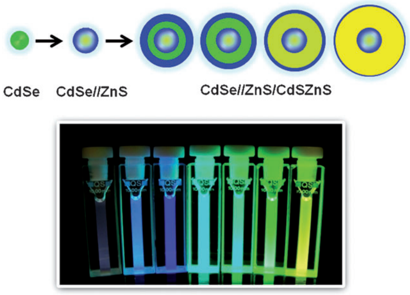
Gels

Fighting the resistance: Biodegradable and injectable/moldable hydrogels with hierarchical nanostructures (see picture) were made with broad-spectrum antimicrobial activities and biofilm-disruption capability. They demonstrate no cytotoxicity in vitro, and show excellent skin biocompatibility in animals. These hydrogels have great potential for clinical use in prevention and treatment of various multidrug-resistant infections.

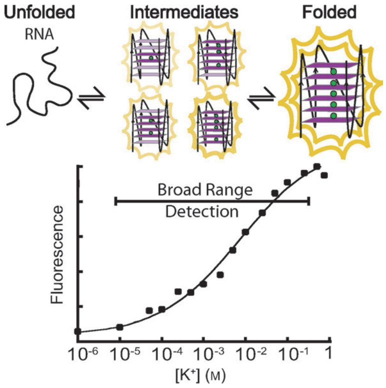


Core–Shell Structures

Color conversion: A quantum dot (QD) structure consisting of an alloy core (CdSe//ZnS) and multishells (CdSZnS) was prepared (see picture). The photoluminescence of the QDs could be tuned especially in the green-light region by controlling the thickness of the inner CdS shell. The alloy core/multishell (AC/MS) QDs showed a quantum efficiency of 100% and a narrow spectrum width.



Keeping a broad (RNA) perspective: Conventional biochemical detection systems only have a 100-fold linear response range. The range of potassium concentrations detected by an RNA G-quadruplex sequence can be broadened by intentionally populating multiple intermediate folding states (see scheme). The folding of the RNA G-quadruplexes was monitored by both circular dichroism and intrinsic fluorescence spectroscopy.



G-Quadruplex Folding

C. K. Kwok, M. E. Sherlock,
P. C. Bevilacqua* ________ **683 – 686**

Decrease in RNA Folding Cooperativity by Deliberate Population of Intermediates in RNA G-Quadruplexes

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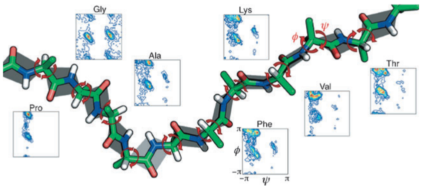
Conformational analysis: An approach to the prediction of RDCs from disordered protein chains, integrating the effect of nearest neighbors and the alignment characteristics of the statistical coil, is reported. NMR residual dipolar couplings (RDC) are sensitive probes of conformational sampling in unfolded proteins (see picture).

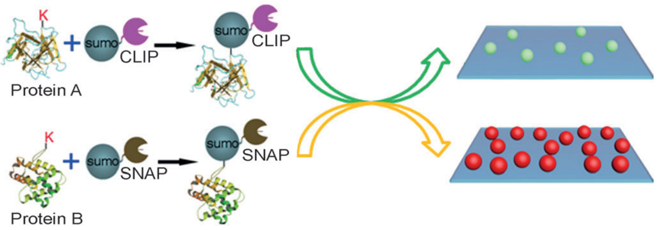


Dipolar Couplings of Proteins

J. R. Huang, V. Ozenne, M. R. Jensen,
M. Blackledge* ________ **687 – 690**

Direct Prediction of NMR Residual Dipolar Couplings from the Primary Sequence of Unfolded Proteins

Inside Back Cover



Two opposing SUMO wrestlers: Simultaneous measurement of multiple SUMOylations was achieved at the single-molecule level by integrating SNAP/CLIP-tag-mediated translation with single-molecule detection (see scheme; SUMO = small ubiquitin-like modifier). This method gives exceptional sensitivity, and is capable of measuring the SUMOylation of different proteins under various physiological conditions.

Posttranslational Modifications

Y. Yang, C. Y. Zhang* ________ **691 – 694**

Simultaneous Measurement of SUMOylation using SNAP/CLIP-Tag-Mediated Translation at the Single-Molecule Level

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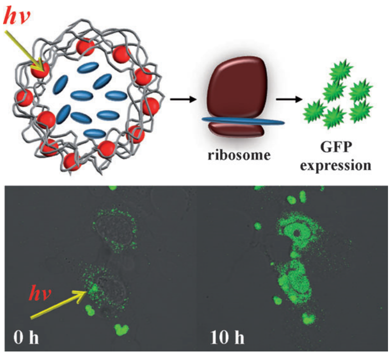


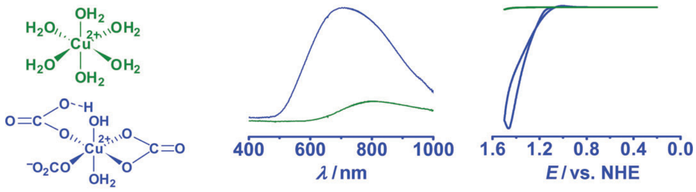
Release me: Polyelectrolyte capsules with different cargo in their cavities and plasmonic and magnetic nanoparticles in their walls were synthesized. Enzymatic reactions were triggered inside cells by light-mediated opening of two individual capsules containing either an enzyme or its substrate, by using photothermal heating. Furthermore, this technique allows controlled release of mRNA from capsules, thereby resulting in synthesis of green fluorescent protein (GFP).

Intracellular Release

M. Ochs, S. Carregal-Romero, J. Rejman,
K. Braeckmans, S. C. De Smedt,
W. J. Parak* ________ **695 – 699**

Light-Addressable Capsules as Caged Compound Matrix for Controlled Triggering of Cytosolic Reactions

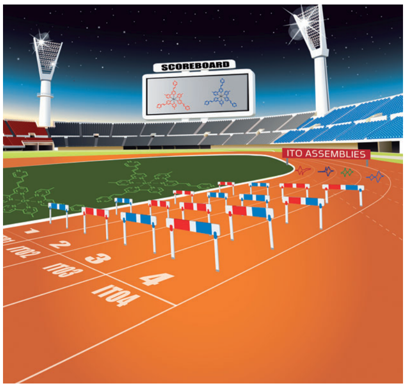
Water Oxidation



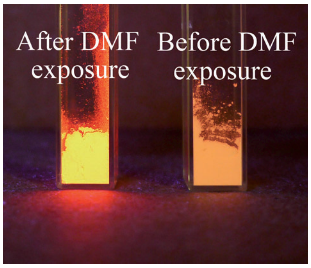
Copper leads to a breakup: Simple Cu^{II} salts are shown to be highly reactive as water oxidation electrocatalysts in neutral to weakly basic aqueous buffer solutions of $CO_2/HCO_3^-/CO_3^{2-}$ or HPO_4^{2-}/PO_4^{3-}. Coordination to the buffer anions under these conditions prevents the precipitation of $Cu(OH)_2$, $CuCO_3$, or $Cu_3(PO_4)_2$ and appears to stabilize higher oxidation states of copper.

Sequence-Dependent Assembly

Variation's what you need: Variation of the assembly sequence in which layers of two isostructural metal complexes are built up leads to molecular materials with electrochemical properties that depend on the assembly sequence. These properties vary from reversible electron transfer to unidirectional current flows and even charge trapping. The sequence-dependent assembly strategy has implications for various disciplines that involve self-assembly.



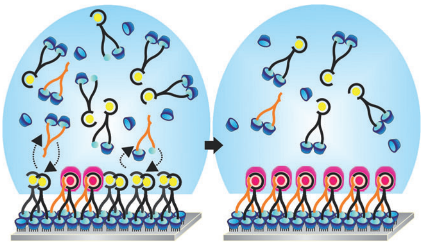
Metal–Organic Frameworks

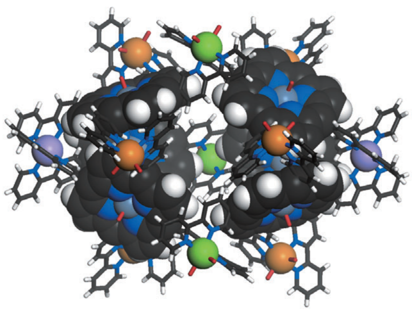


A real turn-on: A luminescent lanthanide metal–organic framework shows strong and fast turn-on responses to *N*,*N*-dimethylformamide (DMF) vapor. The selective turn-on effect is triggered mainly by DMF–ligand interactions, along with the removal of quencher, water, from the metal coordination sphere.

Self-Assembly

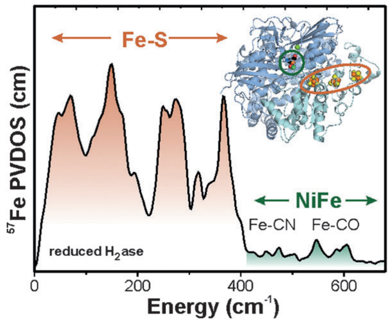
Competition with a monovalent cyclodextrin host (blue cones) in solution drives the multivalent binding of a Eu^{3+} complex and a sensitizer molecule to cyclodextrin monolayers through a nonlinear self-assembly process. Adamantyl groups (light-blue spheres) are attached to the EDTA ligand (black) and the antenna molecule (orange), which has a carboxylate group for coordination to the Eu^{3+} ion (yellow or red in free or complexed form, respectively).





Construction of a self-assembled cage complex through three different Zn^{II} centers is achieved using a Zn porphyrin ligand with four 2,2′-bipyridin-5-yl (bpy) groups. The multiporphyrin cage encapsulates guest molecules unsymmetrically by π–π interactions. Well-balanced aqueous conditions, which allow the formation of both tris(bpy) and hydrated bis(bpy) Zn^{II} units, result in the unsymmetrical yet well-defined supramolecular structure.

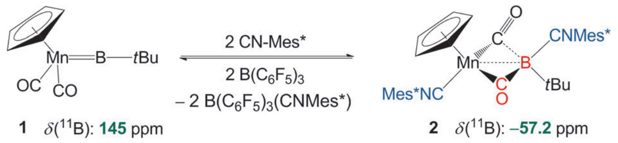
Supramolecular Chemistry



Nuclear inelastic scattering of ^{57}Fe labeled [NiFe] hydrogenase is shown to give information on different states of the enzyme. It was thus possible to detect and assign Fe–CO and Fe–CN bending and stretching vibrations of the active site outside the spectral range of the Fe–S cluster normal modes.

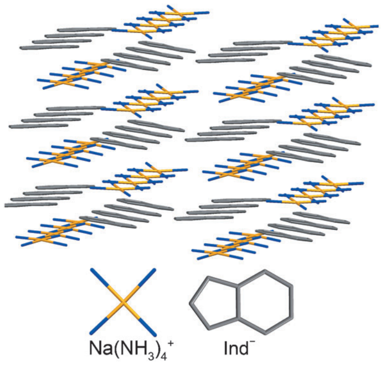
Hydrogenases

Front Cover



Cyclic complex 2 with bridging carbonyl ligands was synthesized from a facile and reversible intermolecular carbonyl–borylene ligand coupling reaction at room temperature. Complex **2** exhibits an unprecedented coordination mode for boron–metal complexes, which is also reflected in its remarkable ^{11}B NMR chemical shift of −57.2 ppm. Findings from spectroscopic, X-ray, and computational studies are presented, along with a proposed mechanism.

Reversible Coupling of :CO and :BR



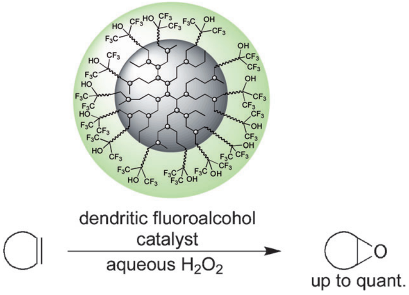
It's hip to be a square! The ammines [Li(NH$_3$)$_4$][Ind] and [Na(NH$_3$)$_4$][Ind] both contain a cation coordinated by four ammonia molecules. Whereas the first shows the anticipated tetrahedral coordination, in the second the metal coordination is unexpectedly square-planar. The solvent-separated ion pair forms a rippled layer structure of alternating planar Na(NH$_3$)$_4$$^+$ cations and indenyl carbanions that is attributed to NH$_3$⋯π hydrogen bonds.

Layered ammines

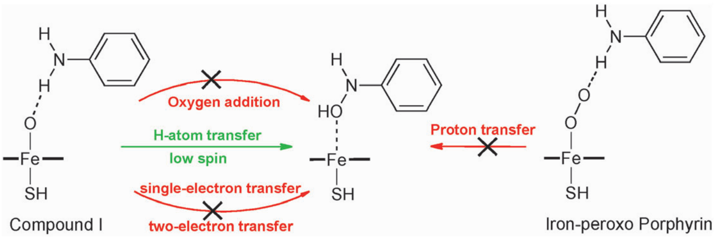
Dendritic Oxidation Catalysts

Inside Cover

Cooperativity is the key for mild catalytic epoxidation: The immobilization of fluoroalcohols on dendritic polyglycerol (by “click chemistry”) provides organocatalysts that can form multiple hydrogen bonds. The epoxidation of alkenes with aqueous hydrogen peroxide proceeds efficiently in the presence of dendritic fluoroalcohol catalysts. The supported catalysts can be separated by membrane filtration and reused.



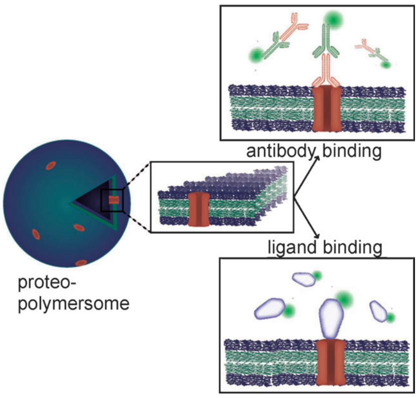
Computational Chemistry



Only one path applies: To date, five different mechanisms have been suggested for the P450-catalyzed N-hydroxylation of primary aromatic amines. Computational analysis employing density functional theory demonstrates that only the H-atom-transfer pathway, that is H abstraction from an amine N followed by a radical rebound step, on a low-spin route can contribute to the aromatic hydroxylamine formation.

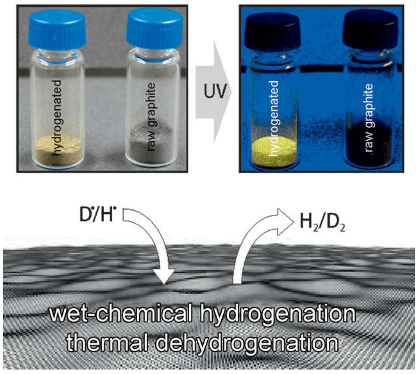
Artificial Membranes

The dopamine receptor D2 (DRD2), a G-protein coupled receptor is expressed into PBd_{22}-PEO_{13} and $PMOXA_{20}$-$PDMS_{54}$-$PMOXA_{20}$ block copolymer vesicles (see scheme). The conformational integrity of the receptor is confirmed by antibody- and ligand-binding assays. Replacement of bound dopamine is demonstrated on surface-immobilized polymersomes, thus making this a promising platform for drug screening.



Graphane

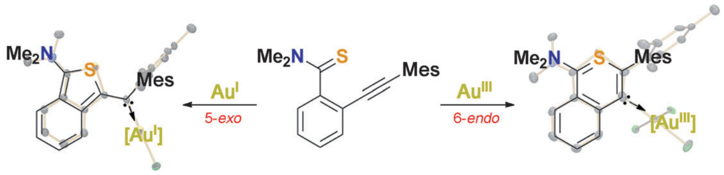
Chemistry meets graphane: A Birch-type reaction using frozen water as a gentle proton source causes the exfoliation of graphite and formation of hydrogenated graphene with electronically decoupled π-nanodomains. This highly functionalized graphene displays pronounced fluorescence.



Gold Complexes

G. Ung, M. Soleilhavoup,
G. Bertrand* ———— **758 – 761**

Gold(III)- versus Gold(I)-Induced Cyclization: Synthesis of Six-Membered Mesoionic Carbene and Acyclic (Aryl)(Heteroaryl) Carbene Complexes



The golden state: Selective 5-*exo*- and 6-*endo*-cyclizations of an alkynyl benzothioamide have been achieved. The selectivity is controlled by the oxidation state of the gold precursor (+I or +III), yielding two new types of carbene ligand: an (aryl)(heteroaryl)carbene and a six-membered mesoionic carbene (see scheme). Mes = 2,4,6-trimethylphenyl.

Click Polymer Ligation

K. K. Oehlenschlaeger, J. O. Mueller,
N. B. Heine, M. Glassner, N. K. Guimard,
G. Delaittre, F. G. Schmidt,
C. Barner-Kowollik* ———— **762 – 766**

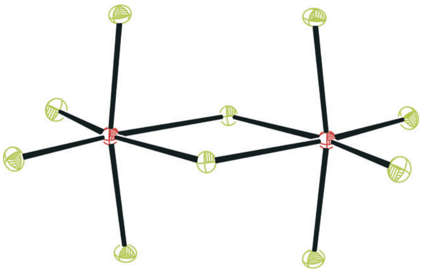
Light-Induced Modular Ligation of Conventional RAFT Polymers

Making light work of RAFT conjugation: A non-activated RAFT agent at the end of RAFT polymers can readily be coupled with *ortho*-quinodimethanes (photoenols) in a photo-triggered Diels–Alder reaction under mild conditions without catalyst (see scheme). The method is universal and opens the door for the conjugation of a large number of RAFT-prepared polymers with photoenol-functionalized (macro)molecules. (RAFT = reversible addition-fragmentation chain transfer.)

Highest Oxidation States

F. Tamadon, K. Seppelt* ———— **767 – 769**

The Elusive Halides VCl_5, $MoCl_6$, and $ReCl_6$



Vanadium pentachloride and molybdenum and rhenium hexachloride are all thermally unstable but can be prepared by metathesis from the corresponding fluorides with BCl_3 at low temperatures. $MoCl_6$ is structurally related to β-WCl_6, and $ReCl_6$ to α-WCl_6. VCl_5 is a dimer in the solid state (see structure; V red, Cl green).

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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Angewandte Corrigendum

Enantioselective Synthesis of Cyclopropanes That Contain Fluorinated Tertiary Stereogenic Carbon Centers: A Chiral α-Fluoro Carbanion Strategy

X. Shen, W. Zhang, L. Zhang, T. Luo, X. Wan, Y. Gu, J. Hu* ______ **6966–6970**

Angew. Chem. Int. Ed. **2012**, *51*

DOI: 10.1002/anie.201202451

In this Communication, the diastereomeric ratio (d.r.) of **2**′ was reported to be $>$99:1, which was determined by ^{19}F NMR spectroscopy using $CHCl_3$ as solvent. During recent investigations on the deuteration of α-fluoro sulfoximines with various N-substituents, the authors found that the reported d.r. of **2**′ ($>$99:1) was incorrect. This error was caused by the coincidental overlap of ^{19}F NMR peaks of two diastereomers of **2**′ (see the Supporting Information accompanying the Communication, pages 3–4). The correct d.r. of **2**′ should be 68:32, as determined by ^{1}H NMR spectroscopy in $CDCl_3$ (see the Supporting Information accompanying this Corrigendum). This corrected d.r. value was also confirmed by the ^{19}F NMR measurement of **2**′ using [D$_6$]DMSO as solvent (see the Supporting Information accompanying this Corrigendum). This correction does not affect the results and conclusions in other parts of the Communication. The authors sincerely apologize for this mistake.