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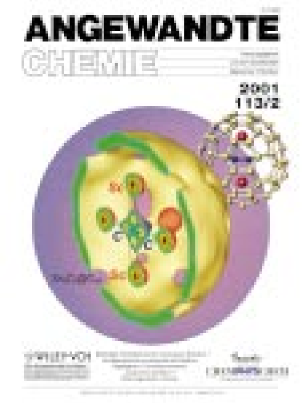
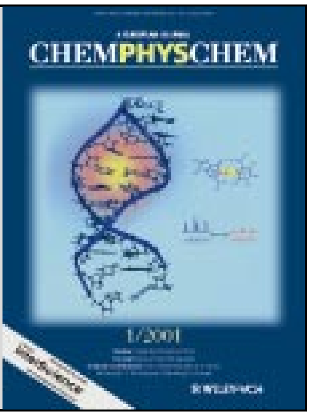
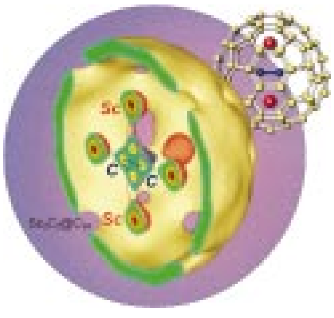


ChemPhysChem* 1/2001 is bound in this issue of *Angewandten Chemie.



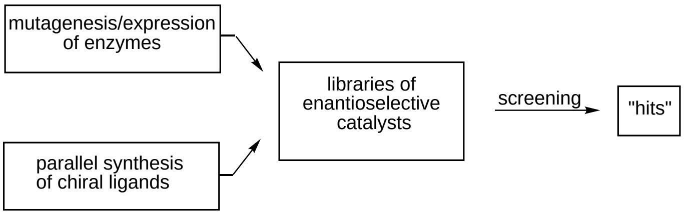
COVER PICTURE

The cover picture shows a section of the electron charge density of the first metal carbide endohedral metallofullerene $(Sc_2C_2)@C_{84}$ obtained from a synchrotron X-ray powder diffraction study by the maximum entropy method (MEM). The several density maxima, which correspond to scandium and carbon atoms, are clearly seen inside the C_{84} carbon cage. The MEM charge density distribution also reveals that the C_{84} cage has D_{2d} symmetry (no. 23) and that the C_2 axis is parallel to the ⟨100⟩ face-centered cubic (fcc) direction of the unit cell. As a consequence of the site symmetry being $4mm$, the C_2 axis of $(Sc_2C_2)@C_{84}$ is oriented to six equivalent ⟨100⟩ directions and shows a merohedral disorder. The resultant $Sc \cdots Sc$ distances and C–C bond lengths of the Sc_2C_2 cluster are 0.429(2) and 0.142(6) nm, respectively. The observed C–C bond length is between that of a typical single and a double bond, and is very close to that of the C–C bond (0.143 nm) combining two pentagons in a C_{60} molecule. More about this fascinating structure can be found in the contribution by Shinohara and co-workers on p. 397 ff.



REVIEWS

The be-all and end-all of both directed evolution of enantioselective enzymes and the combinatorial search for asymmetric homogeneous catalysts is the high-throughput *ee*-screening systems (see scheme). Without them the best evolution or combinatorial technique is useless. Of the various approaches described mass spectrometric and capillary electrophoresis assays appear to be the most promising.



Angew. Chem. **2001**, *113*, 292–320

M. T. Reetz* 284–310

Combinatorial and Evolution-Based Methods in the Creation of Enantioselective Catalysts

Keywords: analytical methods · asymmetric catalysis · combinatorial chemistry · directed evolution · enzyme catalysis · high-throughput screening

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Whereas traditional methods take months the development of valuable catalytic materials with combinatorial methods allows the goal to be reached in days or even a few hours. For the successful implementation of combinatorial methods in catalyst research it is essential that all the components illustrated in the picture are compatible and function smoothly, otherwise bottlenecks develop reducing the overall efficiency of the process.

Angew. Chem. **2001**, *113*, 322–341

S. Senkan* 312–329

Combinatorial Heterogeneous Catalysis—A New Path in an Old Field

Keywords: catalysts · combinatorial chemistry · heterogeneous catalysis · high-throughput screening

ESSAY

Schlenk flask, Schlenk equilibrium, and the Schlenk hydrocarbon are terms familiar to almost every chemist, but who was the man after whom they were all named? Wilhelm Schlenk by the age of 47 was Professor in Berlin, President of the German Chemical Society, and a serious candidate for the Nobel prize, and was known for his innovative experimental techniques and glassware. Within less than a decade he was exiled from Berlin and excluded from research, and his personal history has been largely forgotten. The story of his rise and fall is not only that of a brilliant scientist but also of a man of ethical principles and moral courage.

Angew. Chem. **2001**, *113*, 343–349

T. T. Tidwell* 331–337

Wilhelm Schlenk: The Man Behind the Flask

Keywords: biography · organometallic compounds · radicals

VIPs

The following communications are "Very Important Papers" in the opinion of two referees. They will be published shortly. Short summaries of these articles can be found on the *Angewandte Chemie* homepage at the address http://www.angewandte.com

Synthesis and Structure of a $Ga_{84}R_{20}^{4-}$ Cluster—A link between Metalloid Clusters and Fullerenes?

A. Schnepf, H. Schnöckel*

From Oligomers to Conducting Polymers of the Metal–Dinitrogen Functionality

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

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

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

HIGHLIGHTS

Is the game over or has it just begun? The technical advances related to genomics and proteomics research have provided the scientific community with large sets of sequence-level genetic information with enormous potential for identification of new drug targets. Gene expression and genome-wide gene sequencing have been successfully accomplished. What is the next step? What will be done with this information? Challenges faced are to identify genes or proteins of interest and to determine the functions of a given gene or protein that we only know at the sequence level at the moment.

Angew. Chem. **2001**, *113*, 351–358

P. Arya,* D. T. H. Chou,
M.-G. Baek 339–346

Diversity-Based Organic Synthesis in the Era of Genomics and Proteomics

Keywords: combinatorial chemistry · heterocycles · molecular diversity · natural products · solid-phase synthesis

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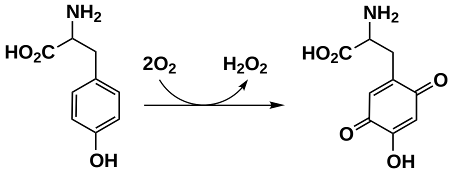
Changing mechanisms: More than half of the known classes of copper oxidase contain a chemically modified amino acid within their active site. Recent experiments by Klinman et al. on the biogenesis of one of these, topaquinone (TPQ; see scheme), have shown that this occurs by a different mechanism from that observed for the aqueous aerobic synthesis of hydroxybenzoquinones in vitro.



TPQ

Angew. Chem. **2001**, *113*, 358–362

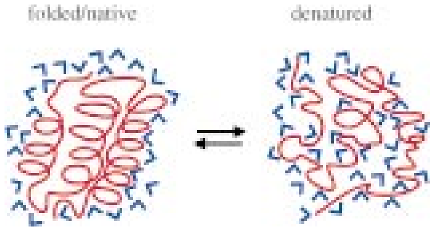
M. A. Halcrow* 346–349

Chemically Modified Amino Acids in Copper Proteins That Bind or Activate Dioxygen

Keywords: amino acids · biosynthesis · copper · enzyme catalysis · radicals

COMMUNICATIONS

Accurate simulation at the atomic level of the folding process of a variety of peptides into different native folds (see picture) can be achieved with a general purpose force field and Newton's equations of motion. The key to understanding this peptide folding lies in the unexpectedly small size of the denatured state and an accurate description thereof.



Angew. Chem. **2001**, *113*, 363–367

W. F. van Gunsteren,* R. Bürgi, C. Peter,
X. Daura 351–355

The Key to Solving the Protein-Folding Problem Lies in an Accurate Description of the Denatured State

Keywords: computer chemistry · molecular dynamics · peptides · protein folding

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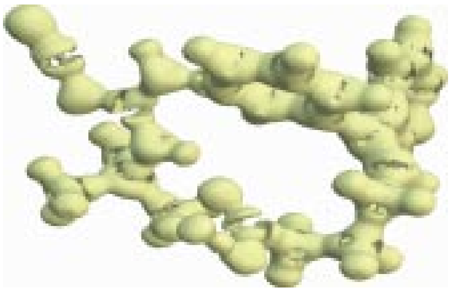
Five instead of 200 days measurement time are sufficient (thanks to area detection rather than conventional scintillation detection) to obtain the accurate charge density distribution of an antithrombotic agent with more than 50 atoms by a high-resolution X-ray diffraction experiment. The preferred sites of intermolecular interactions were identified from various topological properties, such as the reactive surface (zero Laplacian function, see picture) and the electrostatic potential.



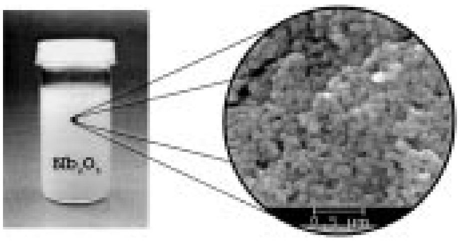
Angew. Chem. **2001**, *113*, 368–371

R. Flaig, T. Koritsánszky, R. Soyka,
L. Häming, P. Luger* 355–359

Electronic Insight into an Antithrombotic Agent by High-Resolution X-Ray Crystallography

Keywords: charge density · drug research · electrostatic interactions · structure–activity relationships · X-ray scattering

Largely monodisperse, crystalline nanoscale oxide particles (for example, Cu_2O, TiO_2, Nb_2O_5) are preparatively accessible with the polyol method (see picture). The colloidal suspensions of the particles thus obtained can be employed readily for the homogeneous coating of various substrates (for example, glass plates, Al_2O_3 powder).



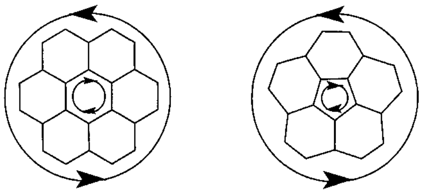
Angew. Chem. **2001**, *113*, 372–374

C. Feldmann,* H.-O. Jungk ... 359–362

Polyol-Mediated Preparation of Nanoscale Oxide Particles

Keywords: colloids • nanostructures • oxides

Explicit ab initio current-density maps contradict the annulene-within-an-annulene model of [*n*]circulenes: in both coronene and corannulene the expected diamagnetic current on the perimeter is opposed by the central, paramagnetic ring current (see schematic representation).



Angew. Chem. **2001**, *113*, 375–379

E. Steiner, P. W. Fowler, L. W. Jenneskens* 362–366

Counter-Rotating Ring Currents in Coronene and Corannulene

Keywords: ab initio calculations • annulenes • magnetic properties • ring currents

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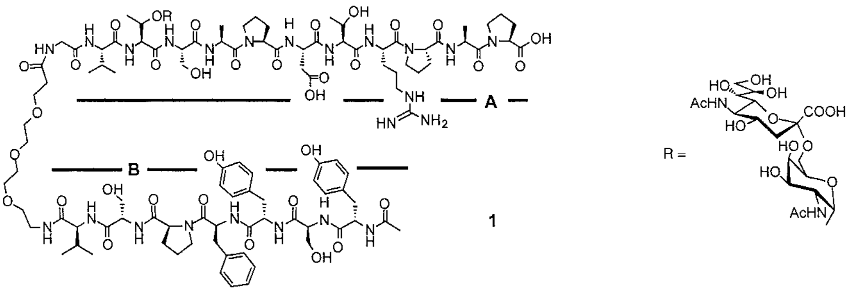
Proliferation of cytotoxic T-cells, a prerequisite for the development of antitumor vaccines, was induced by **1**, but not by its partial structures **A** and **B**. The conjugate **1** containing a tumor-associated Sialyl–T_N–MUC-1 glycopeptide antigen **A** and a T-cell epitope **B** of tetanus toxin was synthesized by fragment condensation on a solid phase.



1

Angew. Chem. **2001**, *113*, 379–382

S. Keil, C. Claus, W. Dippold, H. Kunz* 366–369

Towards the Development of Antitumor Vaccines: A Synthetic Conjugate of a Tumor-Associated MUC1 Glycopeptide Antigen and a Tetanus Toxin Epitope

Keywords: antigens • antitumor agents • glycopeptides • solid-phase synthesis • vaccines

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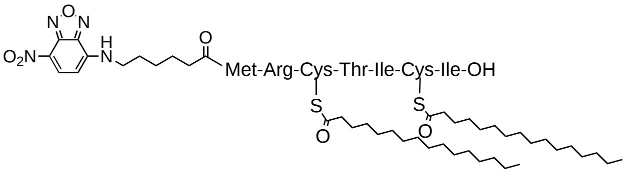
On the trail of the influenza virus! Fluorescent-labeled lipopeptides, such as the characteristic S-palmitoylated partial structure from influenza virus hemagglutinin A (see picture), can be synthesized efficiently by employing a new enzymatic protecting-group technique in the key steps. Their binding to model membranes was determined in a kinetic assay, so leading to a first approximation of the membrane-anchoring ability of the corresponding lipopeptide motif in the parent protein.

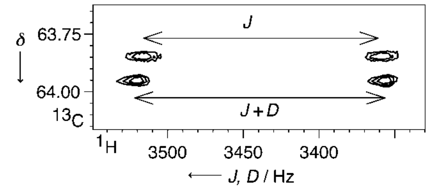


Angew. Chem. **2001**, *113*, 382–386

F. Eisele, J. Kuhlmann, H. Waldmann* 369–373

Synthesis and Membrane-Binding Properties of a Characteristic Lipopeptide from the Membrane-Anchoring Domain of Influenza Virus A Hemagglutinin

Keywords: enzyme catalysis • fluorescence • membranes • peptides • protecting groups



Superimposing the two ^{13}C,^1H correlation maps (see picture) of an unlabeled pentasaccharide acquired in D_2O (upper doublet) and in a magnetically aligned mineral liquid crystal, a colloidal suspension of V_2O_5 (lower doublet), reveals that, in the second case, *D* components appear in addition to the usual splittings *J*. This is a result of the partial alignment of the biomolecule, and provides long-range structural NMR data.

Angew. Chem. **2001**, *113*, 387–389

H. Desvaux,* J.-C. P. Gabriel,*
P. Berthault, F. Camerel 373–376

First Use of a Mineral Liquid Crystal for Measurement of Residual Dipolar Couplings of a Nonlabeled Biomolecule

Keywords: liquid crystals · magnetic properties · NMR spectroscopy · vanadium

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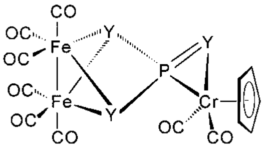
Trithiophosphonato and triselenophosphonato ligands containing mixed Fe/Cr clusters have been synthesized from the reaction of $[Fe_3(CO)_9(\mu_3\text{-}Y)_2]$ (Y = S or Se) with $[CpCr(CO)_2(\eta^3\text{-}P_3]$ in the presence of trimethylamine oxide. This novel approach leads to new clusters containing the first examples of $P(S)S_2$ and $P(Se)Se_2$ ligands in complexed forms (see picture).



Y = S, Se

Angew. Chem. **2001**, *113*, 399–401

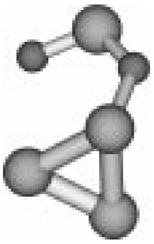
M. Scheer,* S. B. Umbarkar,
S. Chatterjee, R. Trivedi,
P. Mathur* 376–378

Novel Approach to Mixed Group 15/16 Element Ligands—Formation of Unusual Trichalcogenophosphonato Ligands in Mixed Fe/Cr Clusters

Keywords: chalcogens · cluster compounds · coordination chemistry · dinuclear complexes

---

A terra incognita of chemistry is represented by the phosphorus suboxides owing to their high reactivity. The present computational study provides the first insights into this interesting class of compound. The picture shows the most stable isomer of P_4O_2 (the smaller, darker centers denote oxygen atoms)



Angew. Chem. **2001**, *113*, 393–396

B. Engels,* A. R. Soares Valentim,
S. D. Peyerimhoff 378–381

About the Chemistry of Phosphorus Suboxides

Keywords: ab initio calculations · density functional calculations · phosphorus · phosphorus suboxides

---

Solid-supported diazoalkane analogues for the smooth and clean esterifications of carboxylic acids [Eq. (1)] as well as of complex compound mixtures: the alkylating polymers presented here were synthesized as solid-supported 3-alkyl-1-aryltriazenes and are capable of releasing carbenium ions following acidic activation.

Angew. Chem. **2001**, *113*, 390–393

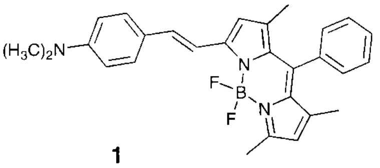
J. Rademann,* J. Smerdka, G. Jung,
P. Grosche, D. Schmid 381–385

Alkylating Polymers: Resin-Released Carbenium Ions as Versatile Reactive Intermediates in Polymer-Assisted Solution-Phase Synthesis

Keywords: alkylation · combinatorial chemistry · diazo compounds · polymeric reagents · solid-phase synthesis

---

The highly fluorescent, unsymmetrically substituted boron–dipyrromethene dye **1** shows emission features that are strongly dependent on the solvent polarity. Thus, **1** can be used for highly sensitive fluorometric probing of solvent polarity and acidity and furthermore can be switched chemically or electrochemically in the near infrared.



1

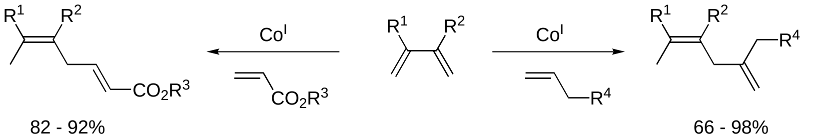
Angew. Chem. **2001**, *113*, 396–399

K. Rurack,* M. Kollmannsberger,
J. Daub* 385–387

Molecular Switching in the Near Infrared (NIR) with a Functionalized Boron–Dipyrromethene Dye

Keywords: donor–acceptor systems · electrochromism · fluorescence · molecular switches · solvatochromism

Not a Diels–Alder reaction but a 1,4-hydrovinylation takes place on treatment of 1,3-dienes with functionalized alkenes in the presence of the catalyst system $[CoBr_2(dppe)]/ZnI_2/Bu_4NBH_4$ (dppe = 1,2-bis(diphenylphosphanyl)ethane). With this reaction the 1,4-dienes with different substituents R^1–R^4 can be obtained in high selectivity and good to excellent yields (see scheme).



Angew. Chem. **2001**, *113*, 408–410

G. Hilt,* F.-X. du Mesnil, S. Lüers 387–389

An Efficient Cobalt(I) Catalyst System for the Selective 1,4-Hydrovinylation of 1,3-Dienes

Keywords: alkenes · cobalt · dienes · hydrovinylation · insertions

---

FlexX and DrugScore are the two computer programs which were applied finally to search for inhibitors of the enzyme carbonic anhydrase II in compound libraries and to predict their binding properties. Subsequently the actual binding affinities of 13 of the best-ranked compounds discovered in this way were measured experimentally. Three of these proved to be subnanomolar, one nanomolar, and seven micromolar inhibitors. The predicted binding mode was confirmed crystallographically for two of the inhibitors.

Angew. Chem. **2001**, *113*, 404–408

S. Grüneberg, B. Wendt, G. Klebe* 389–393

Subnanomolar Inhibitors from Computer Screening: A Model Study Using Human Carbonic Anhydrase II

Keywords: carbonic anhydrase · computer chemistry · drug research · molecular modeling · protein–ligand complexes

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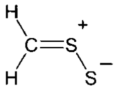
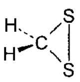
Matrix isolation spectroscopy allows the direct identification of ylide **1** and its cyclic isomer **2**. They were obtained by pyrolysis of 1,2,4-trithiolane under high vacuum; the cyclic compound forms from **1** by thermal ring closure in a kinetically controlled reaction.



1



2

Angew. Chem. **2001**, *113*, 401–404

G. Mlostoń, J. Romański, H. P. Reisenauer, G. Maier* .. 393–396

Thioformaldehyde *S*-sulfide (Thiosulfine)

Keywords: ab initio calculations · heterocycles · matrix isolation · photochemistry · sulfur · ylides

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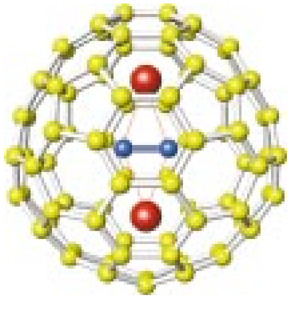
Not $Sc_2@C_{86}$ but $Sc_2C_2@C_{84}$: that is the conclusion of ^{13}C NMR spectroscopic and synchrotron X-ray powder diffraction studies on a new metallofullerene obtained by arc discharge of Sc_2O_3/graphite rods. The picture shows a schematic representation of the deduced structure, in which the novel scandium carbide cluster Sc_2C_2 is encaged in D_{2d}-C_{84}.



Angew. Chem. **2001**, *113*, 411–413

C.-R. Wang, T. Kai, T. Tomiyama, T. Yoshida, Y. Kobayashi, E. Nishibori, M. Takata, M. Sakata, H. Shinohara* 397–399

A Scandium Carbide Endohedral Metallofullerene: $(Sc_2C_2)@C_{84}$

Keywords: carbides · cluster compounds · fullerenes · scandium · structure elucidation

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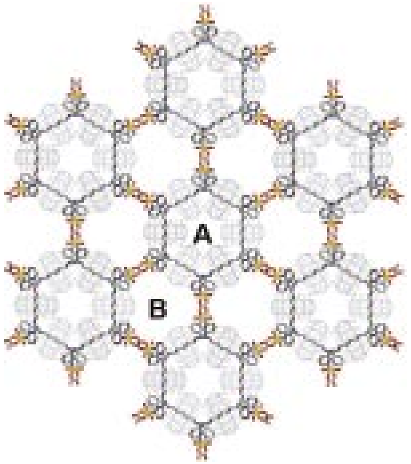
A seven-membered molecular necklace composed of six copper ions and six pseudorotaxane units behaves as a secondary building block in the formation of a two-dimensional polyrotaxane network with large voids (see picture). This novel metal–organic framework allows size-selective anion exchange as well as the exchange of coordinated ligands. Thus a new synthetic strategy has been identified for modular porous solids which utilizes large, rigid, interlocked supermolecules as primary or secondary building blocks.



Angew. Chem. **2001**, *113*, 413–416

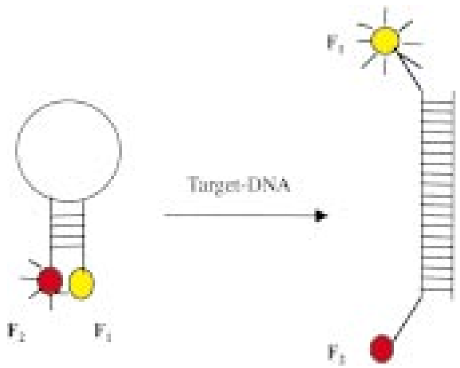
E. Lee, J. Kim, J. Heo, D. Whang, K. Kim* 399–402

A Two-Dimensional Polyrotaxane with Large Cavities and Channels: A Novel Approach to Metal–Organic Open-Frameworks by Using Supramolecular Building Blocks

Keywords: coordination chemistry · copper · rotaxanes · solid-state structures · supramolecular chemistry

1433-7851/01/4002-0272 $ 17.50+.50/0

Fluorescence resonance energy transfer between two fluorophores (F_1 and F_2) attached to the two ends of a molecular beacon DNA probe containing a hairpin structure can be used for quantitative DNA/RNA studies (see scheme). Concentrations of target-DNA as low as 1.7×10^{-10} M could be determined with a commercial spectrometer by using coumarin and 6-carboxyfluorescein as the fluorophores. Measurements on the Förster energy transfer distance for the donor/acceptor pair can also be carried out using these DNA probes.



Angew. Chem. **2001**, *113*, 416–419

P. Zhang, T. Beck, W. Tan* ... 402–405

Design of a Molecular Beacon DNA Probe with Two Fluorophores

Keywords: DNA recognition • donor–acceptor systems • energy transfer • fluorescence spectroscopy

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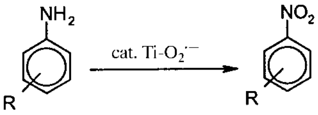
A matrix-bound superoxide radical anion, generated by treating $Ti(OR)_4$ (R = *i*Pr, *n*Bu) with H_2O_2, is a selective heterogeneous catalyst for the oxidation of anilines to the corresponding nitroarenes with 50 % aqueous H_2O_2 [Eq. (1)]. Yields of 82–98 % are obtained, even with anilines bearing electron-withdrawing substituents (R = NO_2, COOH).



(1)

Angew. Chem. **2001**, *113*, 419–422

G. K. Dewkar, M. D. Nikalje,
I. Sayyed Ali, A. S. Paraskar,
H. S. Jagtap, A. Sudalai* 405–408

An Exceptionally Stable Ti Superoxide Radical Ion: A Novel Heterogeneous Catalyst for the Direct Conversion of Aromatic Primary Amines to Nitro Compounds

Keywords: heterogeneous catalysis • nitro compounds • oxidation • radical ions • titanium

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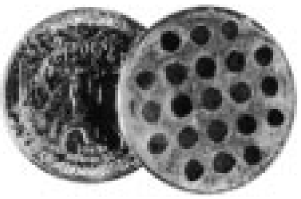
Twenty-one zeolite films were grown on a 2.5 cm alumina disk using a multiwell reactor (see picture). This parallel synthesis from clear organic-free solutions offers an interesting approach to the preparation of catalytic libraries. The morphologies of the films produced were found to be similar to those synthesized under conventional conditions but their X-ray diffraction patterns indicated a lower degree of orientation of crystallites.



Angew. Chem. **2001**, *113*, 422–425

R. Lai, B. S. Kang,
G. R. Gavalas* 408–411

Parallel Synthesis of ZSM-5 Zeolite Films from Clear Organic-Free Solutions

Keywords: combinatorial chemistry • microreactors • zeolite films • zeolites

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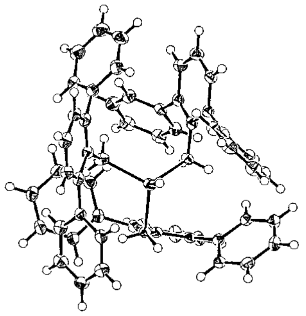
Unique selectivity, hitherto not observable in ordinary radical and ionic reactions, is achieved with the bowl-shaped tris(2,6-diphenylbenzyl)tin hydride (TDTH; see structure), which has been successfully utilized as a new reducing agent.



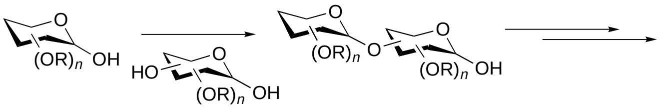
Angew. Chem. **2001**, *113*, 425–428

K. Sasaki, Y. Kondo,
K. Maruoka* 411–414

Bowl-Shaped Tris(2,6-diphenylbenzyl)tin Hydride: A Unique Reducing Agent for Radical and Ionic Chemistry

Keywords: cyclization • radical reactions • reduction • tin

The inherent difference in nucleophilicity between alkyl alcohols and free hemiacetals is capitalized upon in a new approach to chemoselective glycosylation. The strategy employs a controlled dehydrative coupling reaction for the rapid assembly of complex oligosaccharides and obviates the need for the extensive protective group and anomeric leaving group differentiation that is traditionally required (see scheme).



Angew. Chem. **2001**, *113*, 428–431

H. M. Nguyen, J. L. Poole,
D. Y. Gin* 414–417

Chemoselective Iterative Dehydrative Glycosylation

Keywords: carbohydrates · chemoselectivity · dehydrations · glycosylations · oligosaccharides

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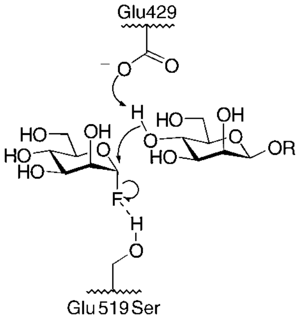
Engineering enzymes: The glutamic acid nucleophile of a retaining β-mannosidase has been replaced with a serine residue to form a β-mannosynthase. When the new enzyme is provided with an α-mannosyl fluoride donor and an appropriate acceptor, β-mannoside linkages are synthesized (see scheme). Remarkably, α-mannosyl fluoride can be generated in situ by providing the mannosynthase with excess fluoride ion.



Angew. Chem. **2001**, *113*, 431–434

O. Nashiru, D. L. Zechel, D. Stoll,
T. Mohammadzadeh, R. A. J. Warren,
S. G. Withers* 417–420

β-Mannosynthase: Synthesis of β-Mannosides with a Mutant β-Mannosidase

Keywords: enzyme catalysis · fluorides · glycosidases · glycosylations · mutagenesis

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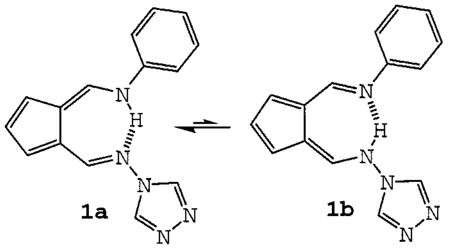
An unusually substantial coupling is observed across the hydrogen bond of fully ^{15}N-labeled compound **1** when it is studied by ^{1}H and ^{15}N NMR spectroscopy. The structure was determined by X-ray diffraction and shown to correspond to tautomer **1a** (both in the solid state and in solution). These results open up a new field of hydrogen-bond research by NMR spectroscopic methods.



Angew. Chem. **2001**, *113*, 434–437

R. M. Claramunt,* D. Sanz,
S. H. Alarcón, M. Pérez Torralba,
J. Elguero, C. Foces-Foces, M. Pietrzak,
U. Langer, H.-H. Limbach 420–423

6-Aminofulvene-1-aldimine: A Model Molecule for the Study of Intramolecular Hydrogen Bonds

Keywords: diimines · hydrogen bonds · isotopic labeling · NMR spectroscopy · tautomerism

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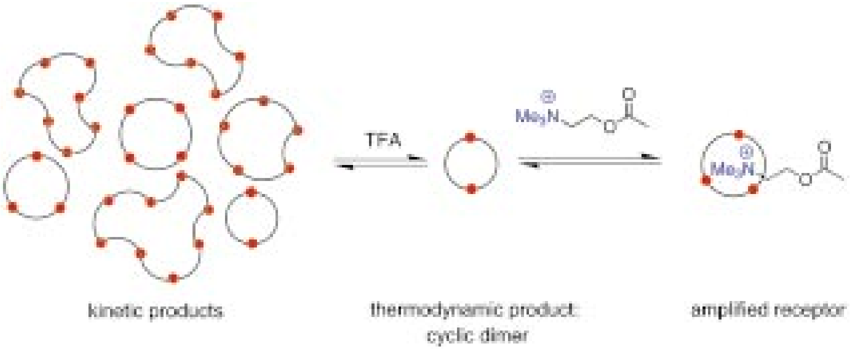
A cyclic pseudo-peptide receptor for acetylcholine has been amplified and isolated from a dynamic combinatorial library by virtue of templated stabilization under thermodynamic control (see scheme, TFA = trifluoroacetic acid). This is a demonstration of significant molecular amplification in dynamic systems to evolve a novel receptor.



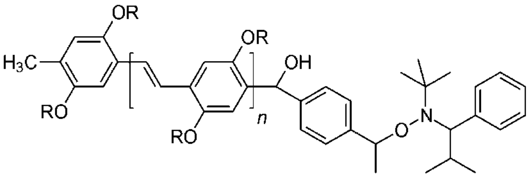
Angew. Chem. **2001**, *113*, 437–442

G. R. L. Cousins, R. L. E. Furlan,
Y.-F. Ng, J. E. Redman,
J. K. M. Sanders* 423–428

Identification and Isolation of a Receptor for *N*-Methyl Alkylammonium Salts: Molecular Amplification in a Pseudopeptide Dynamic Combinatorial Library

Keywords: combinatorial chemistry · hydrazones · molecular evolution · molecular recognition · peptides · receptors

Controlled synthesis of rod–coil block copolymers is possible with a new macroinitiator for “living” nitroxide-mediated radical polymerization (NMRP). The synthesis of the new macroinitiator which contains a rodlike, conjugated poly(*p*-phenylene vinylene) block (see picture) is described. Electron microscopy imaging indicates microphase separation of the resulting block copolymer when cast from chloroform.



Angew. Chem. **2001**, *113*, 442–444

U. Stalmach, B. de Boer, A. D. Post,
P. F. van Hutten,
G. Hadziioannou* 428–430

Synthesis of a Conjugated Macromolecular Initiator for Nitroxide-Mediated Free Radical Polymerization

Keywords: block copolymers · conjugation · polymerization · polymers · radical reactions

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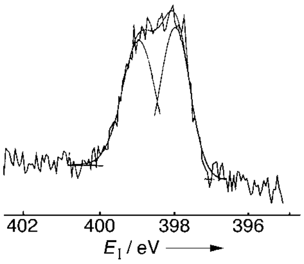
It is ironic that although it is typically a technique that “sees” all elements other than hydrogen atoms, X-ray photoelectron spectroscopy (XPS) acts as a sensitive probe of low-barrier hydrogen bonds, as seen in a study of free-base tetrapyrroles. The nitrogen 1s XPS peaks never quite coalesce, even when the N···H···N hydrogen bonds are almost perfectly symmetrical, as is the case for dibenzo[*cde,mno*]porphycenes (see picture).



Angew. Chem. **2001**, *113*, 445–448

A. Ghosh,* J. Moulder, M. Bröring,
E. Vogel 431–434

X-Ray Photoelectron Spectroscopy of Porphycenes: Charge Asymmetry Across Low-Barrier Hydrogen Bonds

Keywords: bond theory · hydrogen bonds · ionization potentials · photoelectron spectroscopy · porphyrinoids

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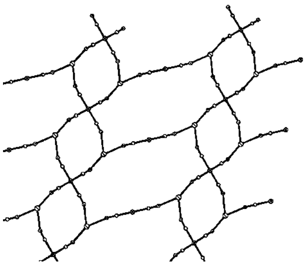
Rings of 24 atoms form part of the two-dimensional structure of the novel compounds $[NdM(bpym)(H_2O)_4(CN)_6]\cdot 3H_2O$ (M = Fe (**1**), Co (**2**); bpym = 2,2′-bipyrimidine). These compounds are the first two-dimensional cyano-bridged species containing lanthanide and transition metal centers (see picture). The structures and magnetic properties are investigated.



Angew. Chem. **2001**, *113*, 448–451

B.-Q. Ma, S. Gao,* G. Su,
G.-X. Xu 434–437

Cyano-Bridged 4f–3d Coordination Polymers with a Unique Two-Dimensional Topological Architecture and Unusual Magnetic Behavior

Keywords: cyanides · lanthanides · magnetic properties · metal–metal interactions

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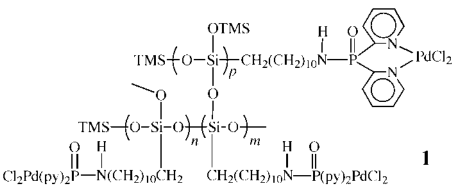
Supported catalysts with controllable solubility were obtained by partial hydrolysis and derivatization of $(MeO)_3Si(CH_2)_{11}N_3$. The soluble Pd complex **1** thus obtained undergoes further hydrolysis to give an insoluble supported complex. Both materials are effective catalysts for the cyclotrimerization of alkynes. Hence, this methodology allows the soluble analogue of a heterogeneous catalyst to be studied by high-resolution solution NMR spectroscopy. TMS = $SiMe_3$, py = 2-pyridyl.



1

Angew. Chem. **2001**, *113*, 451–454

Y.-S. Fu, S. J. Yu* 437–440

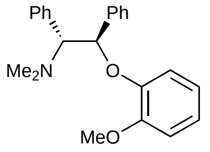
Immobilization of Homogeneous Palladium(II) Complex Catalysts on Novel Polysiloxanes with Controllable Solubility: Important Implications for the Study of Heterogeneous Catalysis on Silica Surfaces

Keywords: cyclization · heterogeneous catalysis · homogeneous catalysis · immobilization · palladium

1433-7851/01/4002-0275 $ 17.50+.50/0

A chiral ligand, a catalytic amount of lithium cation, and no chiral proton source: These are features of the present asymmetric addition–protonation of propenoates with 2-trimethylsilylbenzenethiol. The reaction is catalyzed by a combination of lithium 2-trimethylsilylbenzenethiolate and the chiral ligand **1**. Desulfurization of the product affords 2-substituted propanoates with high *ee* values and without racemization. Furthermore, **1** can be recovered quantitatively for reuse.

Angew. Chem. **2001**, *113*, 454–456



1

K. Nishimura, M. Ono, Y. Nagaoka,
K. Tomioka* 440–442

Catalytic Enantioselective Protonation of Lithium Ester Enolates Generated by Conjugate Addition of Arylthiolate to Enoates

Keywords: asymmetric catalysis · chirality · desulfurization · lithium · protonation

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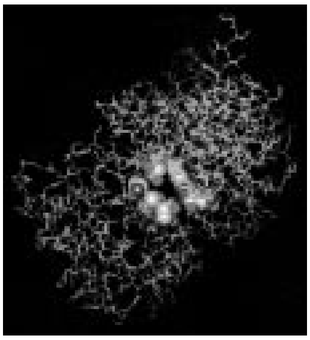
An enzyme-based bio-nanoreactor: By acting as a mineralization template, lumazine synthase, a 60-subunit enzyme complex which has a hollow porous shell, can fabricate nanocrystalline iron oxide. Fe ions can permeate the capsid through hydrophilic funnel-shaped channels lined with glutamic acid residues (see picture) and become encapsulated in the cavity as Fe^{III} oxide. The capsid increases in size from 15 to 30 nm in diameter through formation of a higher order structure as the concentration of Fe^{III} increases.

Angew. Chem. **2001**, *113*, 456–459



W. Shenton, S. Mann,* H. Cölfen,
A. Bacher,* M. Fischer 442–445

Synthesis of Nanophase Iron Oxide in Lumazine Synthase Capsids

Keywords: bioinorganic chemistry · enzymes · ion channels · iron · materials science

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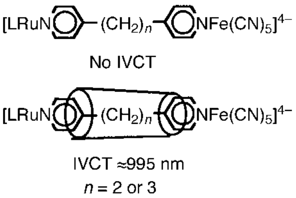
Fe^{II} to Ru^{III} electron transfer is initiated by the inclusion of saturated bridging ligands into the β-cyclodextrin (CD) cavity of [2]rotaxane complexes and is observed as an intervalence charge transfer (IVCT) band in the electronic spectra (see picture). The rotaxanes are synthesized by using Ru^{III} and Fe^{II} complexes as stoppers, β-CD as the cyclic molecular head, and 4,4′-bipyridine derivatives with interrupted π-electron system as the bridging ligand between the metal centers.

Angew. Chem. **2001**, *113*, 460–462



A. D. Shukla, H. C. Bajaj,
A. Das* 446–448

β-Cyclodextrin-Assisted Intervalence Charge Transfer in Mixed-Valent [2]Rotaxane Complexes Having Metal Centers Linked by an Interrupted π-Electron System

Keywords: cyclodextrins · inclusion compounds · metal–metal interactions · mixed-valent compounds · rotaxanes

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Spontaneous decomposition of $[In(\eta^5\text{-}C_5H_5)]$ in the presence of poly(vinyl pyrrolidone) or trioctylphosphane oxide (TOPO) as a stabilizer gave monodisperse indium nanoparticles with a mean diameter of about 5–6 nm. In the case of TOPO, self-organization of the nanoparticles in two- and three-dimensional superlattices is observed (see picture).

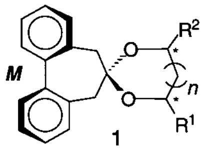
Angew. Chem. **2001**, *113*, 462–465

K. Soulantica, A. Maisonnat,
M.-C. Fromen, M.-J. Casanove,
P. Lecante, B. Chaudret* 448–451

Synthesis and Self-Assembly of Monodisperse Indium Nanoparticles Prepared from the Organometallic Precursor $[In(\eta^5\text{-}C_5H_5)]$

Keywords: colloids · indium · monolayers · nanostructures · self-organization

A quick, simple, and reliable method to assign the absolute configuration of 1,2- and 1,3-diols: all that is needed is to measure the CD sign of the A band (250 nm) of their biphenyldioxolanes **1** ($n = 0,1$). The chirality of the diol induces a preferred sense of twist in the biphenyl moiety (*R*,*R* → *M* and *S*,*S* → *P*), and a positive A band (a probe of *M* twist) reveals an *R* or *R*,*R* configuration of the diol.



1

positive A band → *M* twist → *R*,*R* diol

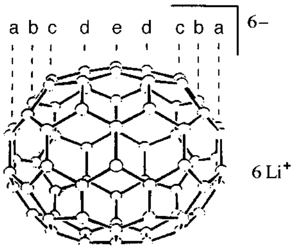
S. Superchi, D. Casarini, A. Laurita, A. Bavoso, C. Rosini* .... 451 – 454

Induction of a Preferred Twist in a Biphenyl Core by Stereogenic Centers: A Novel Approach to the Absolute Configuration of 1,2- and 1,3-Diols

Keywords: atropisomerism • biaryls • circular dichroism • configuration determination • diols

Angew. Chem. **2001**, *113*, 465 – 468

The full NMR assignment by the INADEQUATE method clarifies the reduced aromaticity of the C_{70}^{6-} ion (see picture; a – e indicate the five different carbon environments) relative to the neutral system, as well as the charge delocalization pattern. The reduction process was carried out with lithium in the presence of corannulene, which acts as an “electron shuttle”.



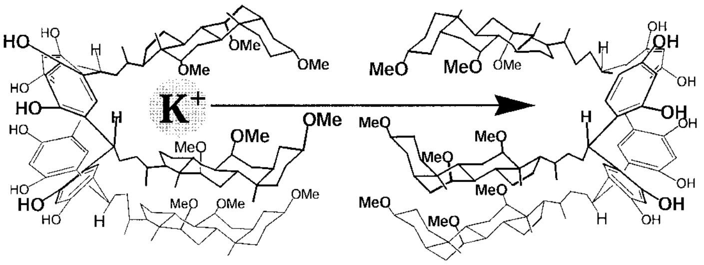
T. Sternfeld, R. E. Hoffman, I. Aprahamian, M. Rabinovitz* .... 455 – 457

Fullerene Anions: Unusual Charge Distribution in C_{70}^{6-}

Keywords: aromaticity • fullerenes • NMR spectroscopy • reduction

Angew. Chem. **2001**, *113*, 469 – 471

Tail-to-tail assembly of two molecules of a resorcin[4]arene resulted in a bilayer membrane with an intramembrane ion channel (see schematic diagram). The steroidal tails introduced here have the advantages of giving a long-lived open state of the pore (2.5 – 4.5 s, as opposed to tens of milliseconds for alkyl tails) and of allowing the hydrophilic pore to be modified without changing the overall structural features.



N. Yoshino, A. Satake, Y. Kobuke* .... 457 – 459

An Artificial Ion Channel Formed by a Macrocyclic Resorcin[4]arene with Amphiphilic Cholic Acid Ether Groups

Keywords: ion channels • macrocycles • potassium • supramolecular chemistry

Angew. Chem. **2001**, *113*, 471 – 473

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

* Author to whom correspondence should be addressed

BOOKS

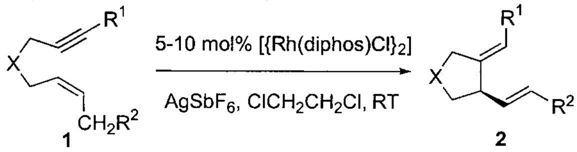
WEB SITES

CORRIGENDA

In the Communication by **J. K. Kochi et al.** in Issue 20 (2000), pp. 3671–3674 we neglected to point out the first experimental (X-ray crystallographic) evidence for C–C hyperconjugation in a rigid adamantyl cation (T. Laube, *Angew. Chem.* **1986**, *98*, 368; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 349 as well as T. Laube, E. Schaller, *Acta. Crystallogr. Sect. B* **1995**, *51*, 177). The authors thank Dr. Thomas Laube for pointing out this oversight.

In the Communication by **X. Zhang et al.** in Issue 22 (2000), pp. 4104–4106, there was a methylene group missing in the structural formula on the left of Scheme 1 as well as in the equation in Table 2 and in the Table of Contents. We would like to apologize for this error. Table 2 is given here in its correct form.

Table 2. Rhodium-catalyzed enantioselective cycloisomerization of 1,6-enynes.[a]



Entry	Substrate	X	R^1	R^2	Ligand	Cat. loading [mol %]	Time [h]	Yield [%]	*ee* [%] (config.)[b]
1	**1a**	O	Ph	H	(*R*,*R*)-Me-DuPhos	5	2	62	96 (−)
2					(*R*,*R*,*R*,*R*)-BICP	5	2	73	74 (−)
3					(*R*,*R*,*R*,*R*)-BICPO	10	1.5	81	65 (+)
4	**1b**	O	C_6H_4(*p*-Me)	H	(*R*,*R*)-Me-DuPhos	10	4	38	77 (−)
5					(*R*,*R*,*R*,*R*)-BICP	10	7	58	87 (−)
6	**1c**	O	C_6H_4(*p*-Cl)	H	(*R*,*R*)-Me-DuPhos	5	2	60	95 (−)
7					(*R*,*R*,*R*,*R*)-BICP	10	0.25	24	83 (−)
8	**1e**	O	C_6H_4(*m*-Cl)	H	(*R*,*R*)-Me-DuPhos	10	0.5	68	93 (−)
9					(*R*,*R*,*R*,*R*)-BICP	10	7	39	79 (−)
10	**1f**	O	C_6H_4(*p*-CF_3)	H	(*R*,*R*)-Me-DuPhos	5	1	60	96 (−)
11					(*R*,*R*,*R*,*R*)-BICP	10	7	47	91 (−)
12	**1g**	O	cyclopentyl	H	(*R*,*R*)-Me-DuPhos	10	12	–	–
13					(*R*,*R*,*R*,*R*)-BICP[c]	5	2	43	95 (−)
14	**1h**	O	C_4H_9	H	(*R*,*R*)-Me-DuPhos	10	12	–	–
15					(*R*,*R*,*R*,*R*)-BICP	5	1	67	98 (−)
16	**1i**	$PhSO_2N$	Me	H	(*R*,*R*,*R*,*R*)-BICPO	3	13	98	82 (−)
17	**1j**	$PhSO_2N$	Et	H	(*R*,*R*,*R*,*R*)-BICPO	3	13	99	80 (−)
18	**1k**	$PhSO_2N$	Me	Me	(*R*,*R*,*R*,*R*)-BICPO	3	13	99	69 (−)

[a] All reactions were carried out in $ClCH_2CH_2Cl$ at room temperature with 0.2 mmol substrate at 0.1M concentration. [{Rh(diphos)Cl}$_2$]/$AgSbF_6$ = 1/1 (diphos = 1,2-bis(diphenylphosphanyl)ethane). $AgSbF_6$ was added to the solution of [{Rh(diphos)Cl}$_2$] after the substrate had been added. [b] The *ee* was determined by GC on a Supelco *β*-390 chiral column and by HPLC. [c] $AgPF_6$ was used.

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