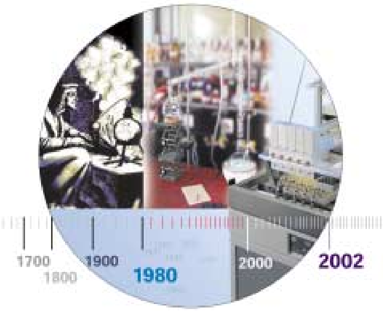
ANGEWANDTE
CHEMIE
A Journal of the
Gesellschaft
Deutscher Chemiker
INTERNATIONAL EDITION
2002
41/21
Pages 3927–4154

COVER PICTURE

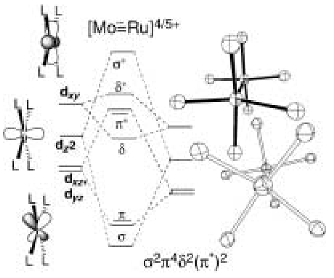
The cover picture shows the progress made in the development of separation techniques over the centuries. The retort and the distillation apparatus symbolize the repertoire of purification methods, which expanded only slightly from the foundations of chemistry to the 1980s. The automated synthesizer symbolizes the increasing demand for the automation of multiparallel techniques, which require simple work-up protocols. Thus, a large variety of specialized separation techniques has been developed. Today the spectrum contains, in addition to classical aqueous work-up, the use of ionic, perfluorinated, or supercritical liquids as well as the application of polymer- and dendrimer-supported separation strategies. An overview of the recent developments and applications of modern separation methods can be found in the Review by W. Bannwarth, R. Haag, et al. on p. 3964 ff.



REVIEWS

Contents

More bonds than metals: The "abnormally" high energies of heterodinuclear bonds in hydrogen halides lead to the concept of electronegativity. Multiple bonds between different transition-metal atoms have not yet given rise to a basic chemical concept but they possess the potential to help elucidate the fundamental properties of interactions between d elements. The picture shows the MO diagram of metal–metal bonding in the Mo–Ru core. Unique to bimetallic complexes of transition metals, the MoRu^{5+} core, when stabilized by porphyrin ligands, exists in the solid state as an equimolar mixture of an eclipsed and a staggered conformer.



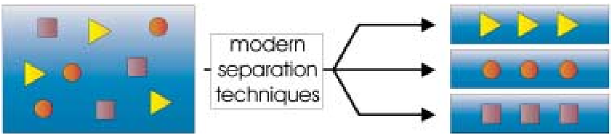
Angew. Chem. **2002**, *114*, 4120–4134

J. P. Collman,*
R. Boulatov 3948–3962

Heterodinuclear Transition-Metal Complexes with Multiple Metal–Metal Bonds

Keywords: bond theory · cluster compounds · electronic structure · metal–metal interactions · transition metals

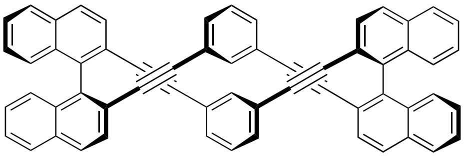
There is no one best method! Rather the best separation strategy for an organic synthesis must be determined on a case by case basis. Herein the advantages and disadvantages of the current important processes—including the application of ionic liquids, supercritical solvents, fluorous systems, and polymer-protected precursors—in regard to their parallelization and automation are described and compared.



Angew. Chem. **2002**, *114*, 4136–4173

Keywords: biphasic catalysis · combinatorial chemistry · parallel synthesis · polymeric supports · separation techniques

HIGHLIGHTS



A bumper crop of “polyunsaturated” cyclophanes has recently been harvested as a result of methodological advances, which have once again fertilized the field of cyclophane chemistry. Features of these designed molecules include structural novelty, strain and its consequences, unusual electronic effects, exploitable physical properties, and stereochemistry. Otera’s “enantiopure double-helical alkynyl cyclophanes” (example shown in picture) are perhaps the pick of the crop.

Angew. Chem. **2002**, *114*, 4175–4178

Keywords: alkynes · arenes · cross-coupling · cyclophanes · strained molecules

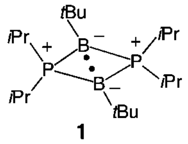
VIPs

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.org

Pd^{II}-Catalyzed Cyclization of Alkynes with Aldehydes, Ketones, or Nitriles Initiated by the Acetoxypalladation of Alkynes	L. Zhao, X. Lu*	◆
Isoprenoid Biosynthesis through the Methylerythritol Phosphate Pathway: The (*E*)-4-Hydroxy-3-methylbut-2-enyl Diphosphate Synthase (GcpE) is a [4Fe–4S] Protein	M. Seemann, B. T. S. Bui, M. Wolff, D. Tritsch, N. Campos, A. Boronat, A. Marquet, M. Rohmer*	◆
Experimental Observation and Confirmation of Icosahedral $W@Au_{12}$ and $Mo@Au_{12}$ Molecules	X. Li, B. Kiran, J. Li, H.-J. Zhai, L.-S. Wang*	
Tuning the Regioselectivity in the Palladium(II)-Catalyzed Isomerization of Alkylidenecyclopropyl Ketones: A Dramatic Salt Effect	S. Ma*, J. Zhang	

1433-7851/02/4121-3930 $ 20.00+.50/0

Make or break: Stable biradicaloid main group element compounds could provide deep insight into fundamental processes of bond making and bond breaking. Whereas for a long time such compounds were only known as highly reactive intermediates or postulated as transition states, recently through the isolation of the stable crystalline 1,3-diphospha-2,4-diborabicyclo[1.1.0]butane (**1**) a decisive step has been taken towards achieving a better understanding of the steps involved in making and breaking bonds.



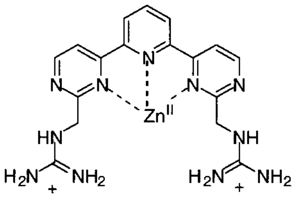
1

Angew. Chem. **2002**, *114*, 4178 – 4184

Keywords: biradicals · bond stretch isomers · main group elements · phosphorus · radicals

COMMUNICATIONS

Cooperation is the key! Multifunctional catalysis with cooperativity approaching that found for enzymes is reported in the hydrolysis of RNA using a synthetic catalyst that includes one zinc atom and two guanidinium groups (see picture).

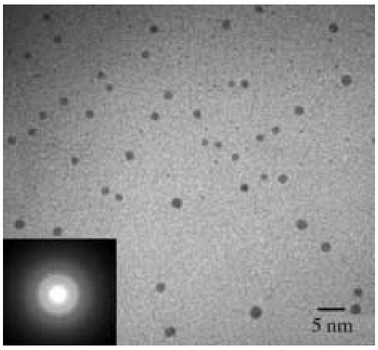


Angew. Chem. **2002**, *114*, 4185 – 4188

Keywords: bioinorganic chemistry · enzyme catalysis · hydrolysis · RNA · zinc

---

Graphite nanoparticles, with diameters as small as 2 nm (see picture) can be fabricated by the carbonization of polypyrrole nanoparticles of similar dimensions, which have been prepared by a low-temperature polymerization technique in which a micellar microemulsion acts as a “nanoreactor”. The graphite nanoparticles exhibit excellent transparent conductive performance in a polycarbonate medium, and may be envisaged as a substitute for carbon nanotubes.



Angew. Chem. **2002**, *114*, 4188 – 4191

Keywords: conducting materials · graphite · micelles · nanostructures · polymers

---

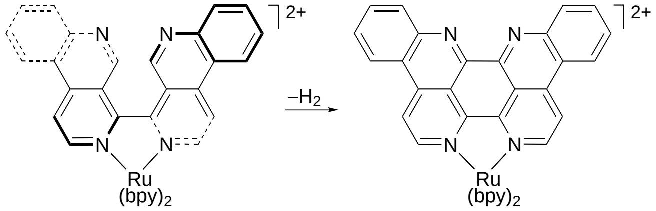
Nanoporous shell or sphere-in-sphere structures have been constructed by consecutive alternating adsorption of polyelectrolytes and SiO_2 on melamine formaldehyde particles, followed by removal of the cores with HCl and SiO_2 with HF. The shells have been distinguished by confocal laser scanning microscopy imaging (see picture) by partially labeling the inner shell with fluorescein (yellow emission) and the outer sphere with rhodamine B (red emission).

Angew. Chem. **2002**, *114*, 4191 – 4194

Keywords: capsules · nanostructures · permeability · polyelectrolytes · self-assembly

1433-7851/02/4121-3931 $ 20.00+.50/0

The fabrication of Ru^{II}–polypyridyl complexes with “large-surface” ligands can be achieved by utilizing metal coordination to facilitate a dehydrogenation reaction (see scheme). This modular methodology efficiently yields biologically active eilatin-containing complexes, as well as Ru^{II} complexes of previously unknown ligands.



Angew. Chem. **2002**, *114*, 4194–4198

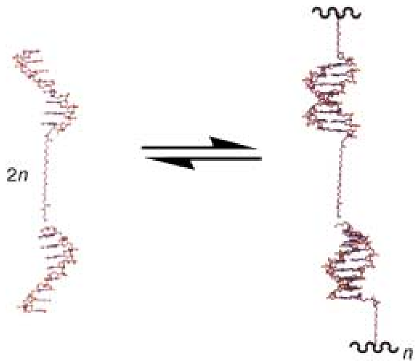
E. C. Glazer, Y. Tor* 4022–4026

Ru^{II} Complexes of “Large-Surface” Ligands

Keywords: bridging ligands · dehydrogenation · ligand design · N ligands · ruthenium

---

Fundamental studies of reversible polymerizations can be achieved with intrinsically modular oligonucleotide-based monomers (OMs) comprised of oligonucleotide sequences that are covalently linked directly or through a synthetic spacer. The thermodynamics and kinetics of association are determined by the variable OM base system. The number of reversible interactions and the conformational flexibility along the polymer backbone are dependent on the spacer.



Angew. Chem. **2002**, *114*, 4198–4200

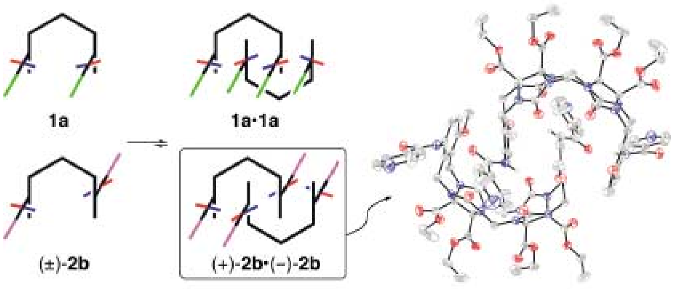
E. A. Fogleman, W. C. Yount, J. Xu, S. L. Craig* 4026–4028

Modular, Well-Behaved Reversible Polymers from DNA-Based Monomers

Keywords: DNA structures · polymers · self-assembly · supramolecular chemistry

---

Clip Art: Achiral (**1a**) and chiral ((±)-**2b**) molecular clips undergo diastereoselective H-bond-mediated self-assembly, both in solution and the solid state, to yield homodimer **1a**·**1a** and the heterochiral aggregate (+)-**2b**·(−)-**2b**. Mixtures of the achiral and chiral clips do not yield heterodimers, but rather undergo an efficient self-sorting process.



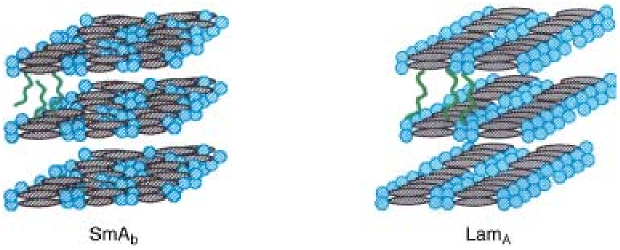
Angew. Chem. **2002**, *114*, 4200–4203

A. Wu, A. Chakraborty, J. C. Fettinger, R. A. Flowers II,* L. Isaacs* 4028–4031

Molecular Clips that Undergo Heterochiral Aggregation and Self-Sorting

Keywords: chirality · hydrogen bonds · pi interactions · self-assembly

Competition between microsegregation and rigidity in bolaamphiphilic biphenyl derivatives bearing lateral semiperfluorinated alkyl chains leads to the formation of novel smectic liquid-crystalline phases, designated SmA$_b$ and Lam$_A$, in which the rigid rodlike segments are organized parallel to the planes of the layers.



Angew. Chem. **2002**, *114*, 4203 – 4207

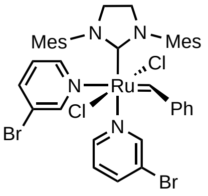
X. H. Cheng, M. K. Das, S. Diele,
C. Tschierske* .... 4031 – 4035

Novel Liquid-Crystalline Phases with Layerlike Organization

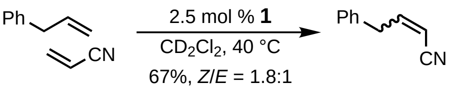
Keywords: amphiphiles · hydrogen bonds · liquid crystals · mesophases · microsegregation

---

The highest initiation rate of any reported ruthenium-based catalyst was found for the new olefin-metathesis catalyst [(H$_2$IMes)(3-Br-py)$_2$(Cl)$_2$Ru=CHPh] (**1**), which was synthesized in one step from commercially available reagents. Complex **1** is highly efficient for the cross metathesis of acrylonitrile, which is generally a poor substrate for metathesis reactions (e.g., see scheme). Mes = 2,4,6-trimethylphenyl.



1



Angew. Chem. **2002**, *114*, 4207 – 4209

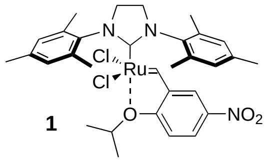
J. A. Love, J. P. Morgan, T. M. Trnka,
R. H. Grubbs* .... 4035 – 4037

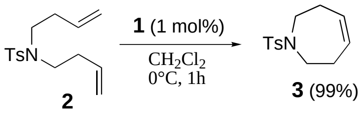
A Practical and Highly Active Ruthenium-Based Catalyst that Effects the Cross Metathesis of Acrylonitrile

Keywords: homogeneous catalysis · metathesis · N ligands · ruthenium

---

A simple three-step synthesis leads to the formation of the active complex **1**, which operates under very mild conditions (even at 0 °C!) and can be successfully applied in various types of olefin metathesis (ring-closing metathesis, cross metathesis, enyne metathesis), for example, in the cyclization of **2** to form **3**.





Angew. Chem. **2002**, *114*, 4210 – 4212

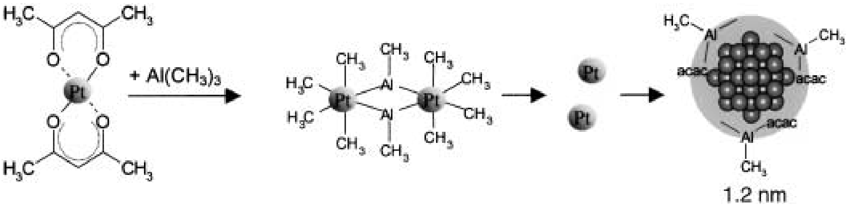
K. Grela,* S. Harutyunyan,
A. Michrowska .... 4038 – 4040

A Highly Efficient Ruthenium Catalyst for Metathesis Reactions

Keywords: alkenes · homogeneous catalysis · metathesis · ruthenium

---

An organometallic compound is the key intermediate during the formation of colloidal Pt particles from [Pt(acac)$_2$] and Al(CH$_3$)$_3$. Additional studies confirm the formation of stable Pt colloids with an average diameter of 1.2 nm, which are stabilized by organoaluminum components (see scheme). Without the stabilizer a Pt nanopowder with a particle size of 1.4 nm is isolated.



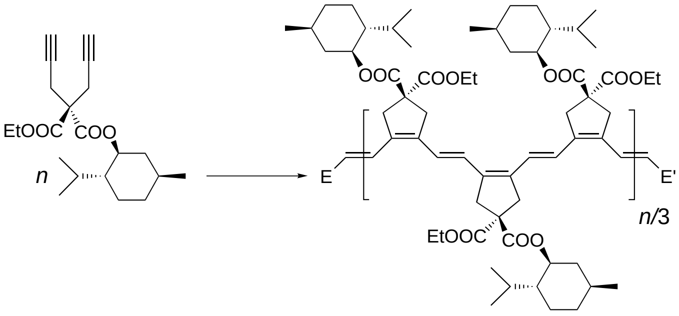
Angew. Chem. **2002**, *114*, 4213 – 4216

K. Angermund, M. Bühl, E. Dinjus,
U. Endruschat, F. Gassner,
H.-G. Haubold, J. Hormes, G. Köhl,
F. T. Mauschick, H. Modrow, R. Mörtel,
R. Mynott,* B. Tesche, T. Vad,
N. Waldöfner,
H. Bönnemann* .... 4041 – 4044

Nanoscopic Pt Colloids in the "Embryonic State"

Keywords: colloids · nanostructures · nucleation · platinum

Taking the sting out of controlling rings: Highly regular, alternating *cis-trans*-polyenes solely containing five-membered rings have been prepared by living alkyne cyclopolymerization of 1,6-heptadiynes using fine-tuned Schrock initiators (see scheme). The resulting polyenes possess interesting physical properties that are different from those of existing poly(heptadiyne) systems.



Angew. Chem. **2002**, *114*, 4226–4230

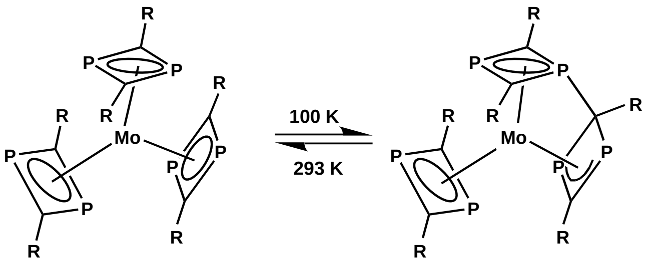
U. Anders, O. Nuyken,*
M. R. Buchmeiser,*
K. Wurst 4044–4047

Stereoselective Cyclopolymerization of 1,6-Heptadiynes: Access to Alternating *cis-trans*-1,2-(Cyclopent-1-enylene)vinylenes by Fine-Tuning of Molybdenum Imidoalkylidenes

Keywords: alkynes • carbene ligands • metathesis • molybdenum • polymerizations

---

Bicycles made in crystals: The phosphorus atoms of the π ligand 1,3-diphosphete turn out to be ambiphilic centers with pronounced intramolecular reactivity. This property results in a temperature-dependent bond formation in [(2,4-di-*t*Bu-1,3-diphosphete)$_3$Mo], which is found to be a topotactic reaction in the single crystal (see scheme). This new reactivity principle can be used to explain a series of complex interligand bond-formation reactions of phosphorus heterocycles.



Angew. Chem. **2002**, *114*, 4221–4226

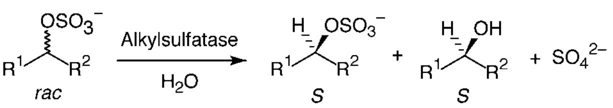
C. Topf, T. Clark,* F. W. Heinemann,
M. Hennemann, S. Kummer, H. Pritzkow,
U. Zenneck* 4047–4052

Ambiphilicity: A Characteristic Reactivity Principle of π-Bound Phosphorus Heterocycles

Keywords: DFT calculations • molybdenum • P ligands • phosphorus heterocycles • pi interactions • solid-state reactions

---

The biocatalytic hydrolysis of (±)-*sec*-alkyl sulfate esters with an alkylsulfatase from *Rhodococcus ruber* DSM 44541 proceeded with high enantioselectivity (up to 99% *ee*) and with absolute stereoselectivity through inversion of configuration. Thus, a *rac* substrate was converted into homochiral *S*-configured products (see scheme).



Angew. Chem. **2002**, *114*, 4230–4231

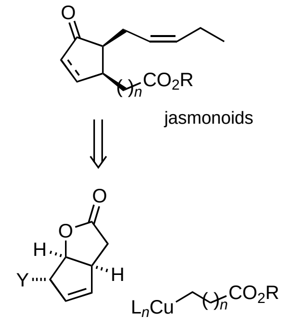
M. Pogorevc, W. Kroutil, S. R. Wallner,
K. Faber* 4052–4054

Enantioselective Stereoinversion in the Kinetic Resolution of *rac-sec*-Alkyl Sulfate Esters by Hydrolysis with an Alkylsulfatase from *Rhodococcus ruber* DSM 44541 Furnishes Homochiral Products

Keywords: alkylsulfatase • biotransformations • configuration inversion • hydrolysis • sulfate ester

---

An important class of phytohormones are jasmonoids. A variety of jasmonoids in the natural *cis* configuration are now accessible by a general strategy. Key building blocks are enantiomerically pure lactones of type **A** with a leaving group Y which can be prepared by a catalytic asymmetric synthesis. Reaction with zinc cyanocuprates affords products with the requisite *cis* configuration that can be transformed into the target compounds in a few steps.



A

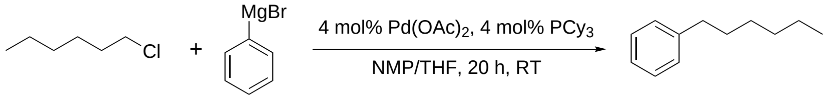
Angew. Chem. **2002**, *114*, 4231–4234

M. Ernst, G. Helmchen* 4054–4056

A New Synthesis Route to Enantiomerically Pure Jasmonoids

Keywords: asymmetric catalysis • asymmetric synthesis • copper • jasmonoids • natural products

Chloroalkanes refined: A simple catalyst system renders the palladium-catalyzed coupling reaction of functionalized alkyl chlorides and Grignard reagents at room temperature (see example in scheme; PCy$_3$ = tricyclohexylphosphane, NMP = *N*-methylpyrrolidinone).



Angew. Chem. **2002**, *114*, 4218–4221

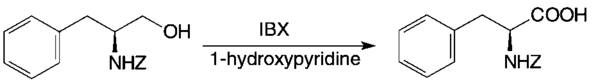
A. C. Frisch, N. Shaikh, A. Zapf,
M. Beller* 4056–4059

Palladium-Catalyzed Coupling of Alkyl Chlorides and Grignard Reagents

Keywords: alkyl halides • cross-coupling • Grignard reaction • Kumada coupling • palladium

---

Under mild conditions and without the use of toxic metals, the oxidation of primary alcohols and aldehydes to the corresponding carboxylic acids with 1-hydroxy-1,2-benziodoxole-3(1*H*)-one-1-oxide (IBX) proceeds in the presence of 1-hydroxypyridine or *N*-hydroxysuccinimide (see scheme). The reaction tolerates a wide variety of functional groups.



Angew. Chem. **2002**, *114*, 4216–4218

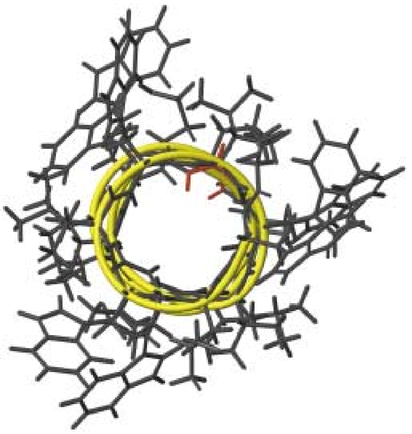
R. Mazitschek, M. Mülbaier,
A. Giannis* 4059–4061

IBX-Mediated Oxidation of Primary Alcohols and Aldehydes To Form Carboxylic Acids

Keywords: alcohols • aldehydes • carboxylic acids • IBX • oxidation

---

Variable ion channels: A 22mer peptide derived from the D,L-peptide gramicidin A changes from an inactive to a highly ion-channel-active conformation (see picture). The helical structure of the active and inactive conformations was characterized by NMR spectroscopy and circular dichroism; conductance measurements led to the conclusion that there are two symmetrical binding sites for the Cs atom in the active form.



Angew. Chem. **2002**, *114*, 4234–4238

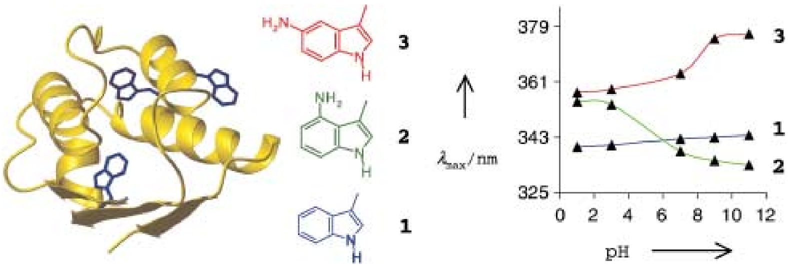
H.-D. Arndt, D. Bockelmann, A. Knoll,
S. Lamberth, C. Griesinger,*
U. Koert* 4062–4065

Cation Control in Functional Helical Programming: Structures of a D,L-Peptide Ion Channel

Keywords: circular dichroism • conformational analysis • ion channels • NMR spectroscopy • peptides

---

Functional protein design: Replacement of the tryptophan indole moiety in proteins with aminoindoles converts pH-insensitive into pH-sensitive fluorescent proteins (see picture). Such global substitution of residues in target proteins by noncanonical amino acids with defined spectral properties offers a unique approach for the design of protein-based molecular sensors.



Angew. Chem. **2002**, *114*, 4238–4242

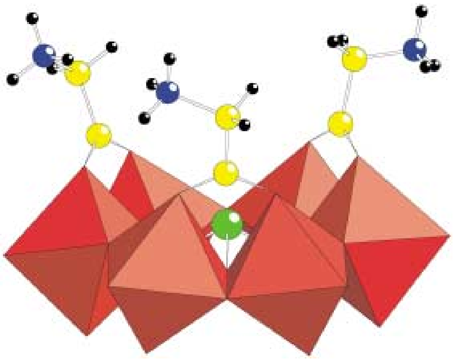
N. Budisa,* M. Rubini, J. H. Bae,
E. Weyher, W. Wenger, R. Golbik,
R. Huber, L. Moroder 4066–4069

Global Replacement of Tryptophan with Aminotryptophans Generates Non-Invasive Protein-Based Optical pH Sensors

Keywords: amino acids • biosensors • gene expression • protein engineering • tryptophan

1433-7851/02/4121-3935 $ 20.00+.50/0

Taming the uncontrollable: The novel heteropolymolybdates, such as the $[Se^{IV}Mo_6O_{21}(O_2CCH_2NH_3)_3]^{2-}$ ion shown, functionalized by amino acids, can be derivatized at two different positions in a controlled manner. In addition, further functionalization of the clusters through the amino groups is possible, thus the 18 new compounds are ideal candidates for pharmaceutical applications.



Angew. Chem. **2002**, *114*, 4246 – 4249

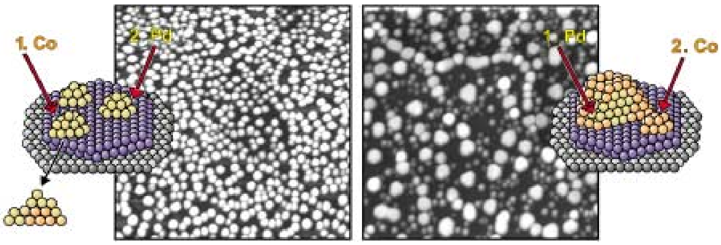
U. Kortz,* M. G. Savelieff, F. Y. A. Ghali,
L. M. Khalil, S. A. Maalouf,
D. I. Sinno .... 4070 – 4073

Heteropolymolybdates of As^{III}, Sb^{III}, Bi^{III}, Se^{IV}, and Te^{IV} Functionalized by Amino Acids

Keywords: amino acids · chirality · cluster compounds · molybdenum · polyoxometalates · structure elucidation

---

Building catalyst models for complex catalytic systems is still a challenging task. In the case of supported bimetallic catalysts, such models can be obtained by taking advantage of nucleation and growth processes during the metal vapor deposition of two metals onto a suitable support (see picture). In this way, the origin of the sometimes surprisingly large changes observed in the adsorption and reaction properties of these systems in comparison to the pure metals can be studied in detail.



Angew. Chem. **2002**, *114*, 4242 – 4245

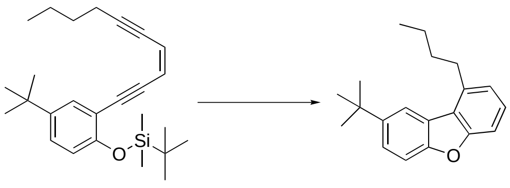
M. Heemeier, A. F. Carlsson,
M. Naschitzki, M. Schmal, M. Bäumer,*
H.-J. Freund .... 4073 – 4076

Preparation and Characterization of a Model Bimetallic Catalyst: Co – Pd Nanoparticles Supported on Al_2O_3

Keywords: adsorption · bimetallic particles · desorption · heterogeneous catalysis · scanning probe microscopy

---

An anionic cycloaromatization reaction provides an efficient method for the synthesis of the dibenzofurans **2** by treatment of the *tert*-butyldimethylsilyl ethers **1** with sodium methoxide or potassium carbonate in methanol at reflux for 16 h, and gives 50 – 94 % yields of **2**.



1 **2**

Angew. Chem. **2002**, *114*, 4251 – 4253

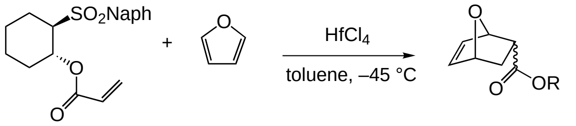
M.-J. Wu,* C.-Y. Lee,
C.-F. Lin .... 4077 – 4079

A Route to 5-Substituted Dibenzofurans by Anionic Cycloaromatization of 2-(6-Substituted 3-Hexene-1,5-diynyl)phenyl *tert*-Butyldimethyl Ethers and Related Molecules

Keywords: cyclization · enediyne · fused-ring systems · heterocycles

---

High yields and high *endo* selectivity of the cycloadducts formed from the Diels – Alder reaction of furan or substituted furans occurs with an $HfCl_4$ catalyst (see scheme). The use of the catalyst allows reactions to be performed at low temperature under kinetic control, as shown for the highly diastereoselective Diels – Alder reaction of a chiral acrylate.



83%, *endo*/*exo* = 68/32, *endo* 87% *de*, *exo* 91% *de*

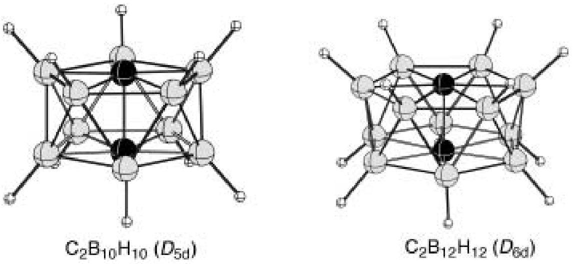
Angew. Chem. **2002**, *114*, 4253 – 4256

Y. Hayashi,* M. Nakamura, S. Nakao,
T. Inoue, M. Shoji .... 4079 – 4082

The $HfCl_4$-Mediated Diels – Alder Reaction of Furan

Keywords: asymmetric synthesis · cycloaddition · furanes · hafnium · pericyclic reaction

Wheel-shaped molecules, exemplified by $C_2B_{10}H_{10}$ (D_{5d}) and $C_2B_{12}H_{12}$ (D_{6d}) (see picture), are predicted by DFT computations to be stable minima. The "axles" of these "wheels" are comprised of conjoined, nearly planar, penta- or hexacoordinate carbon atoms, or their isoelectronic B^-, Al^-, Si, and Ge counterparts.



Angew. Chem. **2002**, *114*, 4256–4259

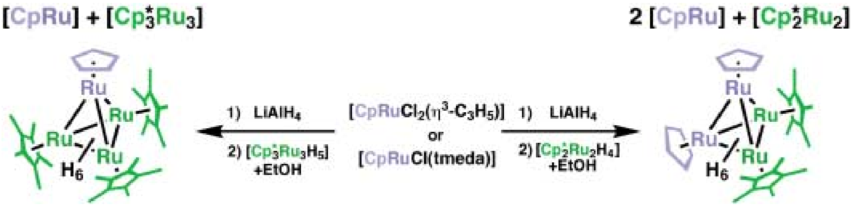
Z.-X. Wang,
P. von R. Schleyer* 4082–4085

Planar Hypercoordinate Carbons Joined: Wheel-Shaped Molecules with C–C Axles

Keywords: boranes · density functional calculations · hypercoordinate carbon · nanostructures

---

A series of tetranuclear ruthenium hexahydride clusters containing several different combinations of Cp (C_5H_5) and Cp* (C_5Me_5) ligands, was systematically synthesized from the reaction of [$CpRuCl_2(\eta^3\text{-}C_3H_5)$] or [CpRuCl(tmeda)] (tmeda = tetramethylethylenediamine) with $LiAlH_4$ followed by treatment with trinuclear, dinuclear, or mononuclear Cp*Ru complexes in the presence of ethanol.



Angew. Chem. **2002**, *114*, 4259–4261

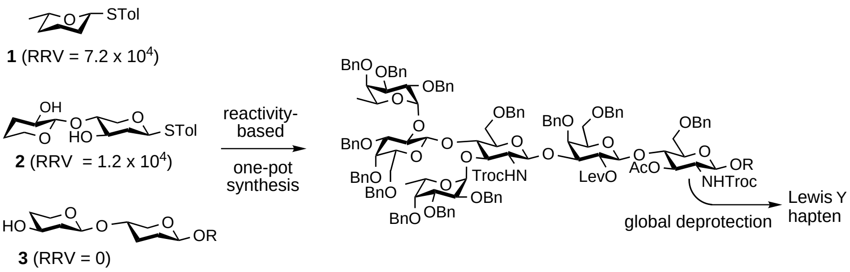
Y. Ohki, N. Uehara,
H. Suzuki* 4085–4087

Rational Synthesis of Tetranuclear Ruthenium Polyhydride Clusters and Their Mixed-Ligand Analogues

Keywords: cyclopentadienyl ligands · hydride ligands · ruthenium · structure elucidation · tetranuclear complexes

---

The stereospecific synthesis of a tumor-related carbohydrate antigenic hapten, Lewis Y, from three basic building units **1**–**3** has been achieved by a reactivity-based one-pot strategy. RRV = relative reactivity value.



Angew. Chem. **2002**, *114*, 4261–4264

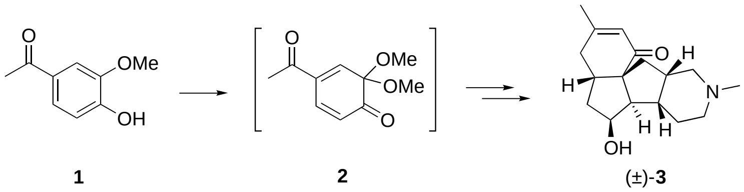
K.-K. T. Mong, C.-H. Wong* 4087–4090

Reactivity-Based One-Pot Synthesis of a Lewis Y Carbohydrate Hapten: A Colon–Rectal Cancer Antigen Determinant

Keywords: antigens · antitumor agents · glycosylation · oligosaccharides · reactivity-based synthesis

---

The power of the masked *o*-benzoquinone Diels–Alder protocol is shown in a total synthesis of magellanine ((±)-**3**). The highly compact molecular architecture of **3** was constructed from acetovanillone (**1**) via a masked *o*-benzoquinone **2** in an overall yield of 12% over 16 steps (or 9% over 14 steps).



Angew. Chem. **2002**, *114*, 4264–4267

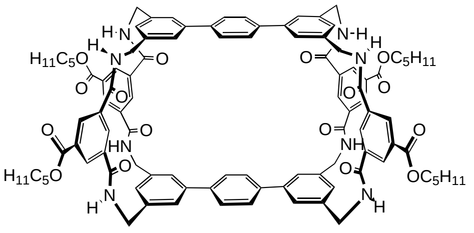
C.-F. Yen, C.-C. Liao* 4090–4093

Concise and Efficient Total Synthesis of *Lycopodium* Alkaloid Magellanine

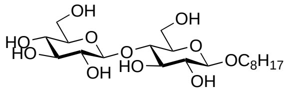
Keywords: cycloaddition · natural products · rearrangement · total synthesis

1433-7851/02/4121-3937 $ 20.00+.50/0

Selective oligosaccharide recognition remains a challenge for supramolecular chemistry. Tricyclic receptor **1** was designed to bind the all-equatorial β-cellobiosyl unit in **2**. Remarkably, it succeeds while showing no detectable affinity for five other mono- and disaccharide substrates.



1



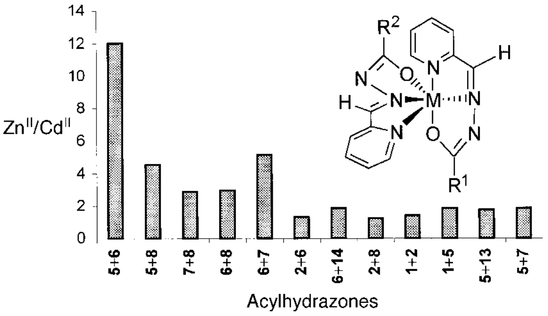
2

Angew. Chem. **2002**, *114*, 4267 – 4270

Keywords: carbohydrates · molecular recognition · oligosaccharides · stereoselectivity · supramolecular chemistry

---

The dynamic nature of metal – ligand interactions facilitates the formation of metal ion acylhydrazone complex libraries. From these libraries, metal ion complexes with two different types of ligands (**1** – **14**; $R^1 \neq R^2$) are shown to have superior extraction properties. Mixed – ligand combinations enhance the selectivity of extraction of Zn^{II} over Cd^{II} (see figure).

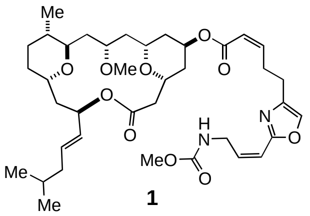


Angew. Chem. **2002**, *114*, 4270 – 4272

Keywords: cadmium · combinatorial chemistry · coordination modes · N ligands · separation processes · zinc

---

A compound that could never be isolated again despite intensive efforts after it was first found in the sponge *Leucascandra caveolata* in 1996 is leucascandrolide A (**1**). An enantioselective, convergent total synthesis of this polyoxygenated marine macrolide proceeds in 23 steps and 2 % overall yield. The strategy relies on the application of modern asymmetric reactions for enantio- and diastereoselective transformations.

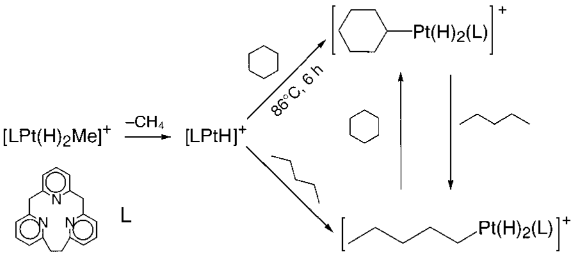


1

Angew. Chem. **2002**, *114*, 4272 – 4275

Keywords: aldol reaction · alkynes · asymmetric synthesis · natural products · total synthesis

Reversible alkane oxidative addition occurs to transient $[LPtH]^+$ (L = [2.1.1]-(2,6)-pyridinophane; see scheme), which is generated at 86 °C from $[LPtMe(H)_2]^+$ in 1:1 hydrocarbon/CD_2Cl_2 mixtures. DFT calculations reveal why $[LPtMe(H)_2]^+$ eliminates methane, not dihydrogen, and why, in contrast to $[LPtMe_2H]^+$, no alkane dehydrogenation occurs.



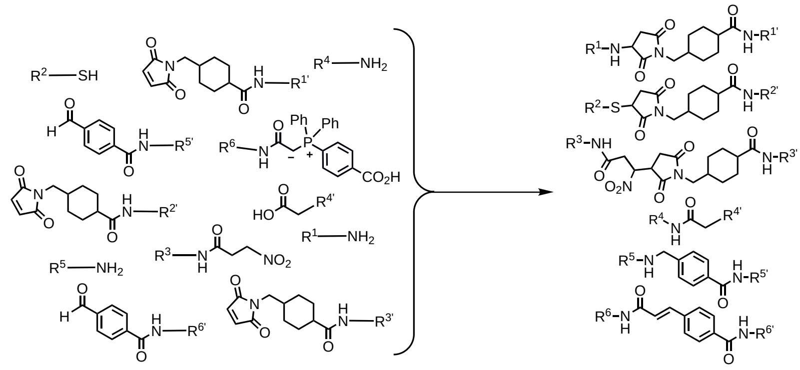
Angew. Chem. **2002**, *114*, 4276–4278

A. N. Vedernikov,*
K. G. Caulton* 4102–4104

Control of H–C(sp^3) Bond Cleavage Stoichiometry: Clean Reversible Alkyl Ligand Exchange with Alkane in $[LPt(Alk)(H)_2]^+$ (L = [2.1.1]-(2,6)-Pyridinophane)

Keywords: alkanes · C-H activation · hydride ligands · platinum · structure-activity relationships

Diversification without spatial separation can be achieved using DNA-templated synthesis. Twelve reactants with functional groups of similar reactivity linked to different DNA sequences (R, R′) were subjected to several different reaction types within the same solution and only six sequence-programmed products out of the more than 28 possibilities were formed (see scheme).



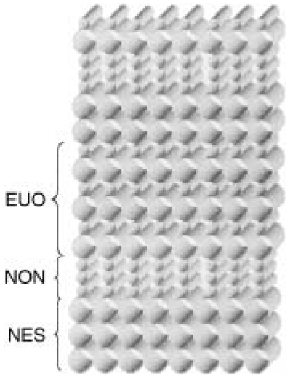
Angew. Chem. **2002**, *114*, 4278–4282

C. T. Calderone, J. W. Puckett,
Z. J. Gartner, D. R. Liu* 4104–4108

Directing Otherwise Incompatible Reactions in a Single Solution by Using DNA-Templated Organic Synthesis

Keywords: combinatorial chemistry · diversification · oligonucleotides · synthetic methods · template synthesis

An intergrowth of three structurally related zeolites with the NON, EUO, and NES framework topologies forms the basis of a structural model for ERS-10 zeolite. The picture shows a roll stacking model of ERS-10; large cylinders: 10-ring channels, small cylinders: 6-ring channels.



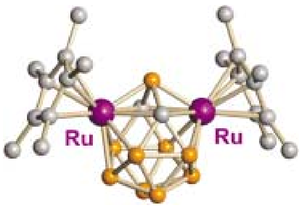
Angew. Chem. **2002**, *114*, 4283–4286

S. Zanardi,* G. Cruciani, L. C. Carluccio,
G. Bellussi, C. Perego,
R. Millini* 4109–4112

Framework Topology of ERS-10 Zeolite

Keywords: structure elucidation · X-ray diffraction · zeolites

Polyhedral expansion of stable 12-vertex *closo*-ruthenacarborane $[(\eta\text{-}C_5Me_5)Ru(C_2B_9H_{11})]^-$ by direct insertion of $[(\eta\text{-}C_5R_5)Ru]^+$ fragments takes place under very mild conditions (−78 °C). The resulting 13-vertex diruthenacarboranes (see picture) are very stable although they have two electrons less than required by Wade's rules.



Angew. Chem. **2002**, *114*, 4286–4288

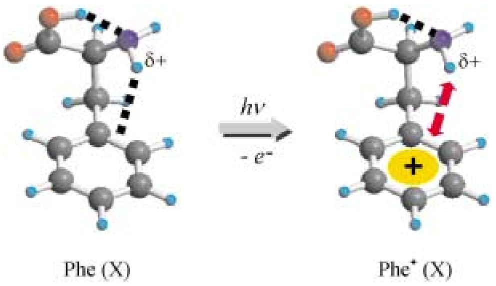
A. R. Kudinov,* D. S. Perekalin,
S. S. Rynin, K. A. Lyssenko,
G. V. Grintselev-Knyazev,
P. V. Petrovskii 4112–4114

Direct Electrophilic Insertion into a Twelve-Vertex Metallacarborane

Keywords: boron · cluster compounds · metallacarboranes · ruthenium

As much as 8 kcal mol^{-1} separates the ionization energies of the lowest energy conformers of L-phenylalanine. This conformation-dependent energy difference, by far the largest reported to date for any molecule, is associated with the drastic change in hydrogen bonding upon ionization (see picture).

Angew. Chem. **2002**, *114*, 4288–4291



K. T. Lee, J. Sung, K. J. Lee, Y. D. Park, S. K. Kim* 4114–4117

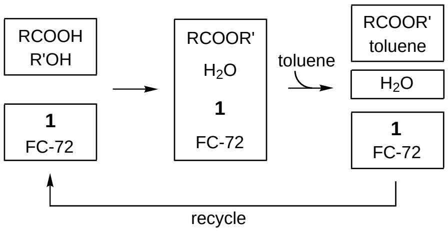
Conformation-Dependent Ionization Energies of L-Phenylalanine

Keywords: amino acids · conformation analysis · hydrogen bonds · ionization potentials

---

A perfectly selective esterification that discriminates between primary and sterically hindered or aromatic carboxylic acids occurs in the presence of the fluoroalkyldistannoxane $[\{\mathrm{Cl(C_6F_{13}CH_2CH_2)_2SnOSn(CH_2CH_2}$-$\mathrm{C_6F_{13})_2Cl}\}_2]$ (**1**). The reaction gives 100 % yield with a strict 1:1 ratio of the carboxylic acid and alcohol reactants, and the catalyst can be recycled without any loss of activity.

Angew. Chem. **2002**, *114*, 4291–4293



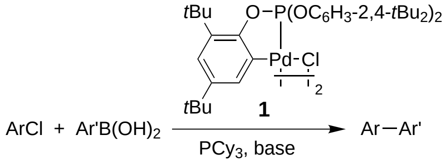
J. Xiang, A. Orita, J. Otera* 4117–4119

Fluorous Biphasic Esterification Directed towards Ultimate Atom Efficiency

Keywords: alcohols · biphasic catalysis · carboxylic acids · esters · tin

---

The most active catalyst yet reported for the Suzuki coupling of activated aryl chlorides, even for electronically deactivated substrates, is generated by addition of tricyclohexylphosphane to the otherwise inactive orthopalladated complex **1** [Eq. (1); for example, $\mathrm{Ar} = \mathrm{C_6H_4}$-4-OMe, $\mathrm{Ar'} = \mathrm{Ph}$].



(1)

Angew. Chem. **2002**, *114*, 4294–4296

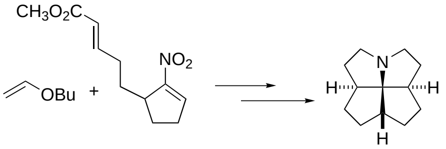
R. B. Bedford,* C. S. J. Cazin, S. L. Hazelwood (néeWelch) 4120–4122

Simple Mixed Tricyclohexylphosphane–Triarylphosphite Complexes as Extremely High-Activity Catalysts for the Suzuki Coupling of Aryl Chlorides

Keywords: C–C coupling · homogeneous catalysis · palladium · Suzuki reaction

---

To provide an opportunity for X-ray analysis of an unsubstituted fenestrane, one of the ring-fusion carbon atoms was replaced with a nitrogen atom to facilitate salt formation; the key strategic step to the first 1-azafenestrane (see scheme) involves the tandem [4+2]/[3+2] cycloaddition of a nitrocyclopentene with butyl vinyl ether. The adduct with borane provided crystals suitable for X-ray analysis, which revealed the planar deformation of the central carbon atom to be modest (116.1 and 116.6°).



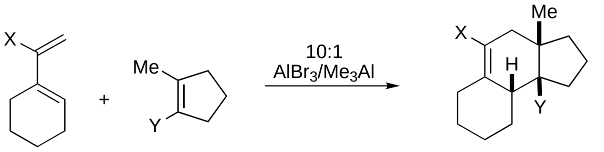
Angew. Chem. **2002**, *114*, 4296–4299

S. E. Denmark,* L. A. Kramps, J. I. Montgomery 4122–4125

Synthesis of *cis,cis,cis,cis*-[5.5.5.5]-1-Azafenestrane

Keywords: anti-van't Hoff/Le Bel compounds · cycloaddition · fenestrane · nitroalkene · polycycles

The right mix! A 10:1 mixture of $AlBr_3$ and $AlMe_3$ promotes the Diels–Alder reaction of hindered dienophiles. For example, the Diels–Alder reaction of an acetyldiene with a *tert*-butyldimethylsilyl (TBS) enol ether gave mainly the *exo* cycloadduct in 77% yield [Eq. (1); X = COMe, Y = OTBS]. Oxidation, hydrolysis, reduction, and desilylation of this cycloadduct afforded a BCD ring analogue of ouabain.



(1)

Angew. Chem. **2002**, *114*, 4299–4302

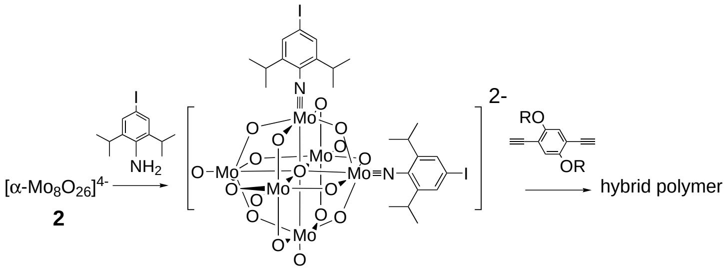
M. E. Jung,* P. Davidov 4125–4128

Efficient Synthesis of a Tricyclic BCD Analogue of Ouabain: Lewis Acid Catalyzed Diels–Alder Reactions of Sterically Hindered Systems

Keywords: cycloaddition · diastereoselectivity · Diels–Alder reaction · Lewis acids · synthetic methods

---

Molybdenum blocks in organic polymers: Bifunctionalized hexamolybdate anions (such as **1**) can be selectively synthesized in high yields by using the octamolybdate anion **2** as the starting material. The ion **1** can then be used in the synthesis of the first main-chain-polyoxometalate-containing hybrid polymer.



Angew. Chem. **2002**, *114*, 4303–4306

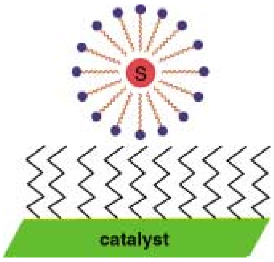
L. Xu, M. Lu, B. Xu, Y. Wei, Z. Peng,* D. R. Powell 4129–4132

Towards Main-Chain-Polyoxometalate-Containing Hybrid Polymers: A Highly Efficient Approach to Bifunctionalized Organoimido Derivatives of Hexamolybdates

Keywords: molybdenum · organic–inorganic hybrid composites · polymers · polyoxometalates

---

No organic solvents are required using this novel concept for the heterogenization of (catalytic) reactions. The method relies on a multiphase transport process, namely on the transport of emulsified hydrophobic substrates to a hydrophobically derivatized sol-gel entrapped catalyst (see figure; S = substrate), and the transport of the resulting emulsified product from the catalyst-entrapping environment back into the aqueous bulk.



Angew. Chem. **2002**, *114*, 4306–4308

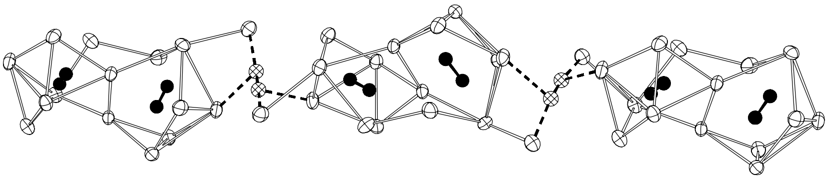
R. Abu-Reziq, D. Avnir,* J. Blum* 4132–4134

A Three-Phase Emulsion/Solid-Heterogenization Method for Transport and Catalysis

Keywords: green chemistry · micelles · phase-transfer catalysis · sol-gel processes · water chemistry

---

The largest known silver(I) cluster with encapsulated acetylide ions, $(Et_4N)_6[\{(Ag_2C_2)_2(AgCF_3CO_2)_8(CF_3CO_2)_3(H_2O)_2\}_2]$, and an infinite anionic silver(I) column with co-intercalation of cyanide and acetylide ions, $(Et_4N)_3[(Ag_2C_2)_2(AgCN)(AgCF_3CO_2)_{11}(CF_3CO_2)_3(H_2O)_6]$ (see picture; black dumbbells C_2^{2-}, cross-hatched dumbbells CN^-), have been synthesized and subsequently characterized by X-ray single-crystal structure analysis.



Angew. Chem. **2002**, *114*, 4309–4311

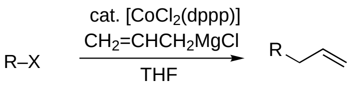
Q.-M. Wang, T. C. W. Mak* 4135–4137

Facile Construction of Anionic Silver(I) Aggregates with Embedded Acetylide and Cyanide Ions

Keywords: aggregation · carbides · clusters · cyanides · silver

1433-7851/02/4121-3941 $ 20.00+.50/0

Facile construction of quaternary carbon centers: The cobalt-catalyzed coupling reaction of not only primary and secondary but also tertiary alkyl halides with allylic Grignard reagents proceeds smoothly (see scheme; dppp = 1,3-bis(diphenylphosphanyl)propane; R = primary, secondary, or tertiary alkyl group). A radical mechanism is proposed for the oxidative addition of alkyl halides to cobalt.



Angew. Chem. **2002**, *114*, 4311 – 4313

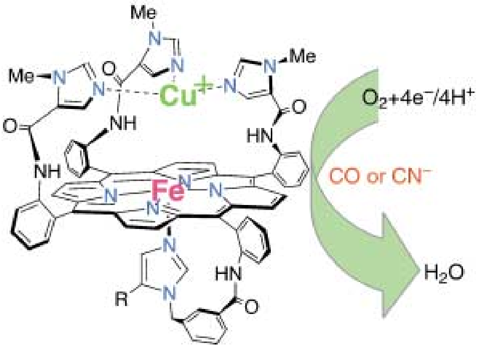
T. Tsuji, H. Yorimitsu, K. Oshima* .... 4137 – 4139

Cobalt-Catalyzed Coupling Reaction of Alkyl Halides with Allylic Grignard Reagents

Keywords: allylation · C–C coupling · cobalt · cross-coupling · radical reactions

---

Iron loses its inhibitions! Comparative voltammetry of close functional heme/Cu$_B$ analogues (see picture) in the FeCu and Cu-free forms revealed a Cu-induced destabilization of CO and CN$^-$ ion binding to the Fe center. During steady-state reduction of O$_2$ under physiologically relevant conditions, an up to fivefold higher concentration of CN$^-$ ion is required to inhibit the same fraction of the FeCu catalyst as of the Cu-free analogues.



Angew. Chem. **2002**, *114*, 4313 – 4316

J. P. Collman,* R. Boulatov, I. M. Shiryaeva, C. J. Sunderland .... 4139 – 4142

Distal Cu Ion Protects Synthetic Heme/Cu Analogues of Cytochrome Oxidase against Inhibition by CO and Cyanide

Keywords: bioinorganic chemistry · electrochemistry · inhibitors · iron · oxidoreductases · porphyrinoids

---

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

* Author to whom correspondence should be addressed

Accelerated publications

BOOKS

1433-7851/02/4121-3942 $ 20.00+.50/0

WEB SITES

SERVICE

Don't forget all the Tables of Contents from 1998 onwards may be still found on the WWW under: http://www.angewandte.org