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:

D. Mössinger, J. Hornung, S. Lei, S. De Feyter, S. Höger**
Molecularly Defined Shape-Persistent Two-Dimensional Oligomers: The Covalent Template Approach to Molecular Spoked Wheels

*O. Iranzo, C. Cabello, V. L. Pecoraro**
Heterochromia in Designed Metallopeptides: Geometry-Selective Binding of Cd^{II} in a De Novo Peptide

B. J. Jankiewicz, A. Adeuya, M. J. Yurkovich, N. R. Vinueza, S. J. Gardner III, M. Zhou, J. J. Nash, H. I. Kenttämaa**
Reactivity of an Aromatic σ,σ,σ-Triradical: The 2,4,6-Tridehydropyridinium Cation

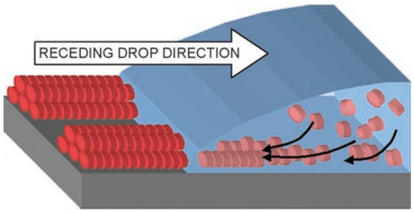
*J.-H. Kim, S. Lee, K. Park, H. Y. Nam, S. Y. Jang, I. Youn, K. Kim, H. Jeon, R.-W. Park, I.-S. Kim, K. Choi, I. C. Kwon**
Protein Phosphorylation-Responsive Polymeric Nanoparticles for Imaging Protein Kinase Activities in Single Living Cells

S. Khanra, M. Kloth, H. Mansaray, C. A. Muryn, F. Tuna, E. C. Sañudo, M. Helliwell, E. J. L. McInnes, R. E. P. Winpenny**
Synthesis of Molecular Vanadium(III) Phosphonates

T. Beweries, V. V. Burlakov, M. A. Bach, S. Peitz, P. Arndt, W. Baumann, A. Spannenberg, U. Rosenthal, B. Pathak, E. D. Jemmis**
Tandem Si–C/C–H Activation for Decamethylhafnocene and Bis(trimethylsilyl)acetylene: Hafnium's Triumph over Titanium and Zirconium

Books

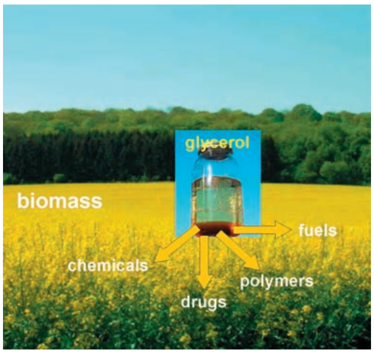
Highlights



When enemies become friends: Hierarchical self-assembly, through the concerted use of different forces that dominate on distinct length scales, allows the generation of functional supramolecular architectures with a high degree of order on both the nano- and macroscopic scales, paving the way towards their application in electronics, catalysis, and medicine.

Surface Patterning

Minireviews



Getting value from glycerol: Over the past 60 years, glycerol (1,2,3-propanetriol) has gone from being a key industrial chemical that faced shortage to a by-product that is formed in surplus during biodiesel production. Recent developments in its applications and its conversion into value-added chemicals highlight the importance of glycerol as a key raw material in biorefineries of the future.

Glycerol Chemistry

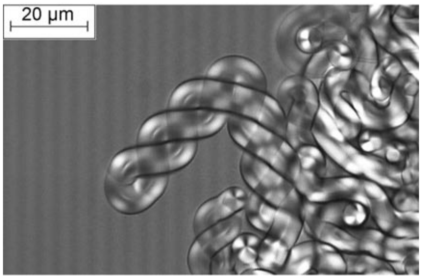
Contents

Reviews

Self-Assembly

I. W. Hamley,* V. Castelletto **4442 – 4455**

Biological Soft Materials



The soft side of life: Recent insights into the self-assembly of biological materials, including proteins, DNA, lipids, and blood cells, are reviewed. The particular focus is on applying concepts from soft-matter physics and chemistry to understand structural self-organization (for example, myelin formation; see image).

Communications

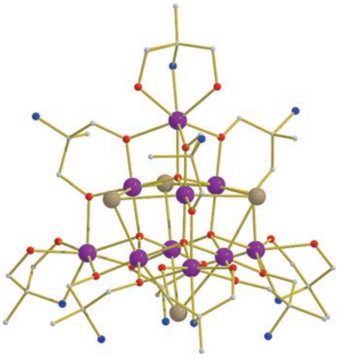
VIP

Cluster Compounds

M. Manoli, R. D. L. Johnstone, S. Parsons, M. Murrie, M. Affronte, M. Evangelisti,* E. K. Brechin* ———— **4456 – 4460**

A Ferromagnetic Mixed-Valent Mn Supertetrahedron: Towards Low-Temperature Magnetic Refrigeration with Molecular Clusters

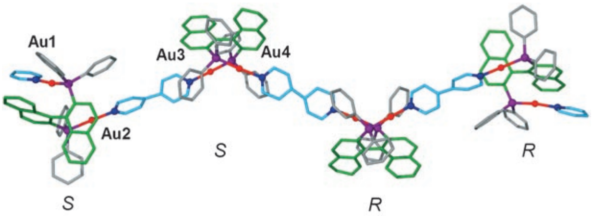
Fridge magnet: A decametallic mixed-valent Mn supertetrahedron (see picture; M purple, O red, N blue, Br brown, C gray) displays dominant ferromagnetic exchange and a spin ground state of $S = 22$. The magnetic behavior of the cluster makes it suitable for use as a low-temperature magnetic refrigerant.



Coordination Polymers

C. A. Wheaton, R. J. Puddephatt* ———— **4461 – 4463**

A Coordination Polymer of Gold(I) with Heterotactic Architecture and a Comparison of the Structures of Isotactic, Syndiotactic, and Heterotactic Isomers



A tactic-al approach: By use of gold chemistry the first organic–inorganic polymer with a heterotactic architecture has been synthesized, and has enabled the first direct structural comparison of coordination polymers with isotactic, syndiotactic, and heterotactic architectures (see picture: naphthyl groups green, 4,4′-bipyridine ligands blue, phenyl gray, Au red, P purple).

For the USA and Canada:
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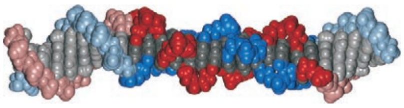
Helical Structures

V. L. Malinovskii, F. Samain,
R. Häner* ______________ 4464 – 4467

Helical Arrangement of Interstrand Stacked Pyrenes in a DNA Framework

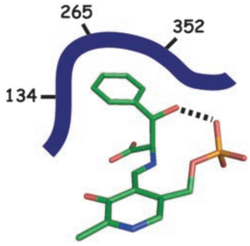


Getting it together: Helical self-organization between oligopyrene strands with 14 consecutive achiral pyrene building blocks embedded in a DNA strand leads to an artificial double helix (see example, oligopyrene regions are shown in dark colors and the flanking DNA regions in light colors). Helicity within the interstrand-stacked oligopyrenes is evident from the observation of exciton-coupled CD signals originating from the pyrene moieties.

Aldolase Optimization

M. D. Toscano, M. M. Müller,
D. Hilvert* ______________ 4468 – 4470

Enhancing Activity and Controlling Stereoselectivity in a Designed PLP-Dependent Aldolase

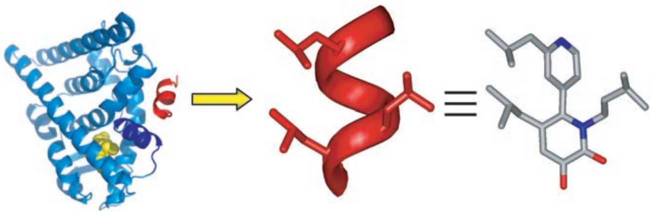


Chop and change: Site-directed mutagenesis has been employed to optimize the activity of an engineered pyridoxal phosphate-dependent aldolase and to invert its inherent *threo* selectivity in the cleavage of D-β-phenylserines. The modification of the active-site residues generates significant retroaldol activity that compares favorably with that of natural enzymes in terms of efficiency and selectivity.

α-Helix Mimetics

J. Becerril, A. D. Hamilton* 4471 – 4473

Helix Mimetics as Inhibitors of the Interaction of the Estrogen Receptor with Coactivator Peptides

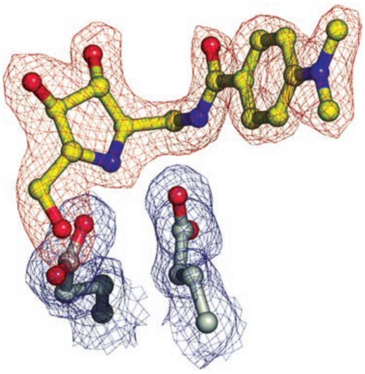


The short and curlies: A new α-helix mimetic based on a pyridylpyridone scaffold has been developed to bind to the estrogen receptor (ER) by mimicking the key leucine side chains of coactivator LXXLL boxes (L = leucine, X = any amino acid). These inhibitors compete with coactivator peptides for the surface of the ER and act as small-molecule inhibitors of the ER–coactivator interaction.

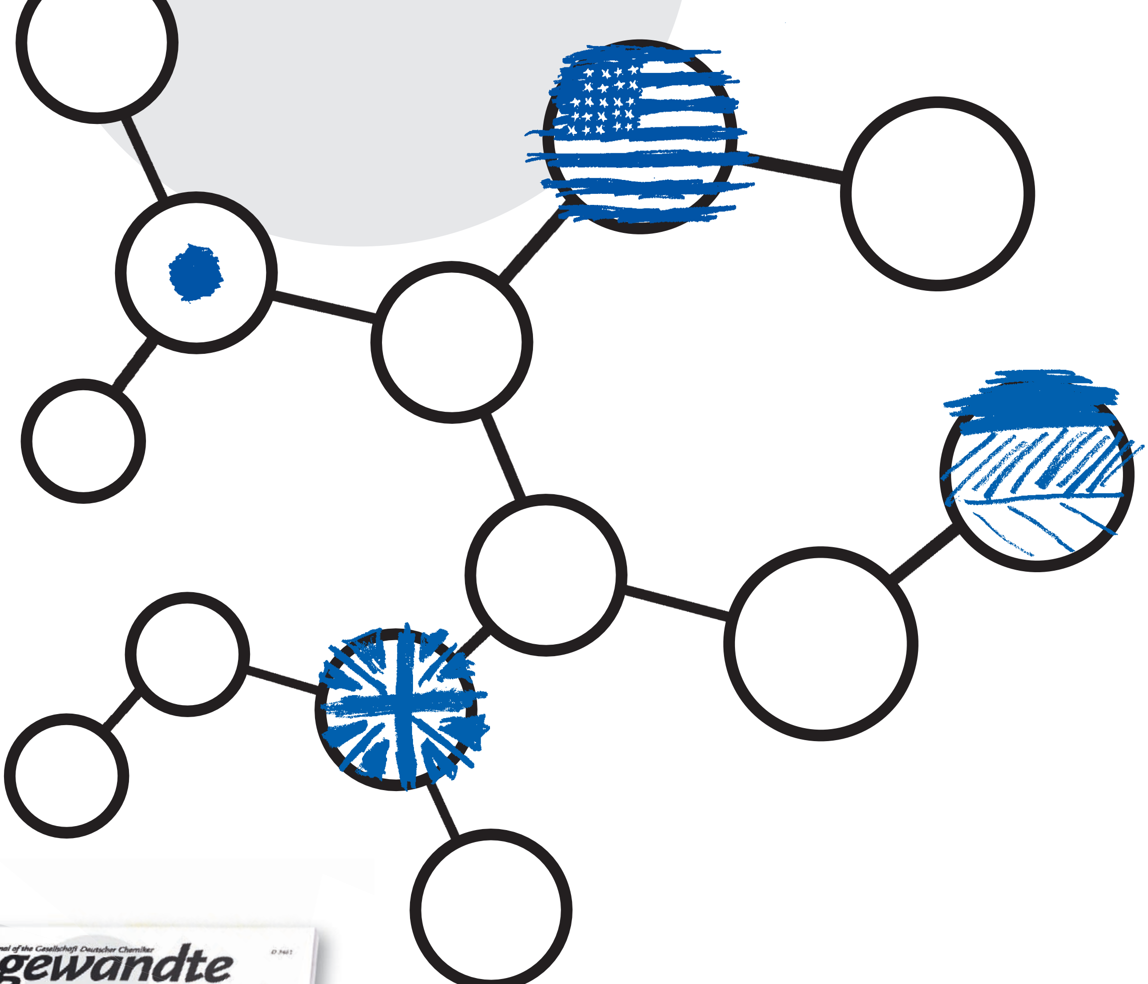
Glycosidase Inhibitors

M. E. C. Caines, S. M. Hancock,
C. A. Tarling, T. M. Wrodnigg, R. V. Stick,
A. E. Stütz, A. Vasella, S. G. Withers,*
N. C. J. Strynadka* _______ 4474 – 4476

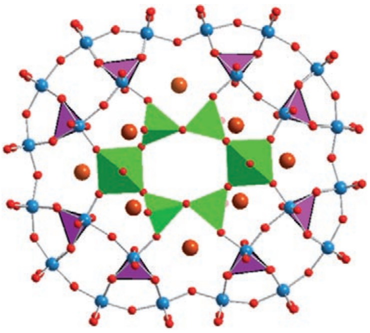
The Structural Basis of Glycosidase Inhibition by Five-Membered Iminocyclitols: The Clan A Glycoside Hydrolase Endoglycoceramidase as a Model System



Fitting five into six: The crystal structure of a glycosidase-bound, five-membered iminocyclitol inhibitor was determined (see picture), and its binding interactions were compared to those of the classical six-membered iminocyclitol inhibitors isofagomine and glucoimidazole and of the glycosyl–enzyme intermediate. This information may be used to develop more potent and specific therapeutically useful glycosidase inhibitors.



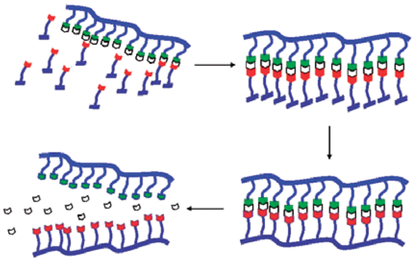
Getting together helps: The wheel-shaped $\{P_8W_{48}\}$ polyoxotungstate (see picture) provides a reaction chamber for the directed assembly of two unprecedented mixed-valence vanadium oxide cavity-capping groups based on linked octahedra and tetrahedra with V^{IV} and V^{V} centers, respectively. The magnetic and electronic properties are controlled by the confined conditions.



Polyoxometalates

A. Müller,* M. T. Pope,* A. M. Todea,
H. Bögge, J. van Slageren, M. Dressel,
P. Gouzerh, R. Thouvenot, B. Tsukerblat,
A. Bell ________ **4477–4480**

Metal-Oxide-Based Nucleation Process under Confined Conditions: Two Mixed-Valence V_6-Type Aggregates Closing the W_{48} Wheel-Type Cluster Cavities



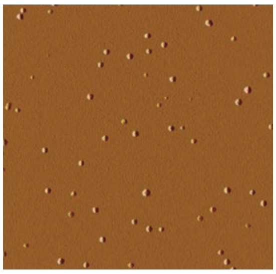
In undergoing a DNA-like replication process, the single-stranded polynorbornene acts as a template for norbornene monomer adhesion through ester linkages (see scheme). Polymerization of the adhered monomers affords the corresponding unsymmetric double-stranded polymer, which produces a complementary polynorbornene carboxylic acid after hydrolysis. The overall process involves a pass of information from the template polymer to the daughter polymer.

Polynorbornene Replication

N.-T. Lin, S.-Y. Lin, S.-L. Lee, C.-h. Chen,
C.-H. Hsu, L. P. Hwang, Z.-Y. Xie,
C.-H. Chen, S.-L. Huang,
T.-Y. Luh* ________ **4481–4485**

From Polynorbornene to the Complementary Polynorbornene by Replication

PEGged as soluble: Potassium graphite (C_8K) is functionalized to yield derivatives that are soluble in either water or organic solvents. For example, treatment of C_8K with 5-bromovaleric acid followed by amine-terminated poly(ethylene glycol) leads to water-soluble nanoplatelets (see AFM image).

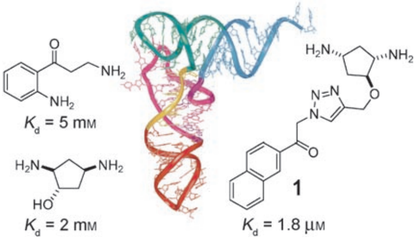


Graphite Functionalization

S. Chakraborty, J. Chattopadhyay, W. Guo,
W. E. Billups* ________ **4486–4488**

Functionalization of Potassium Graphite

Two in one: Two ligands for $tRNA^{Lys3}$ that were identified from a compound library by flow-injection NMR spectroscopic screening and found to have millimolar dissociation constants (on the left in the picture) inspired the fragment-based synthesis of a new family of ligands with the general structural features of both initial compounds. Ligand **1** of this family is a selective D-stem binder of $tRNA^{Lys3}$ with a micromolar K_d value.

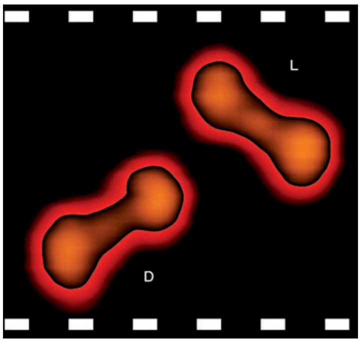


RNA Recognition

F. Chung, C. Tisné,* T. Lecourt, F. Dardel,*
L. Micouin* ________ **4489–4491**

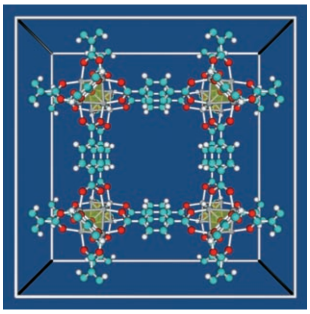
NMR-Guided Fragment-Based Approach for the Design of $tRNA^{Lys3}$ Ligands

Molecular Recognition



Lights, camera, action! The general mechanism of biomolecular recognition introduced by Pauling more than 50 years ago has now been brought to the movie screen (see still frame; D: D-Phe-D-Phe, L: L-Phe-L-Phe). With STM movies, the chiral-recognition process of individual adsorbed di-phenylalanine molecules is followed to illustrate the dynamic induced-fit mechanism at the single-molecule level.

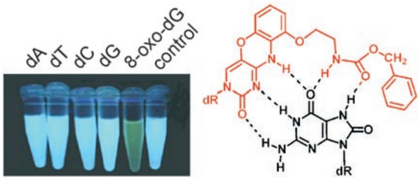
Framework Models



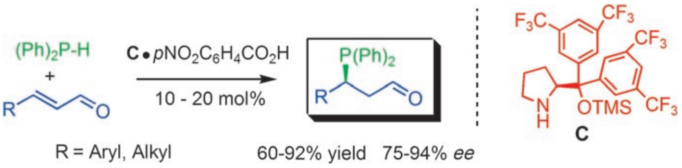
Shrink when heated: A new model for flexible frameworks is used to simulate the structures and adsorption properties of isoreticular metal–organic frameworks (IRMOFs), such as IRMOF-1 (see picture; Zn silver, C cyan, H white, O red). The structural simulations suggest that the IRMOFs have negative thermal-expansion coefficients over their full temperature ranges of stability.

Fluorescent Probes

Marking mutations: Complete discrimination of 8-oxoguanosine (8-oxoG) from other nucleosides has been achieved with a new fluorescent probe, named “8-oxoG-clamp” (see picture). The complex structure between 8-oxoG-clamp and 8-oxoG was confirmed by ^{1}H NMR titration and 2D NMR measurements. A preliminary investigation with use of a detergent for solubilization indicates that 8-oxoG-clamp may be applicable in aqueous media.

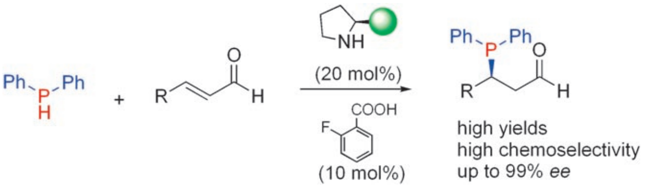


Organocatalysis



Getting round the (periodic) table: A highly chemo- and enantioselective conjugate addition of diphenylphosphine to α,β-unsaturated aldehydes in the presence of a chiral secondary amine **C** provides a direct route to chiral β-phosphino aldehyde intermediates (see scheme, TMS = trimethylsilyl). The synthetic utility of the strategy was exemplified in a rapid one-pot (two-step) synthesis of highly enantioenriched 3-aminophosphines.

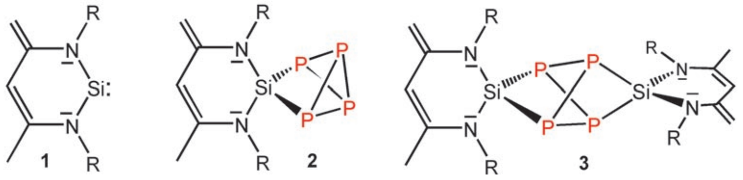
Organocatalysis



high yields
high chemoselectivity
up to 99% *ee*

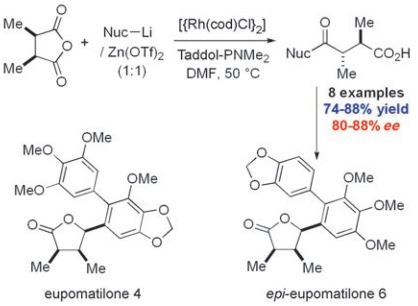
Keeping it simple: Optically active phosphine derivatives can be obtained in high yields and in up to 99% *ee* by using simple chiral amines to catalyze the hydrophosphination of α,β-unsaturated aldehydes (see scheme, green sphere = chiral group). The synthetic utility of this highly chemo- and enantioselective transformation was exemplified by the one-pot asymmetric synthesis of β-phosphine oxide acids.

P_4 Activation



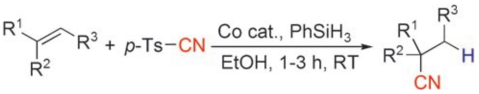
Silylene bites twice in the first insertion of a silylene into a P–P bond of the P_4 tetrahedron. Reaction of the silylene **1** (see scheme; R = 2,6-diisopropylphenyl) with white phosphorus at ambient temperature gives **2** with a tricyclic SiP_4 core. The electronic situation in **2** favors the insertion of a second equivalent of **1** into a P–P bond of the SiP_4 skeleton, affording the novel strained tricyclic silaphosphane **3** with a Si_2P_4 core.

Enantioenriched Keto Acids



The wages of *syn*: The development of a phosphoramidite-ligated rhodium catalyst allows the enantioselective desymmetrization of cyclic anhydrides with organozinc nucleophiles formed in situ. This methodology has been utilized for a concise synthesis of eupomatilones 4 and 7 and of the putative structure of eupomatilone 6, each of which is completed in four steps in greater than 50% overall yield.

Alkene Hydrocyanation

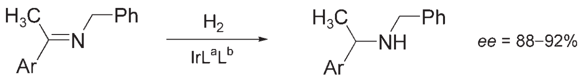


Mild-mannered and well-behaved: A conceptually new hydrocyanation reaction for non-activated olefins provides secondary and tertiary nitriles in good yields under mild conditions. Salient features of this process include broad functional-group tolerance, readily available starting materials, and ease of execution.

Combinatorial Catalysis

M. T. Reetz,* O. Bondarev **4523 – 4526**

Mixtures of Chiral Phosphorous Acid Diesters and Achiral P Ligands in the Enantio- and Diastereoselective Hydrogenation of Ketimines

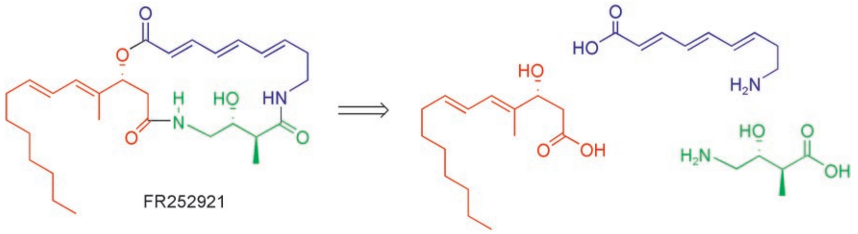


Try this cocktail! Ligand systems comprising a monodentate phosphorous acid diester derived from binol (L^a) and an achiral monodentate P ligand (L^b), such as a phosphite, are surprisingly efficient in the stereoselective Ir-catalyzed hydrogenation of ketimines (see scheme).

Natural Products Synthesis

J. R. Falck,* A. He, H. Fukui, H. Tsutsui, A. Radha **4527 – 4529**

Synthesis and Stereochemical Assignment of FR252921, a Promising Immunosuppressant

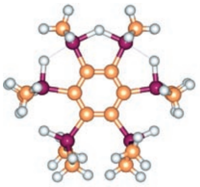


Synthetic detective work: FR252921, an unusual 19-membered lactone–dilactam, and three of its diastereomers were prepared by a versatile, convergent strategy from three key segments (see scheme). Comparison of the synthetic compounds with natural material established conclusively that FR252921 has the configuration 12*S*,13*R*,18*R*.

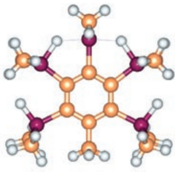
Agostic Interactions

A. Y. Khalimon, Z. H. Lin, R. Simionescu, S. F. Vyboishchikov,* G. I. Nikonov* **4530 – 4533**

Persistent Silylium Ions Stabilized by Polyagostic Si–H···Si Interactions



1



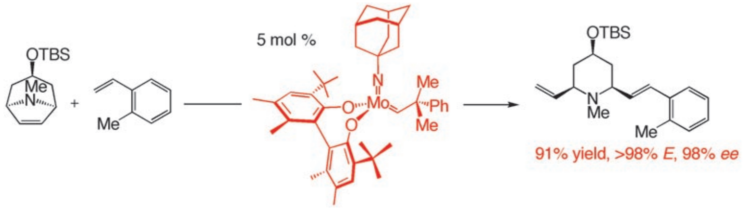
2

Diagnostics for diagostics: The silylium ion **1** (see picture; C orange, Si red, H gray) is highly fluxional at room temperature but at −80 °C exhibits a symmetric structure with a three-center two-electron Si-H-Si bond supported by two additional Si←H-Si agostic interactions. In the related cation **2**, two Si–H bonds coordinate equivalently to the cationic silicon center to afford a symmetrical pentacoordinate silylium ion.

Asymmetric Catalysis

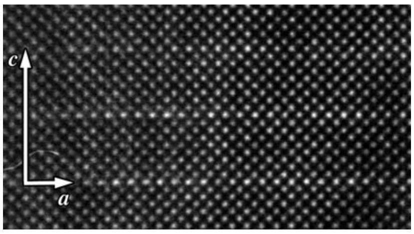
G. A. Cortez, R. R. Schrock, A. H. Hoveyda* **4534 – 4538**

Efficient Enantioselective Synthesis of Piperidines through Catalytic Asymmetric Ring-Opening/Cross-Metathesis Reactions



Mo the better! Chiral Mo complexes promote highly efficient asymmetric ring-opening/cross-metathesis reactions that afford functionalized piperidines in high *E*:*Z* selectivity and enantiomeric purity (see scheme for example; TBS = *tert*-butyldimethylsilyl). In most cases, Ru catalysts are ineffective.

One layer at a time: The sequential pulsed-laser deposition of CaO rock-salt and $CaMnO_3$ perovskite layers on an $SrTiO_3$ substrate allows the growth of the metastable $n=4$, 5, and 6 members of the $Ca_{n+1}Mn_nO_{3n+1}$ Ruddlesden–Popper series (see high-resolution TEM image of $Ca_5Mn_4O_{13}$). The growth process is monitored using reflection high-energy electron diffraction.



Thin-Film Metastable Oxides

L. Yan, H. Niu, C. A. Bridges, P. A. Marshall, J. Hadermann, G. van Tendeloo, P. R. Chalker, M. J. Rosseinsky* ______ **4539 – 4542**

Unit-Cell-Level Assembly of Metastable Transition-Metal Oxides by Pulsed-Laser Deposition

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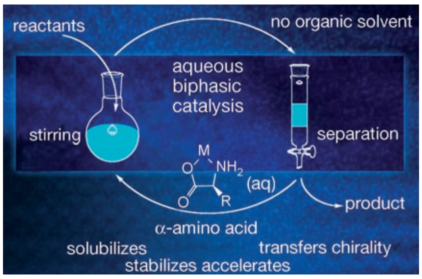

It's as easy as ABC: α-Amino acids may become very important tools in the development of economical and environmentally friendly aqueous biphasic catalysis. Alanine accelerated an $Yb(OTf)_3$-catalyzed Michael addition by a factor of 138. The solubilizing and stabilizing properties of alanine allowed the metal catalyst to be "heterogenized" in the aqueous phase and recycled multiple times without appreciable loss of activity.

Catalysis in Water

K. Aplander, R. Ding, U. M. Lindström,* J. Wennerberg,* S. Schultz _ **4543 – 4546**

α-Amino Acid Induced Rate Acceleration in Aqueous Biphasic Lewis Acid Catalyzed Michael Addition Reactions

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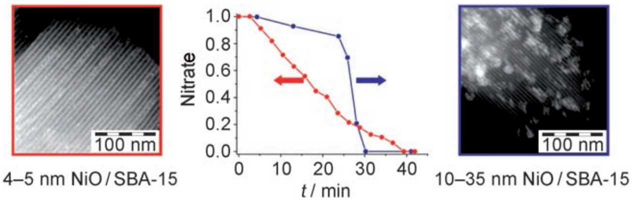

4–5 nm NiO / SBA-15

10–35 nm NiO / SBA-15

Nanoparticles

J. R. A. Sietsma, J. D. Meeldijk, J. P. den Breejen, M. Versluijs-Helder, A. J. van Dillen, P. E. de Jongh, K. P. de Jong* ______ **4547 – 4549**

A need for NO: Moderating the thermal decomposition of supported nitrates with NO (see picture, center) prevents precursor mobility and is a versatile method for the preparation of small NiO (left; compared to the product of the conventional procedure, right) and Co_3O_4 particles. These materials can be used as heterogeneous catalysts and show good activity in the Fischer–Tropsch synthesis.

The Preparation of Supported NiO and Co_3O_4 Nanoparticles by the Nitric Oxide Controlled Thermal Decomposition of Nitrates

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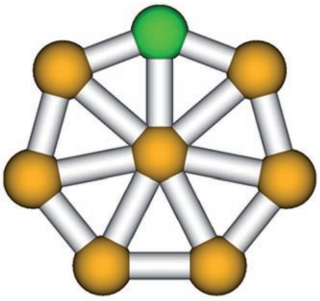
Changing the wheel: Replacing one B^- unit by C in B_8^{2-} is predicted to yield a CB_7^- molecular wheel, which has now been produced by laser vaporization. Ab initio calculations show that CB_7^- has an extremely stable planar C_{2v} structure in which C replaces B^- at the rim of the B_8^{2-} molecular wheel (see picture). The D_{7h} structure with a heptacoordinate C atom lies 63 kcal mol^{-1} above the C_{2v} structure.



CB_7^-, C_{2v}, $^1A_1$

Molecular Wheels

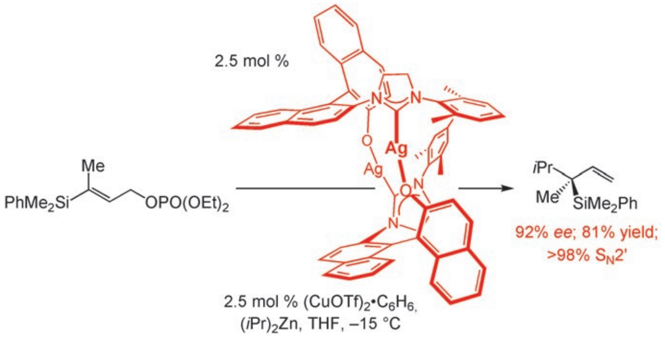
L. M. Wang, W. Huang, B. B. Averkiev, A. I. Boldyrev,* L. S. Wang* **4550 – 4553**

CB_7^-: Experimental and Theoretical Evidence against Hypercoordinate Planar Carbon

Allylic Alkylation

M. A. Kacprzynski, T. L. May, S. A. Kazane,
A. H. Hoveyda* ——— **4554 – 4558**

Enantioselective Synthesis of Allylsilanes Bearing Tertiary and Quaternary Si-Substituted Carbons through Cu-Catalyzed Allylic Alkylations with Alkylzinc and Arylzinc Reagents



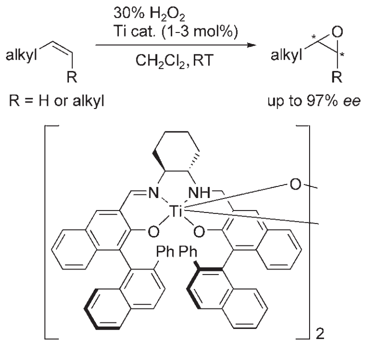
All sorts of allylsilanes including, for the first time, those that contain a Si-bonded quaternary carbon, were synthesized through efficient and highly enantioselective Cu-catalyzed asymmetric allylic alkylations. Reactions may involve dialkyl- as well as diarylzinc reagents and are promoted by various chiral N-heterocyclic carbene complexes.

Asymmetric Epoxidation

Y. Sawada, K. Matsumoto,
T. Katsuki* ——— **4559 – 4561**

Titanium-Catalyzed Asymmetric Epoxidation of Non-Activated Olefins with Hydrogen Peroxide

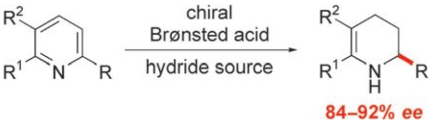
A greener oxidation: A titanium(salalen) complex catalyzes the asymmetric epoxidation of aliphatic (non-activated) olefins using aqueous hydrogen peroxide as the oxidant. Reactions with aliphatic terminal and *Z* olefins furnish the corresponding epoxides in good yields with high enantioselectivities of up to 97% *ee*.



Brønsted Acid Catalysis

M. Rueping,*
A. P. Antonchick ——— **4562 – 4565**

Organocatalytic Enantioselective Reduction of Pyridines



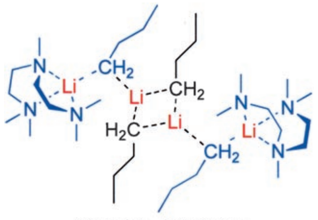
Metal-free at last! The first enantioselective organocatalytic reduction of pyridine derivatives leads to hexahydrochinolinones and tetrahydropyridines in good yields and with excellent enantioselctivities (up to 92% *ee*; see scheme). These compounds are starting materials for the synthesis of various natural products.

Alkyllithium Compounds

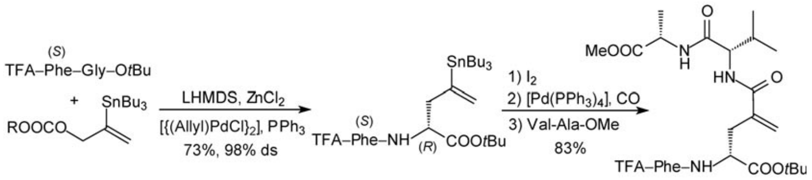
C. Strohmann,*
V. H. Gessner ——— **4566 – 4569**

From the Alkyllithium Aggregate [{(*n*BuLi)$_2$·PMDTA}$_2$] to Lithiated PMDTA

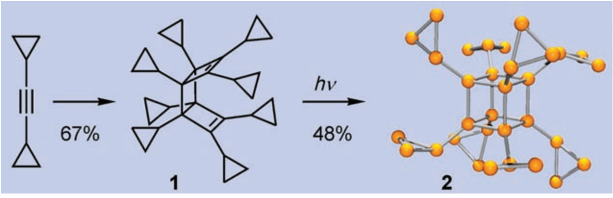
A commonly used deprotonation agent is the combination of *n*-butyllithium and *N*,*N*,*N*′,*N*′′,*N*′′-pentamethyldiethylenetriamine (PMDTA). The highly reactive aggregate [{(*n*BuLi)$_2$·PMDTA}$_2$] crystallizes out of a 2:1 mixture of *n*BuLi and PMDTA. The molecular structure provides insight into the significant influence of the *n*BuLi/PMDTA ratio on the course of some deprotonation reactions.



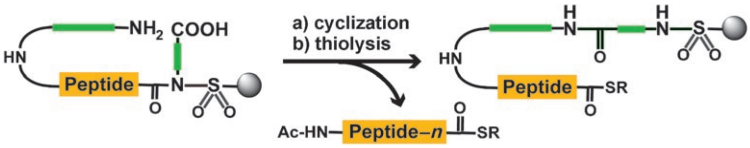
[{(*n*BuLi)$_2$ · PMDTA}$_2$]



In one fell swoop: Stannylated allyl carbonates allow the highly stereoselective synthesis of metalated peptides, which can be further modified by Stille coupling. Tin–iodine exchange generates iodinated peptides which also can be used for C–C coupling reactions. Therefore, only one stereoselective reaction is necessary to generate a wide range of different peptides in stereochemically pure form.



Decorator rocket fuel? Tricyclooctadiene **1**, easily prepared in a single-pot operation from dicyclopropylethyne in 67 % yield, upon irradiation in pentane solution undergoes an intramolecular [2+2] cycloaddition to give octacyclopropylcubane (**2**) in remarkably good yield (48 %). The new cubane derivative with an overall strain energy of $>390\,\mathrm{kcal\,mol^{-1}}$ displays unique physical and chemical properties.



Separating the wheat from the chaff: A cyclization–thiolysis sequence adds a new property to sulfonamide safety-catch resins. Activation of the sulfonamide is used to introduce a carboxy group for subsequent macrocyclization. Truncation products are noncyclic and hence washed away following thiolytic ring opening. Only the full-length peptide thioesters are detached, usually in pure form, in the final step.

Supporting information is available on the WWW (see article for access details).

A video clip is available as Supporting Information on the WWW (see article for access details).

Service