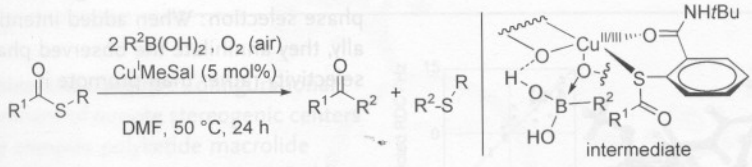
VIP The following Communications have been judged by at least two referees to be "very important papers" and are published online at www.angewandte.org:

Books

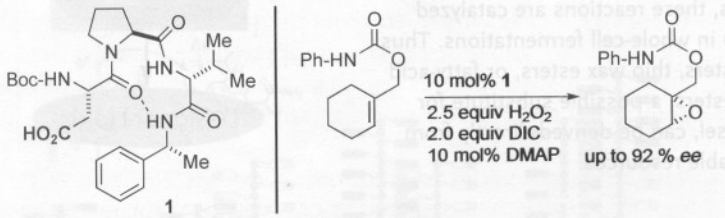
Highlights

C–C Coupling



Getting rid of palladium: Thiol esters can be cross-coupled with boronic acids to generate ketones at neutral pH by using a Cu^{I}-oxygenate catalyst under aerobic and Pd-free conditions (see scheme; S-pendant = NH*t*Bu thiosalicyclamide). The mechanistically unique coupling is likely to proceed by a preorganized, higher oxidation state Cu species that relies on appropriately positioned ligating S-pendant groups on the thiol ester and on an additional equivalent of the boronic acid.

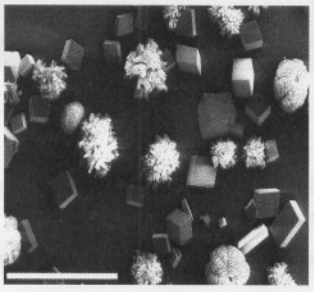
Asymmetric Epoxidation



Oxidation per carboxylic acid: Upon incorporation into a suitable tripeptide, per-aspartate can epoxidize olefins that contain hydrogen-bonding groups with high enantioselectivity (up to 92% *ee*). Catalytic asymmetric epoxidation can be effected with hydrogen peroxide as the terminal oxidant and carbodiimide as the stoichiometric activator for multiple acid/peracid turnovers.

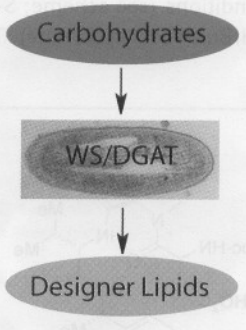
Contents

Correspondence



Like chalk and cheese: Although the model put forward by Lahav and Leiserowitz may be quite reasonable for the crystallization of glycine in the presence of amino acids, it is not the case for the crystallization of $CaCO_3$ (see picture). In the latter case, the amino acids present cannot be considered to be innocent molecules as they are involved as ligands in the coordination chemistry of Ca^{2+}. New results indicate that homochiral impurities are not the driving force for the phase selection: When added intentionally, they annihilate the observed phase selectivity rather than promote it.

Minireviews



For the USA and Canada:
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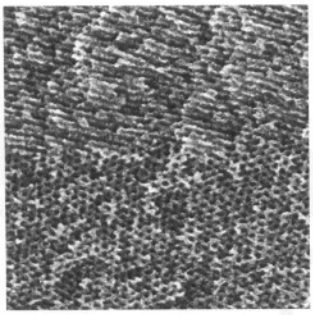
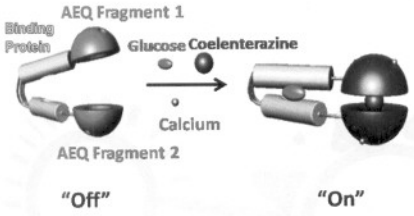
Reviews



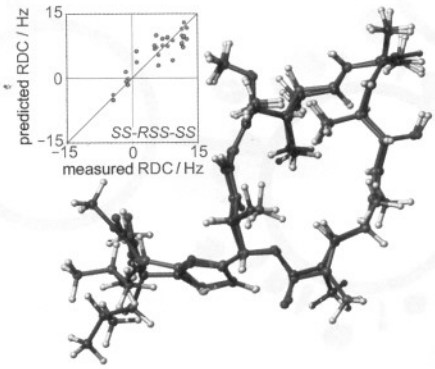
The right combination of new techniques, which use a large variety of hard and soft templates in the controlled synthesis of mesoporous carbon materials with well-defined nanostructures, and surface modification of these materials offers new perspectives for carbon material applications. The picture shows a high-resolution view of the surface structure of a fibrous material formed from phloroglucinol.

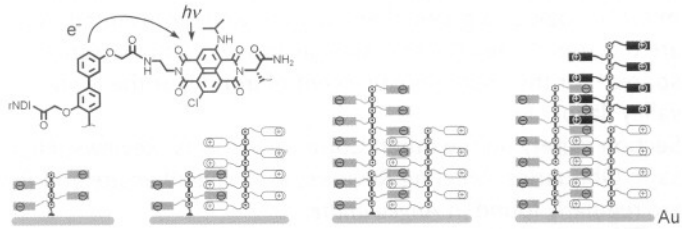
Communications



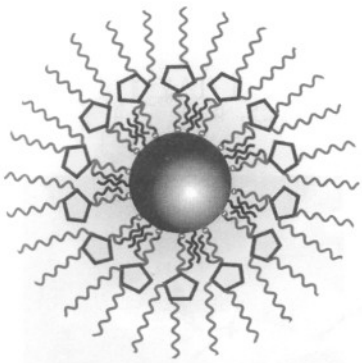
Glowing after a sugar rush: A molecular switch is formed by inserting glucose-binding protein (GBP) into aequorin (AEQ; see picture). This switch is triggered by recognition of glucose by the GBP. For the first time, AEQ is rationally split into two fragments that, upon a molecular recognition event, come together and emit bioluminescence.

Combine and conquer: Configurational assignment of remote stereogenic centers in the complex polyketide macrolide archazolide A (see structure; red O, blue N, yellow S) was accomplished by a purely NMR-based approach relying on a combination of nuclear Overhauser effects, *J* couplings, and residual dipolar couplings (RDCs).





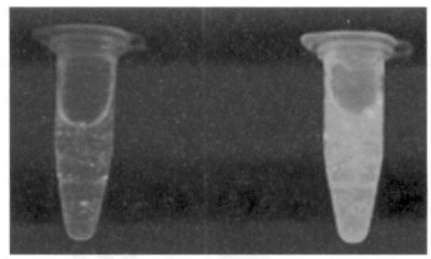
Zipped up: Supramolecular 3D organization on gold with interdigitating intra- and interlayer recognition motifs (see picure, black *p*-oligophenyl rods; red, blue naphthalenediimide (NDI) stacks) is designed to access supramolecular cascade n/p-heterojunctions or the adaptable directionality needed to control fill factors in current–voltage curves.



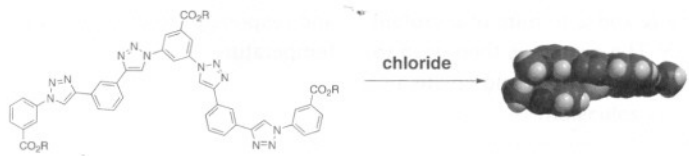
No fear of water: Hydrophobic nanocrystals (NCs) are converted into hydrophilic ones by dual-interaction ligands, which bind onto the surface of NCs by coordinate bonding and hydrophobic van der Waals interactions. The resulting NCs have high stability in aqueous solutions over a wide pH range (1–14), salt concentrations, and thermal treatments. Quantum dots coated with these ligands are excellent fluorescence labels for immunostaining tests.

Water-Soluble Nanocrystals

No destaining required: The luminescence properties of an iridium(III)–2-phenylpyridine complex can be utilized for the detection of proteins in sodium dodecyl sulfate–polyacrylamide gels. Emissive gel images obtained upon staining with the complex are visible under UV light. The high detection sensitivity for histidine-rich proteins (right vial, compared to a non-histidine-tagged protein) suggests potential applications in the signaling of biomolecules.

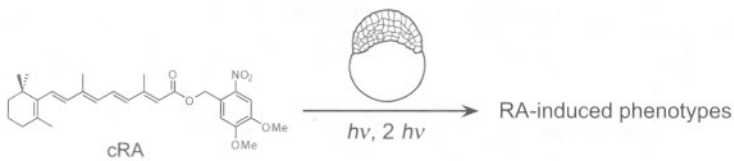


Luminescent Probes



A new folder: The electropositive CH groups of diaryl triazoles interact favourably with chloride, leading to anion-induced helical folding in aryl triazole oligomers. Triazoles thus provide an alternative to conventional protic hydrogen bonds and coordination complexes as functional components in anion receptors.

Molecular Recognition

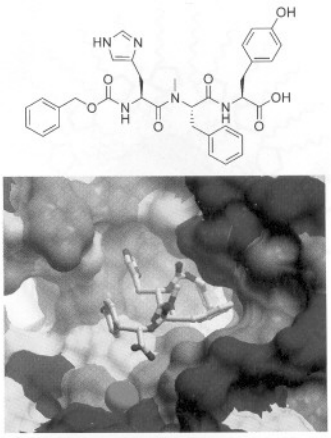


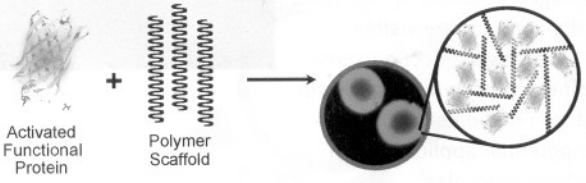
Escaping the cage: Retinoic acid (RA), a crucial signaling molecule for the embryogenesis of vertebrates, can be photoreleased from a simple caged derivative (cRA) upon illumination. In zebrafish embryos, cRA causes RA-induced phenotypes with one- and two-photon excitation (see picture), which opens a route to the noninvasive generation of controlled RA concentration patterns in vivo.

Embryogenesis

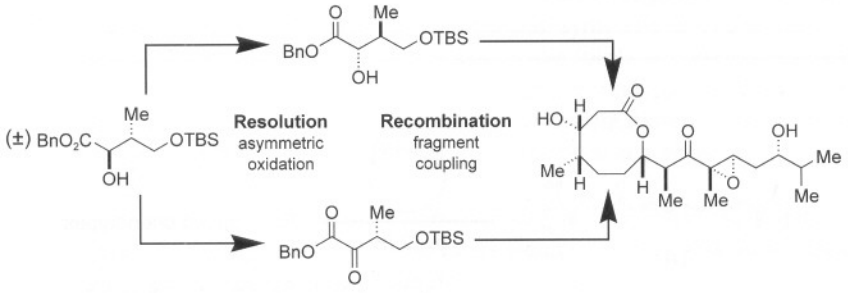
Contents

Stopping the transfer: Based on the structure of pepticinnamin E, specific inhibitors of Rab geranylgeranyl transferase (RabGGTase) with activity in cells were developed, and the first crystal structure of the enzyme in complex with an inhibitor is reported (see inhibitor structure and positioning in the active site of the enzyme). The findings may have implications for the chemical-biological study of Rab prenylation and vesicular transport and the involvement of RabGGTase in the establishment of disease.

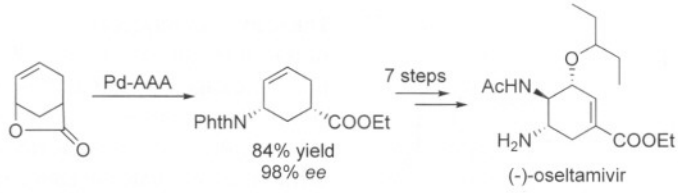




Creating a greener future: A strategy for creating hybrid materials of polymers and proteins relies on orthogonal reactions to activate the N and C termini of a protein concurrently. The protein is then used to cross-link polymer chains and create a hydrogel (see picture). A model hybrid hydrogel containing enhanced green fluorescent protein is both biodegradable and responsive to changes in pH and temperature.

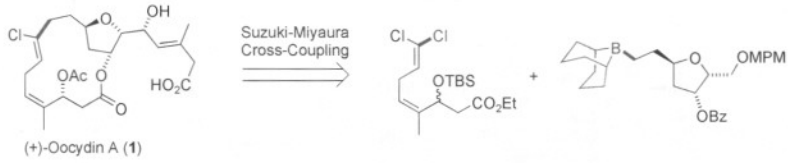


Both products of the kinetic resolution were used in the resolution/recombination approach shown in the scheme for the enantioselective total synthesis of (−)-octalactin A. Bn = benzyl, TBS = *tert*-butyldimethylsilyl.



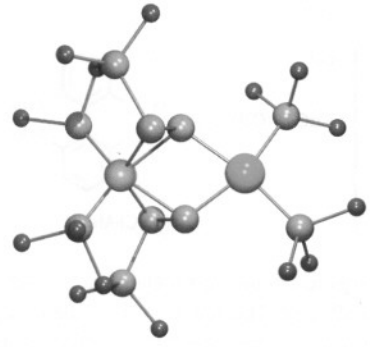
Tackling the supply problem: A short and efficient synthesis of (−)-oseltamivir has been developed which requires eight steps from commercially available starting material and proceeds with an overall yield of 30%. Key transformations include a novel palladium-catalyzed asymmetric allylic alkylation reaction (Pd-AAA, see scheme) as well as a chemo-, regio-, and stereoselective aziridination reaction. Phth = phthaloyl.

Drug Synthesis



Two sensitive fragments were coupled in the mild title reaction to create the *Z*-chlorovinyl functionality of the target macrolide oocydin A (**1**; see scheme). Another highlight in the total synthesis of **1** was an efficient stereoselective Pd^0-catalyzed cyclization to form the highly substituted tetrahydrofuran ring. Bz = benzoyl, TBS = *tert*-butyldimethylsilyl, MPM = 4-methoxyphenylmethyl.

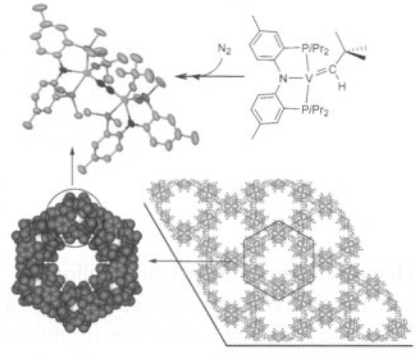
Natural Product Synthesis



White phosphorus is sequentially activated and functionalized by stepwise reaction with cobalt and platinum metal complexes. The two zwitterionic diphenyl(alkyl)phosphonium(+)diphosphenide(−) molecules generated act as bridging side-on/end-on ligands that tether two different metal units (see picture of the complex core: C black, Co pale green, P orange, Pt green).

P_4 Activation

Honeycomb architectures from N_2 sequestration! The V^{III}–bis-neopentyl complex $[(PNP)V(CH_2tBu)_2]$ (PNP = N[4-Me-2-($PiPr_2$)$C_6H_3]_2^-$) is a synthon to terminal V^V alkylidene complexes when treated with two-electron oxidants such as N_2CPh_2, O^{2-} sources such as $OPPh_3$ and N_2O, and sulfide sources like S_8 and $SPPh_3$. The likely V^{III}–alkylidene intermediate, [(PNP)V=CH*t*Bu], can also activate N_2 to form a honeycomb-like packing rearrangement along the N_2 unit (see picture).



Vanadium(V) Alkylidenes

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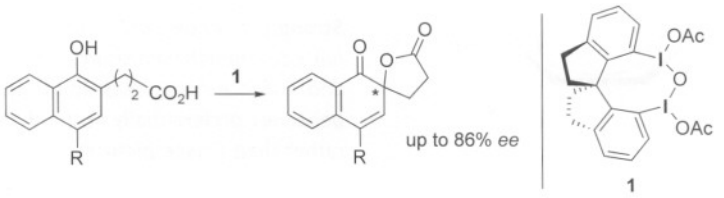
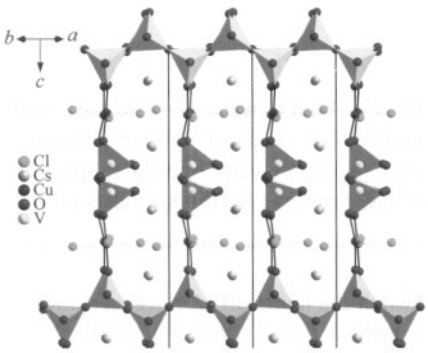


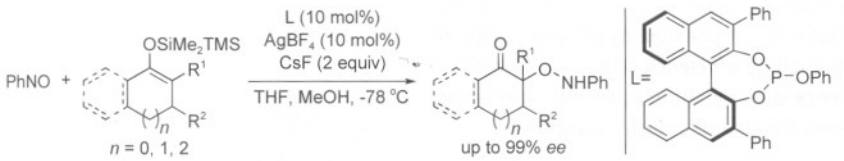
The hype about iodine(III): A chiral hypervalent iodine(III) reagent (**1**) is reported to enantioselectively dearomatize phenols in a highly selective manner (see scheme). This result clearly supports existence of the associative pathway in hypervalent iodine(III)-induced phenolic oxidations.

Oxidation

Acentric vanadates: Three unique structure types of the vanadate-based mixed-metal oxide systems (salt)·Mn^{II}-V^{V}-O and (salt)·Cu^{II}-V^{V}-O are presented, with a focus on the role of the asymmetric vanadate units (yellow polyhedra). The two structure types found in the $(AX)_2M(VO_3)_2$ series differ in the propagation direction of the metavanadate chains, which is thought to be due to the presence (or absence) of a Jahn–Teller distortion of the metal (d^9 Cu^{2+} vs. d^5 Mn^{2+}) ion.

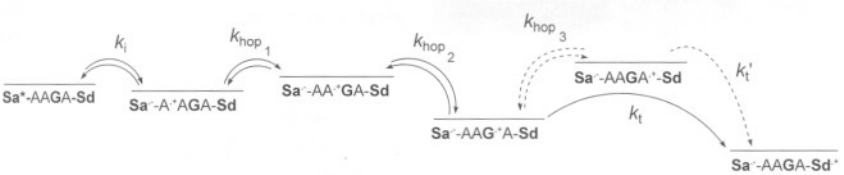


Noncentrosymmetric Vanadates



New nucleophiles for the O-nitroso aldol reaction in the form of readily prepared disilanyl enol ethers make this transformation more practical and more versatile. A silver catalyst with a chiral biaryl phosphite ligand promotes the title reaction with high enantio- and regioselectivity (see scheme). R^1,R^2 = H, Ar; TMS = trimethylsilyl.

Asymmetric Catalysis



Stopover at G base: The efficiency of photoinduced charge separation between donor and acceptor chromophores separated by a polyadenine sequence containing a single guanine (G) is sensitive to the location of G and the total length of the polypurine sequence. Quantum yields provide support for a stepwise mechanism in which G serves as a temporary resting place in the overall process (Sa: stilbenedicarboxamide electron acceptor, Sd: stilbenediether electron donor).

Electron Transfer

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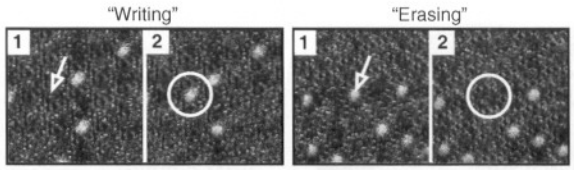
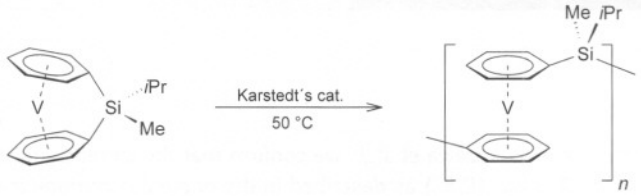


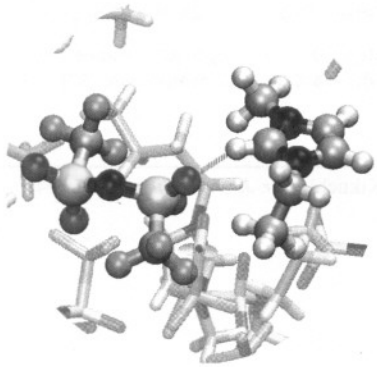
Host–Guest Chemistry

Now you see it, now you don't: A molecular monolayer polymorph of an oligopyridine forms a host–guest network with copper(II) phthalocyanine at the solid–liquid interface with controllable phthalocyanine occupation. The slow movement of the phthalocyanine guest molecules and the competition between oligopyridine and phthalocyanine guest molecules make it possible to manipulate individual guest molecules in analogy to "writing" and "erasing".



Ansa Complexes

Salt-elimination reactions led to the formation of highly strained [1]bora- and [1]silavanadoarenophanes, which undergo different types of ring-opening reactions with low-valent platinum complexes. Whereas the boron-bridged derivative opened stoichiometrically by cleavage of the V–C_{arene} bond, the [1]silavanadoarenophane reacted at the Si–C_{ipso} bond to afford a polymer containing spin-active metal centers in the main chain (see scheme).



Ionic Liquids

Bending and stretching: The nature of intermolecular interactions in imidazolium-based ionic liquids has been studied by far-infrared spectroscopy. The lowest frequencies can be assigned to the bending and stretching vibrational modes of the cation–anion interaction, which describes the cohesion energy.

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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Service

Corrigendum

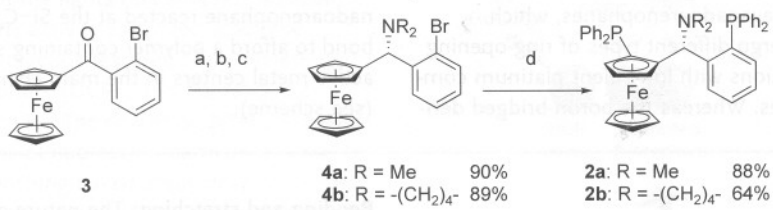
Ferrocenyl Ligands with Two Phosphanyl Substituents in the α,ε Positions for the Transition Metal Catalyzed Asymmetric Hydrogenation of Functionalized Double Bonds

T. Ireland, G. Grossheimann, C. Wieser-Jeunesse, P. Knochel ——— **3212–3215**

Angew. Chem. Int. Ed. **1999**, *38*

DOI 10.1002/(SICI)1521-3773(19991102)38:21<3212::AID-ANIE3212>3.0.CO;2-9

Following a remark by Fukuzawa et al.,[1] we confirm that the stereochemistry of ferrocenyl ligands **2** is not (R,S_{Fc}) as described in the original communication, but (R,R_{Fc}) as indicated by the X-ray structure of the [Rh(nbd)(**2a**)]BF_4 complex included in the manuscript. Thus, the ferrocene derivatives **2a** and **2b** have (R,R_{Fc}) configuration (Scheme 1).



3

4a: R = Me 90%
4b: R = -$(CH_2)_4$- 89%

2a: R = Me 88%
2b: R = -$(CH_2)_4$- 64%

Scheme 1. a) CBS catalyst (0.3 equiv), BH_3–Me_2S, 0 °C, 2 h; b) Ac_2O, pyridine, 12 h; c) HNR_2, CH_3CN, H_2O, 12 h; d) *t*BuLi (3.5 equiv), −78 °C to room temperature (RT), 1 h; then $ClPPh_2$ (2.5 equiv), −78 °C to RT, 1 h.

[1] S. Fukuzawa, M. Yamamoto, M. Hosaka, S. Kikuchi, *Eur. J. Org. Chem.* **2007**, 5540.

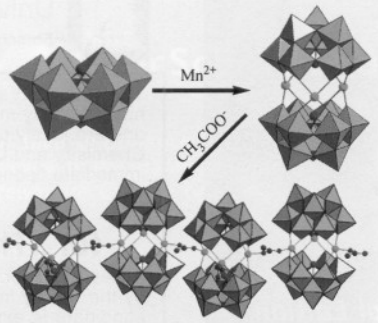
Spotlights ...

Polyoxometalates

J.-P. Wang, P.-T. Ma, J. Li, H.-Y. Niu, J.-Y. Niu*

Self-Assembly of $[B\text{-}SbW_9O_{33}]^{9-}$ Subunit with Transition Metal Ions (Mn^{2+}, Cu^{2+}, Co^{2+}) in Aqueous Solution: Syntheses, Structures and Magnetic Properties of Sandwich Type Polyoxometalates with Subvalent Sb^{III} Heteroatom

Chem. Asian J.
DOI: **10.1002/asia.200700363**



Fast-food chains: A series of new 1D, 2D, or 3D extended structural sandwiched compounds built from *B*-α-$[SbW_9O_{33}]^{9-}$ or *B*-β-$[SbW_9O_{33}]^{9-}$ building blocks (see figure) can be prepared by rational self-assembly being interconnected by either a carboxylate-bridge or a transition-metal covalent bond.

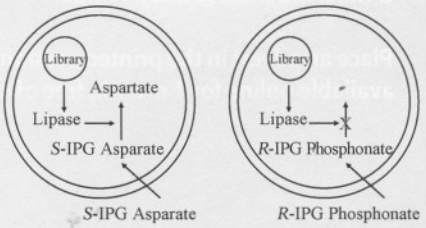
Directed Evolution

Y. L. Boersma, M. J. Dröge, A. M. van der Sloot, T. Pijning, R. H. Cool, B. W. Dijkstra, W. J. Quax*

A Novel Genetic Selection System for Improved Enantioselectivity of *Bacillus subtilis* Lipase A

ChemBioChem
DOI: **10.1002/cbic.200700754**

Enhancing enzyme enantioselectivity: A novel method for selecting enzymes with altered enantioselectivity was developed. A mutant library of lipases transformed to an *E. coli* aspartate auxotroph was grown on (*S*)-(+)-IPG-aspartate ester. Dual selection by using an (*R*)-(−)-IPG phosphonate inhibitor was shown to increase selection pressure towards improved enantioselectivity to (*S*)-(+)-IPG.

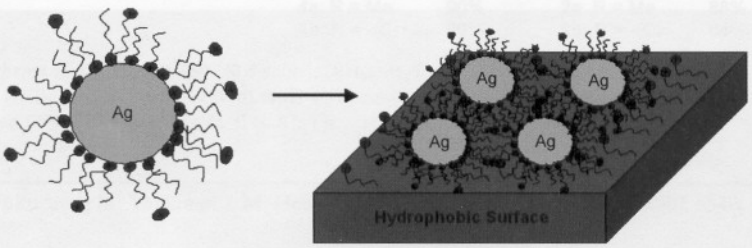


Nanocavities

M. Kahraman, N. Tokman, M. Çulha*

Silver Nanoparticle Thin Films with Nanocavities for Surface-Enhanced Raman Scattering

ChemPhysChem
DOI: **10.1002/cphc.200800007**



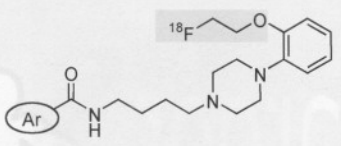
Nanocavities: The presence of nanometer-sized gaps between silver nanoparticles is critical for optimum enhancement in surface-enhanced Raman scattering (SERS). In thin films prepared on hydrophobic surfaces from concentrated silver colloidal suspensions, such gaps are generated using cationic surfactant molecules as spacers (see picture).

Imaging Agents

C. Hocke,* O. Prante, I. Salama, H. Hübner, S. Löber, T. Kuwert, P. Gmeiner

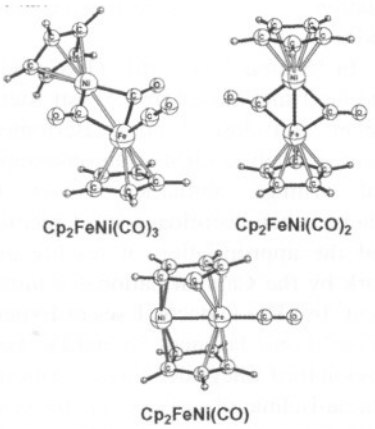
^{18}F-Labeled FAUC 346 and BP 897 Derivatives as Subtype-Selective Potential PET Radioligands for the Dopamine D3 Receptor

ChemMedChem
DOI: **10.1002/cmdc.200700327**



The dopamine D3 receptor has attracted special attention in recent year because of its potential importance in psychiatric illness. However, there exists a lack of subtype-selective ligands for the D3 receptor. Based on 3D-QSAR models predicting subtype selectivities of dopaminergic test compounds, the [^{18}F]labeled D3 receptor ligands [^{18}F]**4a–d** were synthesized and tested in vitro.

Using density functional theory (BP86) the global minima of both $Cp_2FeNi(CO)_3$ and $Cp_2FeNi(CO)_2$ are found to have two bridging CO groups. The coaxial structure of $Cp_2FeNi(CO)$ prefers an open-shell high spin state whereas the isoelectronic $Cp_2Co_2(CO)$ prefers a closed shell state with a Co≡Co triple bond. However, the global minimum for the monocarbonyl is a singlet perpendicular $Cp_2FeNi(CO)$ structure with an iron-bonded terminal CO group.

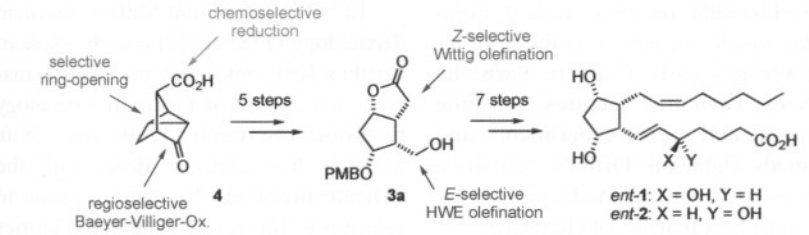


Multiple Metal–Metal Bonds

J. D. Zhang, Z. Chen, R. B. King, H. F. Schaefer, I.

Comparison of Isoelectronic Heterometallic and Homometallic Binuclear Cyclopentadienylmetal Carbonyls: The Iron–Nickel vs. the Dicobalt Systems

Eur. J. Inorg. Chem.
DOI: **10.1002/ejic.200701065**



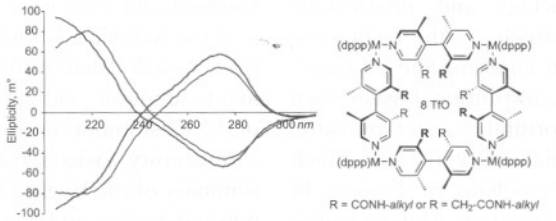
The all-*cis* substituted Corey lactone analogue **3a** was synthesized by a five-step sequence starting from enantiomerically pure nortricyclanone **4**. Further application of this chiral building block is demonstrated in the total syntheses of two diastereomeric isoprostanes belonging to the 5-F_2 family (*ent*-**1** and *ent*-**2**).

Isoprostane Synthesis

P. Elsner, P. Jetter, K. Brödner, G. Helmchen*

Stereoselective Synthesis of a *cis*-1,2-Dialkylcyclopentane Building Block and Its Application in Isoprostane Synthesis (5-*ent*-F_{2c}-IsoP)

Eur. J. Org. Chem.
DOI: **10.1002/ejoc.200800010**



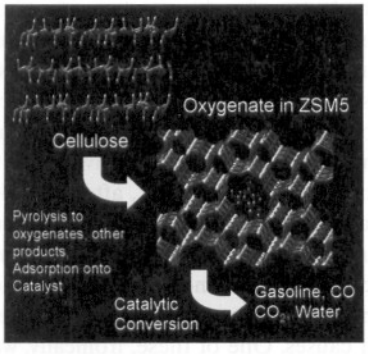
A preferred choice: Prochiral 3,3′,5,5′-tetramethyl-4,4′-bipyridine can be converted into two types of axially chiral 4,4′- bipyridine compounds, separable into enantiomers by chiral HPLC. The obtained enantiopure bipyridines were sufficiently stable in solution to be used in the self-assembly of chiral metallo-supramolecular squares, which reveal a remarkable preference for one of ten possible structures.

Supramolecular Chemistry

A. Rang, M. Engeser, N. M. Maier, M. Nieger, W. Lindner, C. A. Schalley*

Synthesis of Axially Chiral 4,4′-Bipyridines and Their Remarkably Selective Self-Assembly into Chiral Metallo-Supramolecular Squares

Chem. Eur. J.
DOI: **10.1002/chem.200800113**



A fuelling success: High-quality aromatic fuel additives can be produced directly from solid biomass feedstocks by catalytic fast pyrolysis in a single catalytic reactor at short residence times. High heating rates and catalyst-to-feed ratios are needed to ensure that pyrolized biomass compounds enter the pores of the ZSM5 catalyst and that thermal decomposition is avoided. Product selectivity is a function of the active site and pore structure of the catalyst.

Heterogeneous Catalysis

T. R. Carlson, T. P. Vispute, G. W. Huber*

Green Gasoline by Catalytic Fast Pyrolysis of Solid Biomass Derived Compounds

ChemSusChem
DOI: **10.1002/cssc.200800018**