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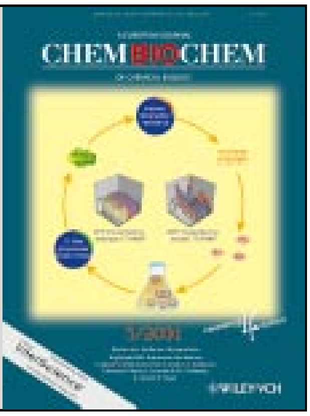
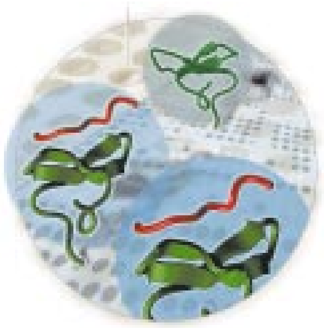
Pages 805–968

ChemBioChem* 3/2001 is bound in this issue of *Angewandte Chemie.



COVER PICTURE

The cover picture shows an array of several hundred synthetically produced variants of the 44 amino acids comprising the hyAP-WW protein domain. The array was produced by a stepwise SPOT synthesis on a cellulose membrane. At each synthesis site (spot) a WW domain is bound to the membrane through a C-terminal ester bond. The secondary structure of the WW domain is shown in green as a ribbon. The domains of the single spots differ only by a single amino acid. All the domains were tested simultaneously for their ability to bind to a peptide motif (red) common to many proteins. The binding was evident when visualized by chemoluminescence, with the Spots having various intensities. The systematic analysis undertaken here enabled molecular biology to be carried out that would have otherwise have required great effort, or not been done at all. This chemical technique also allows the construction of many non-genetically coded building blocks. Through the use of modern synthetic techniques for the coupling of peptides this method should also allow the synthesis of proteins. The combination of molecular biological and chemical methods opens up opportunities for the preparation of protein chips for diagnostics and drug discovery. More about this can be found in the article by Schneider-Mergener et al. on p. 897ff.



From chemical curiosities to highly sought synthetic building blocks: Anti-Bredt alkenes are accessible in one step from acyclic precursors by using the type 2 intramolecular Diels–Alder (IMDA) reaction described herein [Eq. (1)]. Unlike with the normal Diels–Alder reaction this variant allows high regio- and stereoselectivities. This provided the prerequisite for bridgehead alkenes to play a key role in the synthesis of a large number of complex natural products. Medium-sized rings are also readily accessible by using this method, and the bridges can be selected such that they can be cleaved after the synthesis.


(1)

Angew. Chem. **2001**, *113*, 864–894

B. R. Bear, S. M. Sparks,
K. J. Shea* 820–849

The Type 2 Intramolecular Diels–Alder Reaction: Synthesis and Chemistry of Bridgehead Alkenes

Keywords: bridgehead alkenes · cycloaddition · natural products · strained molecules · synthetic methods

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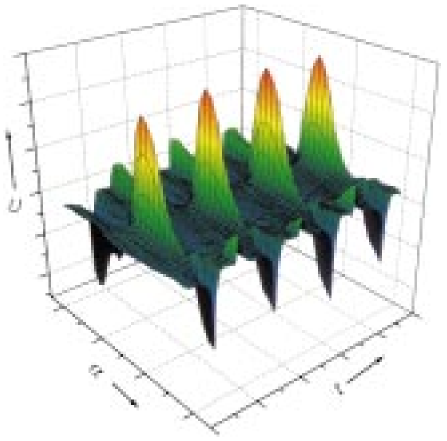
Spontaneous formation of ordered reactivity patterns at the electrode/electrolyte interface can occur in a variety of electrochemical reactions. Depending on the reaction conditions, different modes of spatial couplings necessary for cooperative behavior become dominating. This variability explains many of the multifaceted, spatiotemporal structure formations observed. The picture shows the spatiotemporal evolution of the potential at a Pt electrode during the oxidation of H_2 in the presence of Cu^{2+} and Cl^- ions after subtraction of the homogeneous oscillating part.



Angew. Chem. **2001**, *113*, 842–863

K. Krischer,* N. Mazouz,
P. Grauel 850–869

Fronts, Waves, and Stationary Patterns in Electrochemical Systems

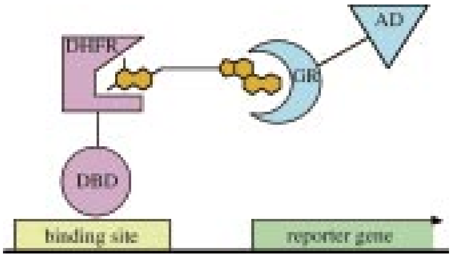
Keywords: autocatalysis · electrochemistry · nonlinear dynamics · pattern formation · self-organization

VIPs

The following communications are “Very Important Papers” in the opinion of two referees. They will be published shortly (those marked with a diamond will be published in the next issue). Short summaries of these articles can be found on the *Angewandte Chemie* homepage at the address http://www.angewandte.com

Formation of Super Wires of Clusters by Self-Assembly of Transition Metal Cluster Anions with Metal Cations	T. Nakajima, A. Ishiguro, Y. Wakatsuki*	◆
Highly Efficient and Ultrafast Phototriggers for cAMP and cGMP by Using Long-Wavelength UV/Vis Activation	V. Hagen,* J. Bendig, S. Frings, T. Eckardt, S. Helm, D. Reuter, U. B. Kaupp	◆
Isolation and Structural Characterization of the Endohedral Fullerene $Sc_3N@C_{78}$	M. M. Olmstead, A. de Bettencourt-Dias, J. C. Duchamp, S. Stevenson, D. Marciu, H. C. Dorn,* A. L. Balch*	
Synthesis of Conformationally Locked Carbohydrates: A Skew-Boat Conformation of L-Iduronic Acid Governs the Antithrombotic Activity of Heparin	S. K. Das, J.-M. Mallet, J. Esnault, P.-A. Driguez, P. Duchaussoy, P. Sizun, J.-P. Hèrault, J.-M. Herbert, M. Petitou,* P. Sinaÿ*	
The First Phosphine Oxide Ligand Precursors for Transition Metal Catalyzed Cross-Coupling Reactions: C–C, C–N, and C–S Bond Formation on Unactivated Aryl Chlorides	G. Y. Li*	
Copper(I) Carbenes: The Synthesis of Active Intermediates in Copper-Catalyzed Cyclopropanation	B. F. Straub, P. Hofmann*	
Cyclic Dimers of Metalloporphyrins as Tunable Hosts for Fullerenes: A Remarkable Effect of Rhodium(III)	J.-Y. Zheng, K. Tashiro, Y. Hirabayashi, K. Kinbara, K. Saigo,* T. Aida,* S. Sakamoto, K. Yamaguchi	

HIGHLIGHTS



The scope of cell-based assays is being expanded to allow the detection of interactions between proteins and DNA, RNA, or small molecules. The yeast two-hybrid assay, which normally detects protein–protein interactions, can be modified to detect interactions between ligands (the two dark yellow shapes in the diagram) and receptors (DHFR or GR). A small bridging molecule (made up of the ligands joined together) is used to join two fusion proteins (DHFR–DBD and AD–GR), thereby activating the reporter gene.

Angew. Chem. **2001**, *113*, 895–899

H. Lin, V. W. Cornish* 871–875

In Vivo Protein–Protein Interaction Assays: Beyond Proteins

Keywords: dimerization · molecular recognition · proteins · protein–protein interactions

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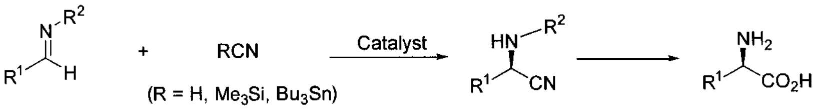
150 years after its discovery, a truly efficient three-component asymmetric version of the Strecker reaction has finally been accomplished; there has also been significant progress in recent years in two-component Strecker-type systems: Enantiopure amino acids can now be obtained from enantioselective catalysis of the Strecker reaction with different cyanide sources and aldimines (see scheme).



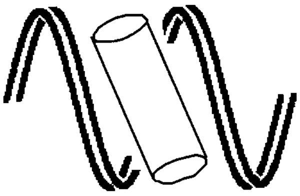
Angew. Chem. **2001**, *113*, 900–902

L. Yet* 875–877

Recent Developments in Catalytic Asymmetric Strecker-Type Reactions

Keywords: amino acids · asymmetric catalysis · cyanides · Schiff bases · Strecker reaction

COMMUNICATIONS



In the groove! A tetracationic supramolecular cylinder, $[Fe_2L_3]^{4+}$ ($L = C_{25}H_{20}N_4$), with a triple-helical architecture is just the right size to fit into the major groove of DNA (see picture) and too big to fit into the minor groove. NMR spectroscopic data confirm that the cylinder binds in the major groove. Linear dichroism shows that very low loadings of $[Fe_2L_3]^{4+}$ have a dramatic bending effect on the DNA and atomic force microscopy images show that this is an intramolecular effect resulting in coils of DNA.

Angew. Chem. **2001**, *113*, 904–908

M. J. Hannon,* V. Moreno,* M. J. Prieto, E. Moldrheim, E. Sletten,* I. Meistermann, C. J. Isaac, K. J. Sanders, A. Rodger* 880–884

Intramolecular DNA Coiling Mediated by a Metallo-Supramolecular Cylinder

Keywords: bioinorganic chemistry · DNA recognition · DNA structures · helical structures · supramolecular chemistry

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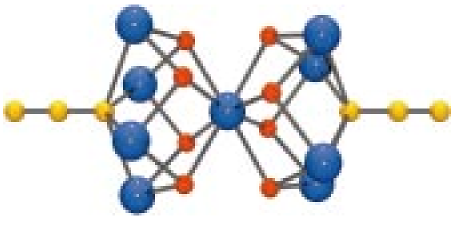


μ_4 end-on coordination (through the N atom) of the pseudohalogeno ligands $X^- = N_3^-$ and NCO^- has been observed in the isostructural nonanuclear Co^{II} cages with the general formula $[Co_9\{(2\text{-}C_5H_4N)_2\text{-}CO_2\}_4(O_2CMe)_8X_2]$ (see picture); this mode is imposed by the trapping of anions X^- into cavities formed inside the cage. The change of X^- modulates the magnetic behavior of the cage from antiferromagnetic coupling to a ferrimagnetic high-spin ground state.

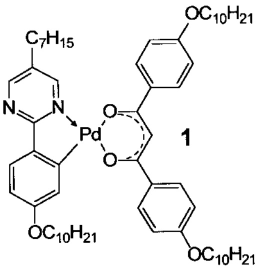
Angew. Chem. **2001**, *113*, 908–910

G. S. Papaefstathiou, S. P. Perlepes, A. Escuer,* R. Vicente, M. Font-Bardia, X. Solans 884–886

Unique Single-Atom Binding of Pseudohalogeno Ligands to Four Metal Ions Induced by Their Trapping into High-Nuclearity Cages

Keywords: azides · cage compounds · cobalt · high-spin molecules · magnetic properties

Molecular self-organization, driven by attractive face-to-face interactions between **1** and 2,4,7-trinitrofluorenone, leads to the formation of an optically biaxial smectic A liquid crystalline phase—a long-predicted new state of ordered soft matter.



Angew. Chem. **2001**, *113*, 911 – 914

T. Hegmann, J. Kain, S. Diele, G. Pelzl, C. Tschierske* . . . . 887 – 890

Evidence for the Existence of the McMillan Phase in a Binary System of a Metallomesogen and 2,4,7-Trinitrofluorenone

Keywords: donor – acceptor systems · liquid crystals · mesophases · metallomesogens · palladium

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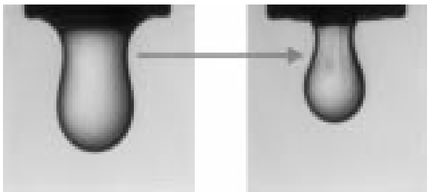
Folded drops: A skinlike folded drop surface is formed by the coadsorption of two components from different phases at the chloroform/water interface (see picture). Both pure β-lactoglobulin and mixtures of α-dipalmitoylphosphatidylcholine (DPPC) and β-lactoglobulin can form the skinlike film; the lipid accelerates this process by coadsorption with the protein. Atomic force microscopy provided information on the morphology of the complex film and confirmed the formation of a multilayer film at the liquid/liquid interface.



Angew. Chem. **2001**, *113*, 915 – 918

J. B. Li,* Y. Zhang, L. L. Yan . . 891 – 894

Multilayer Formation on a Curved Drop Surface

Keywords: atomic force microscopy · emulsions · multilayers · phospholipids · proteins · surface chemistry

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The chirality of the sugar moiety is responsible for the chiral molecular recognition on formation of a metalloanthocyanin from *Salvia patens.* This mechanism was revealed by using the synthetic apigenin 7,4′-diglucosides derived from D- or L-glucose. The supermolecule (see picture) consists of six malonylawobanin molecules (blue) coordinated to two Mg^{2+} ions (red) with an *M*-helical arrangement of six 7,4′-diglucoside molecules (yellow) intercalated.

Angew. Chem. **2001**, *113*, 918 – 922

T. Kondo,* K.-i. Oyama, K. Yoshida . . . . 894 – 897

Chiral Molecular Recognition on Formation of a Metalloanthocyanin: A Supramolecular Metal Complex Pigment from Blue Flowers of *Salvia patens*

Keywords: chirality · glycosylation · metalloanthocyanins · molecular recognition · natural products

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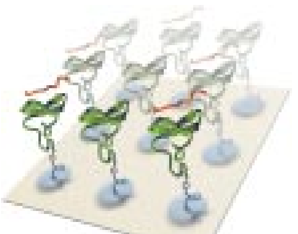
Comprehensive structure – function analyses are possible with an array comprising more than 800 synthetic variants of a protein domain composed of 44 amino acids. This array was produced by SPOT synthesis on a cellulose membrane (see schematic representation) and successfully employed for a parallel ligand-binding assay.



Angew. Chem. **2001**, *113*, 922 – 925

F. Toepert,* J. R. Pires, C. Landgraf, H. Oschkinat, J. Schneider-Mergener* . . . . 897 – 900

Synthesis of an Array Comprising 837 Variants of the hYAP WW Protein Domain

Keywords: peptides · peptide synthesis · proteins · solid-phase synthesis

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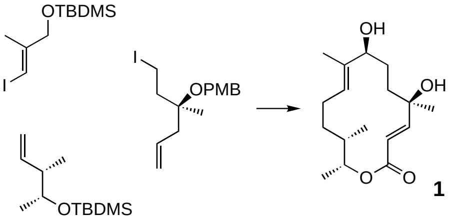
Three building blocks are coupled convergently in the first total synthesis of the macrolide antibiotic 5,6-tetrahydrocineromycin B (**1**); the facial selective allylation of a methyl ketone is the key step of the synthesis. TBDMS = *tert*-butyldimethylsilyl, PMB = *p*-methoxybenzyl.



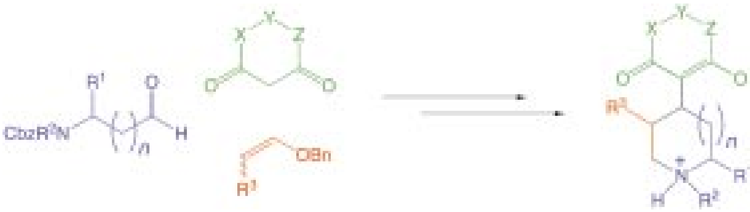
Angew. Chem. **2001**, *113*, 925 – 927

L. F. Tietze,* L. Völkel . . . . 901 – 902

Total Synthesis of the Macrolide Antibiotic 5,6-Dihydrocineromycin B

Keywords: allylation · antibiotics · lactones · macrolides · total synthesis

Advantages of solid-phase and liquid-phase synthesis are combined in a new concept of combinatorial chemistry: a domino sequence comprising Knoevenagel and hetero-Diels–Alder reactions with subsequent hydrogenation starting from protected aminoaldehydes, 1,3-dicarbonyl compounds, and enol ethers leads to N-heterocycles of high diversity with a betaine structure, which are isolated in highly pure form by precipitation with diethyl ether (see scheme). Cbz = benzyloxycarbonyl, Bn = benzyl.



Angew. Chem. **2001**, *113*, 927–929

L. F. Tietze,* H. Evers,
E. Töpken 903–905

A Novel Concept in Combinatorial Chemistry in Solution with the Advantages of Solid-Phase Synthesis: Formation of N-Betaines by Multicomponent Domino Reactions

Keywords: amino aldehydes · betaines · combinatorial chemistry · domino reactions · multicomponent reactions

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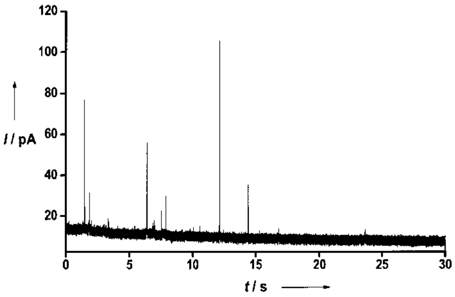
Positioning a carbon-fiber microelectrode with optimized stiffness and vibration characteristics in close proximity to an individual biological cell is achieved by using a shear-force-based constant-distance control in the scanning electrochemical microscope. With the properly positioned microelectrode, the discrete release of neutrotransmitters from individual cells can be monitored (see diagram; I = oxidation current).



Angew. Chem. **2001**, *113*, 942–946

A. Hengstenberg, A. Blöchl, I. D. Dietzel,
W. Schuhmann* 905–908

Spatially Resolved Detection of Neurotransmitter Secretion from Individual Cells by Means of Scanning Electrochemical Microscopy

Keywords: electrochemistry · exocytosis · microelectrodes · neurotransmitters · scanning probe microscopy

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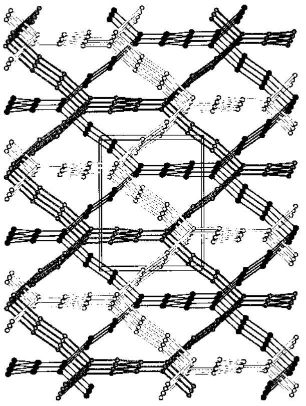
Inseparably interwoven are three independent polymeric diamond-type $U(P_2S_6)_2$ frameworks in the structure of the title compound (see picture). The linear P_2S_6 units act as molecular rods linking the pseudotetrahedral U^{4+} centers. $U(P_2S_6)_2$ may be viewed as a coordination polymer which is formed from U/P/S melts by the solid-state equivalent of the self-assembly reactions in solution.



Angew. Chem. **2001**, *113*, 946–948

C. Gieck, F. Rocker, V. Ksenofontov,
P. Gütlich, W. Tremel* 908–911

"Supramolecular" Solid-State Chemistry: Interpenetrating Diamond-Type Frameworks of U^{4+} Ions Linked by *S,S′*-Bidentate $P_2S_6^{2-}$ Molecular Rods in UP_4S_{12}

Keywords: chalcogenides · networks · solid-state structures · supramolecular chemistry · uranium

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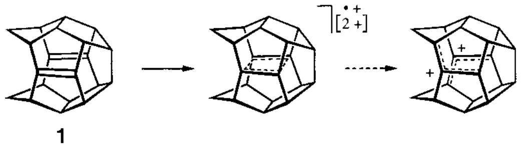
For the seco-dodecahedradiene 1, in which the distance $d_{\pi\pi}$ between the carbon atoms of the two double bonds ranges from 2.90 to 3.20 Å and pyramidalization angles Φ range from 14.9 to 35.5°, the geometrical prerequisites for in-plane (σ)-homoconjugative (σ-bishomoaromatic) electron delocalization in 4C/3(2)e cations could be better defined. Whilst the 4C/3e radical cation is persistent in a matrix, the 4C/2e dication in superacid medium is, at best, an intermediate en route to the stable bisallylic dication.



1

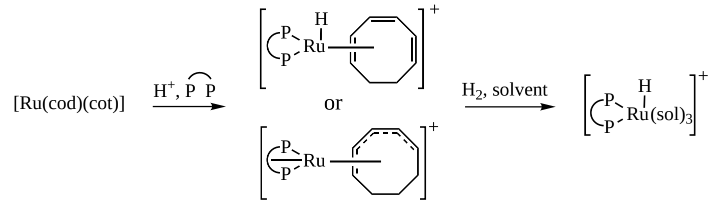
Angew. Chem. **2001**, *113*, 930–933

H. Prinzbach,* J. Reinbold, M. Bertau,
T. Voss, H.-D. Martin, B. Mayer,
J. Heinze, D. Neschchadin, G. Gescheidt,
G. K. S. Prakash, G. A. Olah .. 911–914

σ-Bishomoconjugation (σ-Bishomoaromaticity) in 4C/3(2)e Cations—Scope and Limitations

Keywords: aromaticity · cage compounds · cyclic voltammetry · photoelectron spectroscopy · superacidic systems

Simple and efficient: Protonation of [Ru(1,2:5,6-η-cod)(η^6-cot)] (cod = 1,5-cyclooctadiene, cot = 1,3,5-cyclooctatriene) with $HBF_4 \cdot Et_2O$ and then reaction with chiral bisphosphane ligands ($\widehat{P\,P}$ = Me-DuPHOS, BINAP, Tol-BINAP, JOSIPHOS) affords the corresponding $[Ru(\widehat{P\,P})(H)(\eta^6\text{-cot})]^+$ or $[Ru(\widehat{P\,P})(1,2,3,4,5\text{-}\eta\text{-}C_8H_{11}')]^+$ (C_8H_{11}' = 2,4-cyclooctadienyl; see scheme). Exposure of these cations to H_2 in solvents (sol) such as acetone, methanol, and THF affords $[Ru(\widehat{P\,P})(H)(sol)_3]^+$, which are catalysts for (amongst other things) enantioselective hydrogenations of alkenes.



Angew. Chem. **2001**, *113*, 937–942

J. A. Wiles, S. H. Bergens,*
K. P. M. Vanhessche, D. A. Dobbs,
V. Rautenstrauch* 914–919

A Versatile and High-Yield Route to Active and Well-Defined Catalysts $[Ru(bisphosphane)(H)(solvent)_3](BF_4)$

Keywords: asymmetric catalysis · homogeneous catalysis · hydrogenation · P ligands · ruthenium

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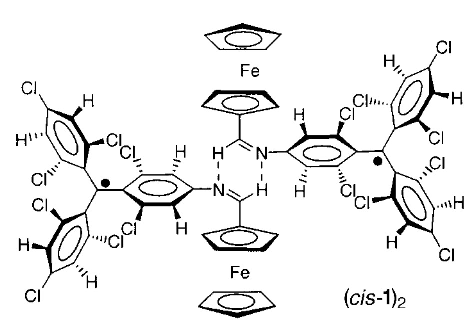
An irreversible *trans*→*cis* isomerization of the imino group occurs during the irradiation of the new ferrocenyl Schiff-base polychlorotriphenylmethyl radical **1** by light. Low-temperature ESR investigations of frozen solutions revealed that the *cis* isomer exists as the (*cis*-**1**)$_2$ dimer with strong antiferromagnetic interactions. The radical **1** constitutes an example of a one-way photoswitchable magnetic system in which a conversion between a doublet and a singlet ground-state species is promoted by a photoinduced self-assembly process driven by the formation of hydrogen bonds.


(*cis*-**1**)$_2$

Angew. Chem. **2001**, *113*, 933–936

I. Ratera, D. Ruiz-Molina,
J. Vidal-Gancedo, K. Wurst, N. Daro,
J.-F. Létard, C. Rovira,
J. Veciana* 919–922

A New Photomagnetic Molecular System Based on Photoinduced Self-Assembly of Radicals

Keywords: isomerization · magnetic properties · photochemistry · radicals · self-assembly

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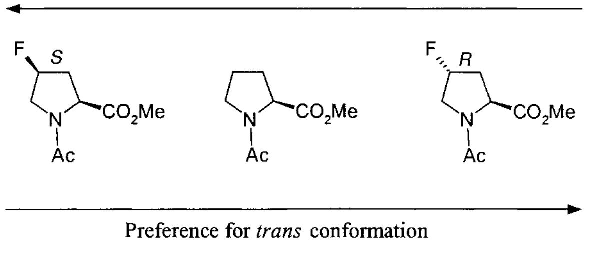
The preference of the peptidyl–fluoroproline amide bond for the *cis* or *trans* conformation in the model compounds *N*-acetyl-4-fluoroproline methyl esters (see scheme) fully correlates with the thermostability of the related mutants of the model protein barstar. Thus, the (4*S*)-L-FPro mutants show a higher and the(4*R*)-L-FPro mutants a lower thermal stability than barstar.



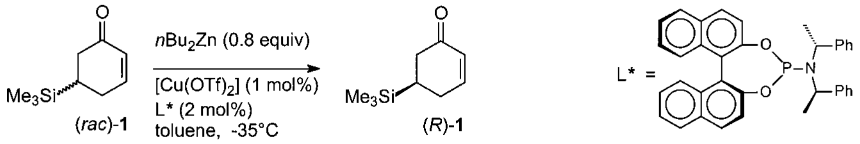
Angew. Chem. **2001**, *113*, 949–951

C. Renner, S. Alefelder, J. H. Bae,
N. Budisa, R. Huber,
L. Moroder* 923–925

Fluoroprolines as Tools for Protein Design and Engineering

Keywords: fluorine · isomerization · NMR spectroscopy · proline · proteins

A variety of substituted 2-cyclohexenones, such as (R)-**1**, is obtained enantiomerically pure by employing the chiral copper–phosphoramidite complex $[Cu(OTf)_2L^*]$ as a highly efficient catalyst for their kinetic resolution (>99% *ee* at 52% conversion, selectivity $S > 200$). These important building blocks can be obtained on a synthetically interesting scale, as was demonstrated by the successful multigram resolution of 5-methyl-2-cyclohexenone. Tf = trifluoromethanesulfonyl.



Angew. Chem. **2001**, *113*, 953–956

R. Naasz, L. A. Arnold, A. J. Minnaard,
B. L. Feringa* 927–930

Highly Enantioselective Copper–Phosphoramidite Catalyzed Kinetic Resolution of Chiral 2-Cyclohexenones

Keywords: asymmetric catalysis · copper · enones · kinetic resolution · phosphoramidites

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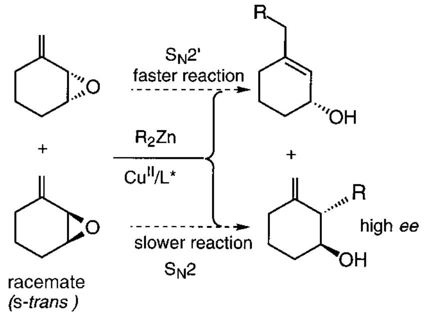
Chiral recognition leads to enantio- and regiodivergent reactivity: An unusual regiodivergent catalytic kinetic resolution has been accomplished for the first time in an organometallic reaction in which a C–C bond is formed. Chiral copper complexes of the non-racemic phosphoramidite ligand L* discriminate the enantiomers of semirigid vinyloxiranes (having a blocked s-*cis* or s-*trans* conformation) to give separable regioisomeric products with very high stereocontrol in a two-step process (see scheme).



Angew. Chem. **2001**, *113*, 956–958

F. Bertozzi, P. Crotti, F. Macchia,
M. Pineschi,* B. L. Feringa* .. 930–932

Highly Enantioselective Regiodivergent and Catalytic Parallel Kinetic Resolution

Keywords: asymmetric catalysis · copper · elimination · kinetic resolution · phosphoramidites

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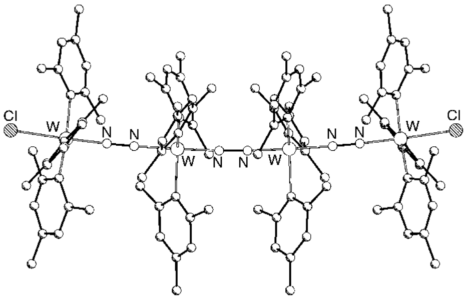
A new avenue is opened up in the potential use of dinitrogen. Oligomerization of the metalla–dinitrogen functionality leads to the formation of polymers based on a $[-(Mes)_3W-N_2-]_n^q$ moiety (see picture).



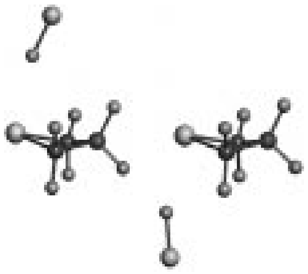
Angew. Chem. **2001**, *113*, 958–960

E. Solari, J. Hesschenbrouck,
R. Scopelliti, C. Floriani,*
N. Re 932–934

From Oligomers to Conducting Polymers of the Metal–Dinitrogen Functionality

Keywords: dinitrogen · metallacycles · oligomers · tungsten

Two different conformers (axial (in the left picture) and equatorial (right)) are formed in a supersonic jet stream when trimethylene sulfide, a floppy molecule with a large-amplitude ring-puckering motion, is complexed to hydrogen chloride. The axial conformer is the most stable. The relaxation from the equatorial to the axial conformational has been observed using different carrier gases.



Angew. Chem. **2001**, *113*, 961–964

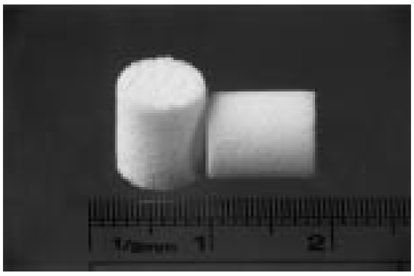
M. E. Sanz, A. Lesarri, J. C. López,
J. L. Alonso* 935–938

Hydrogen Bond in Molecules with Large-Amplitude Motions: A Rotational Study of Trimethylene Sulfide···HCl

Keywords: conformational analysis · hydrogen bonds · large-amplitude motions · rotational spectroscopy

A new resin support generated by co-sintering resin beads with an inert polymer (see picture) facilitates resin handling. A wide range of reactions was carried out to demonstrate its applicability and its comparability to the free resin.

Angew. Chem. **2001**, *113*, 964–967



B. Atrash, M. Bradley,* R. Kobylecki,*
D. Cowell, J. Reader 938–941

Revolutionizing Resin Handling for Combinatorial Synthesis

Keywords: combinatorial chemistry • polymer supports • synthetic methods

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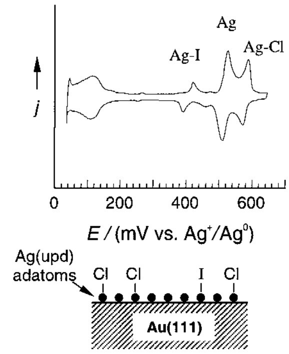
A new strategy for detecting halides is presented that employs gold electrodes plated to expose a monolayer of silver atoms. Cl^-, Br^-, and I^- ions each adsorb onto this surface and stochastically produce electrochemical changes (see picture; upd = underpotentially deposited) in the stripping characteristic of the silver layer that reflect the identity and surface coverage of these halides. The latter provides measurements that relate to the solution concentrations of the halides.

Angew. Chem. **2001**, *113*, 967–970



R. Michalitsch, P. E. Laibinis* . 941–944

Adsorption-Mediated Electrochemical Sensing of Halides

Keywords: cyclic voltammetry • electrochemistry • halides • sensors • silver

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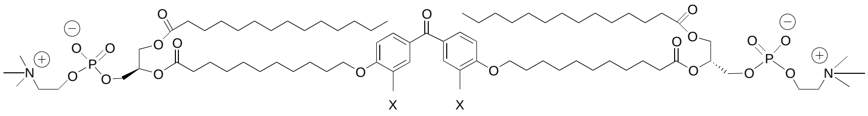
The tandem use of the photosensitive bola-amphiphile 1 ($X = {}^3H$) and cholesterol enabled the determination of the center of the transmembrane domain of glycophorin A (131 amino acid residues) in a membrane by selective functionalization of the protein within a phospholipid bilayer.



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Angew. Chem. **2001**, *113*, 970–972

Y. Ogawa, W. Hahn, P. Garnier,
N. Higashi, D. Massotte,
M.-H. Metz-Boutigue, B. Rousseau,
J. Sunamoto, G. Ourisson,
Y. Nakatani* 944–946

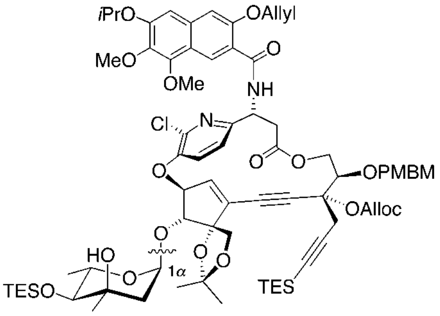
Mid-Membrane Photolabeling of the Transmembrane Domain of Glycophorin A in Phospholipid Vesicles

Keywords: cross-coupling • liposomes • membrane proteins • photolabeling • protein structures

---

The α-selective effect and potency of $AgPF_6$ on readily prepared 2-deoxythioglycosides allows the direct attachment of a partially protected *allo*-sugar, such as L-mycarose, to an advanced and hindered aglycon unit of kedarcidin (see picture). This method also permits access to other 2-deoxyglycosides in an expedient and mild manner. PMBM = *p*-methoxybenzyloxymethyl, Alloc = allyloxycarbonyl, TES = triethylsilyl.

Angew. Chem. **2001**, *113*, 972–975

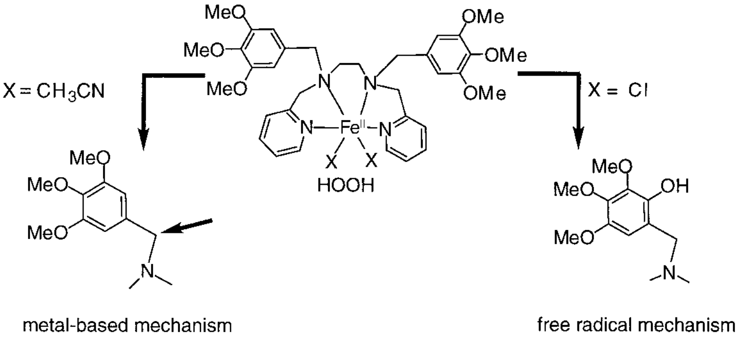


M. J. Lear, F. Yoshimura,
M. Hirama* 946–949

A Direct and Efficient α-Selective Glycosylation Protocol for the Kedarcidin Sugar, L-Mycarose: $AgPF_6$ as a Remarkable Activator of 2-Deoxythioglycosides

Keywords: deoxy sugars • glycosylation • kedarcidin • silver hexafluorophosphate • stereoselectivity

Manipulation of the coordination sphere of an Fe^{II} ion can be used to tune the balance between different catalytic pathways for oxidation (OH$^\bullet$ versus iron-based oxidant; see scheme). This reinvestigation of Fenton chemistry uses the iron complex shown as a mechanistic probe.



Angew. Chem. **2001**, *113*, 975–978

Y. Mekmouche, S. Ménage,*
C. Toia-Duboc, M. Fontecave,
J.-B. Galey, C. Lebrun,
J. Pécaut 949–952

H_2O_2-Dependent Fe-Catalyzed Oxidations: Control of the Active Species

Keywords: homogeneous catalysis · hydrogen peroxide · hydroxylation · iron · reaction mechanisms

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Photolysis of a diazogermylene generates a germylene–carbene species, a resonance form of a germyne (see scheme). Support for the intermediacy of the triply bonded form in the trapping reaction with an alcohol is provided by the fact that the diazo precursor does not behave as a germylene and that its photolysis product does not react with carbene traps such as 2,3-dimethylbutadiene. Hence, this is the first chemical evidence for a germyne. Ar = 2,6-(iPr$_2$NCH$_2$)$_2$C$_6$H$_3$; R = Me, *t*Bu.

$$\mathrm{Ar\underset{\bullet\bullet}{Ge}C(N_2)SiMe_3} \xrightarrow[-N_2]{h\nu} \left[\mathrm{Ar\underset{\bullet\bullet}{Ge}\underset{\bullet\bullet}{C}SiMe_3} \longleftrightarrow \mathrm{ArGe{\equiv}CSiMe_3}\right] \xrightarrow{2\,\mathrm{ROH}} \mathrm{ArGe(OR)_2CH_2SiMe_3}$$

Angew. Chem. **2001**, *113*, 978–980

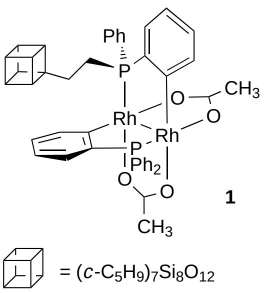
C. Bibal, S. Mazières, H. Gornitzka,
C. Couret* 952–954

A Route to a Germanium–Carbon Triple Bond: First Chemical Evidence for a Germyne

Keywords: carbenes · diazo compounds · germanium · multiple bonds · photolysis

---

Supported, air stable, and reusable hydroformylation catalysts have been prepared by immobilizing dinuclear rhodium(II) complexes bearing *ortho*-metalated arylphosphane ligands on amorphous silica and mesoporous MCM-41 supports by phosphane tethers. The oligosilsesquioxane model complex of the catalytic site **1** has been prepared analogously and characterized by single-crystal X-ray diffraction analysis.



Angew. Chem. **2001**, *113*, 981–984

M. Nowotny,* T. Maschmeyer,*
B. F. G. Johnson, P. Lahuerta,
J. M. Thomas, J. E. Davies 955–958

Heterogeneous Dinuclear Rhodium(II) Hydroformylation Catalysts—Performance Evaluation and Silsesquioxane-Based Chemical Modeling

Keywords: heterogeneous catalysis · hydroformylation · immobilization · mesoporosity · rhodium

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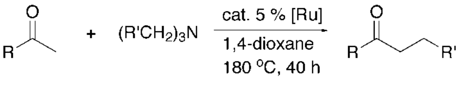
A new reaction: A ruthenium-catalyzed transfer of an alkyl group from a trialkylamine to the α-carbon atom of a ketone leads in good yields to α-alkylated ketones [Eq. (1)]. The reaction is applicable to a wide range of alkyl(alkyl), alkyl(aryl), and cyclic ketones, and in the case of unsymmetrical ketones it takes place regioselectively at the less hindered α-position.



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Angew. Chem. **2001**, *113*, 984–986

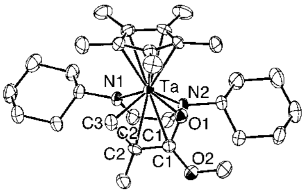
C. S. Cho,* B. T. Kim, M. J. Lee,
T.-J. Kim, S. C. Shim* 958–960

Ruthenium-Catalyzed Regioselective α-Alkylation of Ketones: The First Alkyl-Group Transfer from Trialkylamines to the α-C Atom of Ketones

Keywords: alkylation · amines · homogeneous catalysis · ketones · ruthenium

Activation with $AlMe_3$ at low temperature converts half-metallocene complexes of tantalum with methyl methacrylate (MMA) and diazadiene ligands such as [$Cp^*Ta(\eta^2$-Cy-DAD)(η^4-MMA)] (structure shown) into effective catalysts for the polymerization of MMA. Polymerization is complete after 10 min at -20°C and gives a poly(methyl methacrylate) of narrow polydispersity. $Cp^* = \eta^5$-C_5H_5, Cy-DAD = 1,4-dicyclohexyl-1,4-diaza-1,3-butadiene.

Angew. Chem. **2001**, *113*, 986 – 988



Keywords: diazadienes · homogeneous catalysis · metallocenes · polymerization · tantalum

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

* Author to whom correspondence should be addressed

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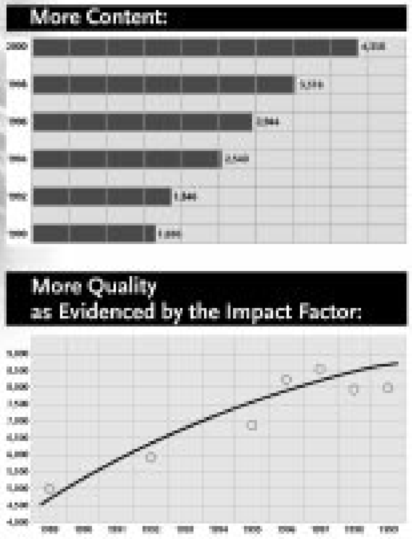
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