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## COVER PICTURE

**The cover picture shows** the molecular modeling of a star-shaped metallo-supramolecular polymer and the schematic drawing of a linear analogue. These molecules are of great interest because of their unique properties. Metallo-supramolecular polymers emerge by the well-directed combination of polymers, the properties of which have dominated the development of materials in recent years, with supramolecular ligands, which have the ability to organize spontaneously and form unique structures on a molecular level, and transition-metal ions, which, through their physical properties bring characteristic functionalities. The well-known properties of the individual components allow the use of established methods, such as UV/Vis spectroscopy, NMR spectroscopy, and gel permeation chromatography for characterization. However, the combination also requires the application of new methods, such as analytical ultracentrifugation or MALDI-TOF mass spectrometry. More about metallo-supramolecular polymers based on bipyridine and terpyridine complexes can be found in the review by U. S. Schubert and C. Eschbaumer on p. 2892 ff.

## REVIEWS

Contents

**Evolution leads the way**: The structure of proteins is based on a limited number of folds (see picture). Natural products have been evolutionarily selected to bind to such protein domains, therefore, they represent biologically validated starting points for the design of combinatorial compound libraries, which allow a higher hit rate despite smaller library sizes.

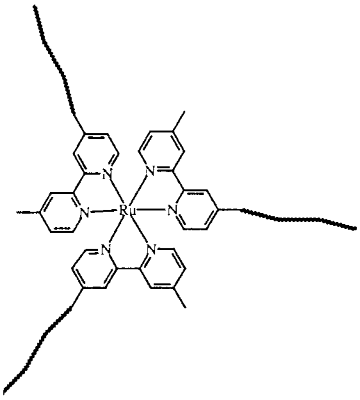
*Angew. Chem.* **2002**, *114*, 3002–3015

R. Breinbauer, I. R. Vetter,
H. Waldmann* ............. 2878–2890

From Protein Domains to Drug Candidates—Natural Products as Guiding Principles in the Design and Synthesis of Compound Libraries

**Keywords:** bioorganic chemistry · combinatorial chemistry · natural products · protein structures · solid-phase synthesis

**Functional architectures and "intelligent" materials** can be constructed from polymer complexes with bipyridine (see picture) and terpyridine ligands, compounds that play an important role in modern macromolecular and supramolecular chemistry. This review provides an overview of the current status of the synthesis, characterization, and application of this class of compounds.



*Angew. Chem.* **2002**, *114*, 3016–3050

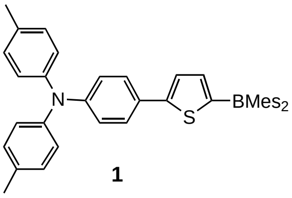
Ulrich S. Schubert,*
C. Eschbaumer ............. 2892–2926

Macromolecules Containing Bipyridine and Terpyridine Metal Complexes: Towards Metallosupramolecular Polymers

**Keywords:** bipyridine ligands · coordination chemistry · polymers · supramolecular chemistry · terpyridine ligands

# MINIREVIEW

**Molecular and polymeric boron-containing systems** are proving to display interesting optical and electrooptical properties. Molecules such as thiophene **1** with a donor (4-[bis(4-methylphenyl)amino]phenyl) and an acceptor (dimesitylboryl) substituent, are strongly electroluminescent, and have been incorporated into organic electronic devices.



**1**

*Angew. Chem.* **2002**, *114*, 3051–3056

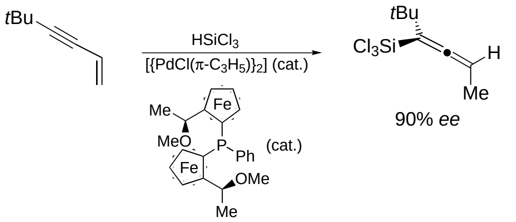
C. D. Entwistle,
T. B. Marder* .............. 2927–2931

Boron Chemistry Lights the Way: Optical Properties of Molecular and Polymeric Systems

**Keywords:** amorphous materials · boron · electroluminescence · fluorescence · nonlinear optics

# HIGHLIGHT

**A breakthrough** in the catalytic enantioselective synthesis of allenes was recently reported by Hayashi and co-workers: chiral trichlorosilyl allenes were generated with up to 90% *ee* by palladium-catalyzed hydrosilylation of but-1-en-3-ynes in the presence of a chiral ferrocenyl phosphane [Eq. (1)]. This transformation, as well as further recent highlights in enantioselective allene synthesis, are summarized in this account.



(1)

*Angew. Chem.* **2002**, *114*, 3057–3059

A. Hoffmann-Röder,
N. Krause* ................. 2933–2935

Enantioselective Synthesis of and with Allenes

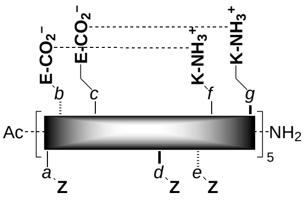
**Keywords:** allenes · asymmetric catalysis · copper · hydrosilylation · transition metals

# 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.org

| | |
|---|---|
| Metallabenzenes and Valence Isomers: Synthesis and Characterization of a Platinabenzene | V. Jacob, T. J. R. Weakley, M. M. Haley* |
| Syntheses and Crystal Structures of the New Ag-S Clusters $[Ag_{70}S_{16}(SPh)_{34}(PhCO_2)_4(triphos)_4]$ and $[Ag_{188}S_{94}(PnPr_3)_{30}]$ | X.-J. Wang, T. Langetepe, C. Persau, B.-S. Kang, D. Fenske* |
| Protonated Benzene: IR Spectrum and Structure of $C_6H_7^+$ | N. Solcà, O. Dopfer* |

**Substitution in the outer surface** of the six-helix peptide bundle improved the solubility and enhanced the anti-HIV-1 activity of SC peptides. The E and K residues at positions *b*, *c*, *f*, and *g* (see scheme) stabilize the α-helix conformation critical to inhibition; the Z residues at positions *a*, *d*, and *e* interact with the inner strand.



Angew. Chem. **2002**, *114*, 3062 – 3064

A. Otaka,* M. Nakamura, D. Nameki, E. Kodama, S. Uchiyama, S. Nakamura, H. Nakano, H. Tamamura, Y. Kobayashi, M. Matsuoka, N. Fujii* ..... 2938 – 2940

Remodeling of gp41-C34 Peptide Leads to Highly Effective Inhibitors of the Fusion of HIV-1 with Target Cells

**Keywords:** antiviral agents · drug design · helical structures · HIV · peptides

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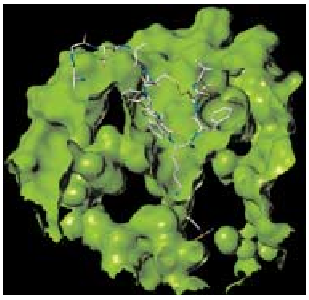
**The salient structural features** of urotensin II (U II) required for stimulation of its G-protein-coupled receptor were obtained from biological evaluation of synthetic derivatives of U II. This approach led to a plausible U-II – receptor complex (see picture), which inspired the installation of nonnatural amino acids in place of key residues. Notably, replacement of tyrosine with (2-naphthyl)-L-alanine resulted in a sixfold potency improvement compared to U II.



Angew. Chem. **2002**, *114*, 3064 – 3068

W. A. Kinney,* H. R. Almond, Jr., J. Qi, C. E. Smith, R. J. Santulli, L. de Garavilla, P. Andrade-Gordon, D. S. Cho, A. M. Everson, M. A. Feinstein, P. A. Leung, B. E. Maryanoff ............ 2940 – 2944

Structure – Function Analysis of Urotensin II and Its Use in the Construction of a Ligand – Receptor Working Model

**Keywords:** G proteins · protein models · structure – activity relationships · urotensin II · vasoactive peptides

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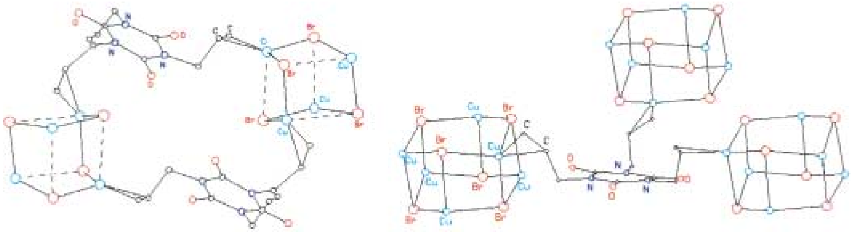
**Temperature determines the product**: The reaction of triallyl-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione with CuBr at 60°C affords a copper(I) – olefin coordination polymer with a $Cu_4Br_4$ open cubane (left) as a connecting node; when the reaction is repeated at 90°C a $Cu_6Br_6$ prismane unit is formed in a coordination polymer (right).



Angew. Chem. **2002**, *114*, 3068 – 3070

X. Xue, X.-S. Wang, R.-G. Xiong,* X.-Z. You, B. F. Abrahams,* C.-M. Che, H.-X. Ju .................... 2944 – 2946

A Cluster Rearrangement of an Open Cubane ($Cu_4Br_4$) to a Prismane ($Cu_6Br_6$) in a Copper(I) – Olefin Network

**Keywords:** cluster compounds · copper · crystal engineering · cubanes · supramolecular chemistry

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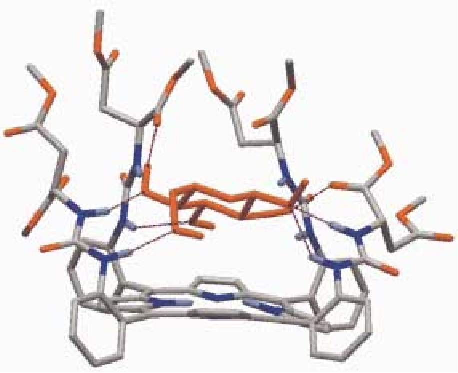
**Sugar receptors**: Urea-appended porphyrins were the most effective binding agent for pyranosides in chloroform and still very effective even in the presence of hydroxylic cosolvents. The combination of a rigid porphyrin skeleton and acyclic, flexible, yet preorganized polar urea groups aligned in a rigid platform (see picture) enabled three-dimensional recognition of carbohydrates.



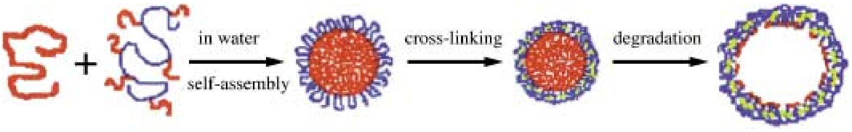
Angew. Chem. **2002**, *114*, 3071 – 3074

Y.-H. Kim, J.-I. Hong* ...... 2947 – 2950

Molecular Recognition of Carbohydrates through Directional Hydrogen Bonds by Urea-Appended Porphyrins in Organic Media

**Keywords:** carbohydrates · host – guest systems · hydrogen bonds · molecular recognition · porphyrinoids

**A block-copolymer-free strategy** has been used to form micelles by the self-assembly of poly($\varepsilon$-caprolactone) (PCL) and a graftlike copolymer which has a hydrophilic backbone and short PCL side-chains (see schematic representation). Affinity between the PCL homopolymer and the PCL short branches appears to stabilize the micelles. The hydrophobic polyester core can be selectively hydrolyzed by lipase to give hollow spheres, as shown by transmission electron microscopy.



*Angew. Chem.* **2002**, *114*, 3074–3077

X. Liu, M. Jiang,* S. Yang, M. Chen, D. Chen, C. Yang, K. Wu .... 2950–2953

Micelles and Hollow Nanospheres Based on $\varepsilon$-Caprolactone-Containing Polymers in Aqueous Media

**Keywords:** electron microscopy · micelles · nanostructures · polymers · self-assembly

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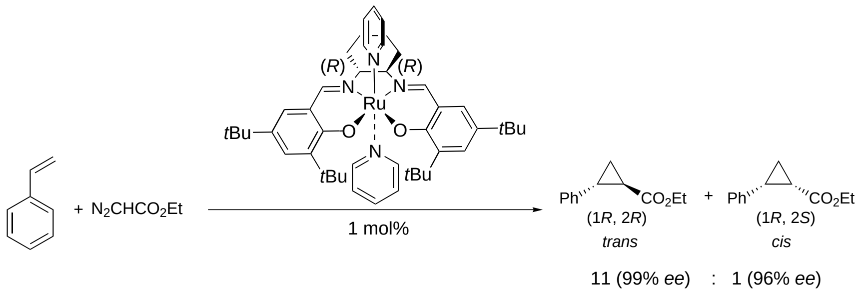
**Both electron-rich and electron-deficient olefins**—such as styrene and methyl methacrylate—undergo efficient (yields $>90\%$) cyclopropanation with ethyl diazoacetate as the carbene source to give predominantly *trans* products with exceptionally high enantioselectivity when the (salen)Ru catalyst shown is used (see scheme).



*Angew. Chem.* **2002**, *114*, 3077–3080

J. A. Miller, W. Jin, S. T. Nguyen* .............. 2953–2956

An Efficient and Highly Enantio- and Diastereoselective Cyclopropanation of Olefins Catalyzed by Schiff-Base Ruthenium(II) Complexes

**Keywords:** asymmetric catalysis · cyclopropanation · N,O ligands · ruthenium

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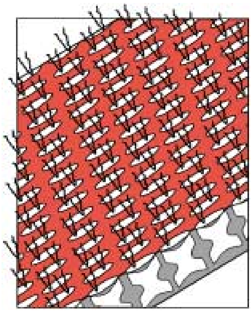
**Ionic self-assembly**: Oligopeptides with a small number of charged sites can be precipitated from water by complexation with oppositely charged surfactants, as exemplified here with oxidized glutathione, GSSG. These complexes are well-defined 1:1 species, dissolve in organic solvents, and form highly organized supramolecular aggregates (solution; see schematic representation) or mesophases (solid-state films). This ionic self-assembly with surfactants represents a simple access to new peptide superstructures with structural features on the nanometer scale.



*Angew. Chem.* **2002**, *114*, 3081–3084

S. General, M. Antonietti* .. 2957–2960

Supramolecular Organization of Oligopeptides, through Complexation with Surfactants

**Keywords:** nanostructures · oligopeptides · self-assembly · superhelices · surfactants

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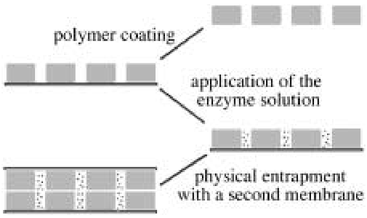
**The conversion of enzymes** into enantioselective receptors by mutagenesis opens the way for resolution of racemates by using enantioselective membranes: the transport of one enantiomer is accelerated through the membrane, while the other enantiomer diffuses across much more slowly. As an example, histidine ammonia lyase and phenylalanine ammonia lyase were rendered catalytically inactive and incorporated in artificial membranes (see figure). The facilitated transport of L-histidine and L-phenylalanine resulted in a maximum 14-fold enantiomeric enrichment.



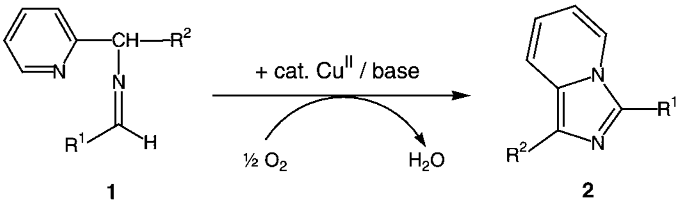
*Angew. Chem.* **2002**, *114*, 3094–3096

A. Skolaut, J. Rétey* ....... 2960–2962

Use of Enzymes Deactivated by Site-Directed Mutagenesis for the Preparation of Enantioselective Membranes

**Keywords:** amino acids · chiral resolution · enantioselective transport · lyases · membranes

**Starting from Schiff bases 1**, a wide variety of heterobicycles, which can be applied as pharmaceuticals or as ligands for catalysts, is accessible by copper-catalyzed oxidation with atmospheric oxygen. The scheme shows, for example, the synthesis of imidazo[1,5-*a*]pyridines **2** ($R^1$ = 2-hydroxy-3-methoxyphenyl, *t*Bu, 2-hydroxyphenyl, 2-aminophenyl; $R^2$ = 2-pyridyl, Me, phenyl).



*Angew. Chem.* **2002**, *114*, 3104–3107

M. E. Bluhm, M. Ciesielski, H. Görls,
M. Döring* ................ 2962–2965

Copper-Catalyzed Oxidative Heterocyclization by Atmospheric Oxygen

**Keywords:** copper · homogeneous catalysis · metalloenzymes · oxygen · Schiff bases

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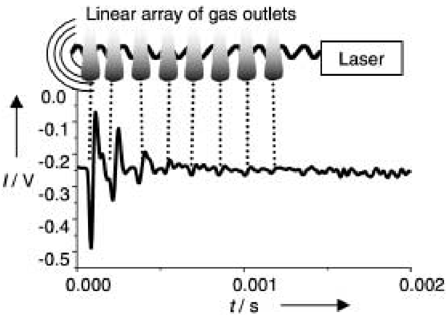
**Photoacoustic parallel detection** is introduced as a novel analysis technique for high-throughput experimentation in catalysis (see picture). Libraries of mixed-metal oxides were generated by a novel process based on activated carbon and thus novel CO-oxidation catalysts were discovered.



*Angew. Chem.* **2002**, *114*, 3096–3100

T. Johann, A. Brenner, M. Schwickardi,
O. Busch, F. Marlow, S. Schunk,
F. Schüth* ................ 2966–2968

Real-Time Photoacoustic Parallel Detection of Products from Catalyst Libraries

**Keywords:** amorphous materials · CO oxidation · heterogeneous catalysis · high-throughput screening · photoacoustics

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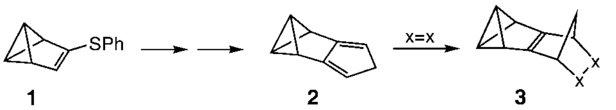
**A strong pyramidalization of the double bond** in the Diels–Alder adducts **3**, as suggested by quantum-chemical calculations and NMR spectroscopic data, is probably the reason why these very reactive compounds are observable at best at low temperatures. The title compound **2**, required for preparation of **3**, was prepared in five steps from benzvalene **1**.



*Angew. Chem.* **2002**, *114*, 3091–3093

T. Fischer, U. Kunz, S. E. Lackie,
C. Cohrs, D. D. Palmer,
M. Christl* ................ 2969–2971

1,2,3,5-Tetrahydro-1,2,3-methenopentalene, a Valence Isomer of Isoindene: Synthesis and Diels–Alder Reactions

**Keywords:** benzvalene · cycloaddition · Pauson–Khand reaction · polycycles · rearrangement

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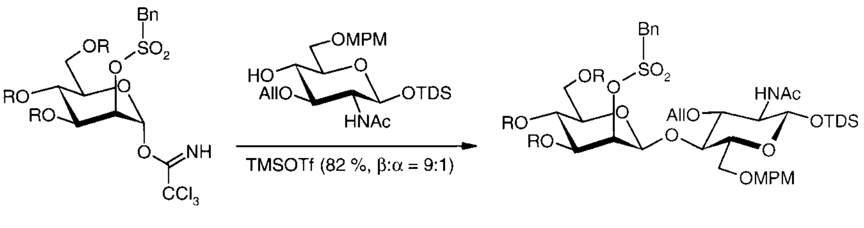
**An electron-withdrawing protecting group** at the O-2 atom and a good anomeric leaving group at the mannopyranosyl donor are required for a new, practical approach to the production of β-linked mannopyranoside units (see scheme, MPM = *para*-methoxybenzyl, TDS = thexylmethysilyl, TMS = trimethylsilyl, All = β-D-allose, OTf = trifluoromethanesulfonate). Many attempts to solve this problem in a direct manner have failed. β-Mannopyranoside units are found, for instance, in N-glycopeptides.



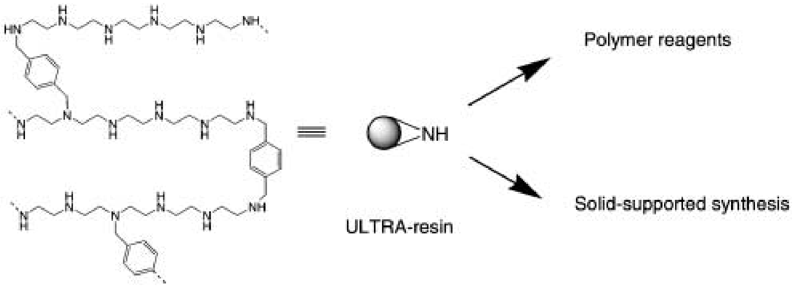
*Angew. Chem.* **2002**, *114*, 3100–3103

A. A.-H. Abdel-Rahman, S. Jonke,
El S. H. El Ashry,*
R. R. Schmidt* ............ 2972–2974

Stereoselective Synthesis of β-D-Mannopyranosides with Reactive Mannopyranosyl Donors Possessing a Neighboring Electron-Withdrawing Group

**Keywords:** asymmetric synthesis · C-glycosides · mannopyranosides · protecting groups · stereoelectronic effects

**ULTRA resins** (see picture), useful for making polymer reagents, heterocycles, and peptides, were prepared by thermodynamically controlled cross-linking of linear poly(ethylene imine)s with a loading of up to 15 mmol g$^{-1}$. During characterization, the secondary amines in the resin backbone of the novel carriers were found to be very accessible to chemical modification.



*Angew. Chem.* **2002**, *114*, 3087–3090

J. Rademann,* M. Barth .... 2975–2978

ULTRA Loaded Resins Based on the Cross-Linking of Linear Poly(ethylene imine): Improving the Atom Economy of Polymer-Supported Chemistry

**Keywords:** combinatorial chemistry · polymers · solid-phase synthesis · synthetic methods

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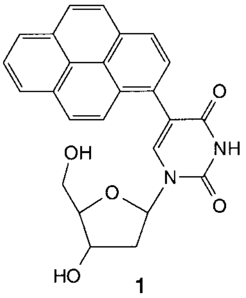
**Ultrafast intramolecular electron transfer** results from the excitation of the pyrene-modified nucleoside **1**. The dynamics and pH dependence of this process were investigated by steady-state fluorescence and femtosecond time-resolved transient absorption spectroscopy. These studies suggest that reductive electron transfer through DNA is not coupled to protonation.

*Angew. Chem.* **2002**, *114*, 3084–3087



**1**

N. Amann, E. Pandurski, T. Fiebig,*
H.-A. Wagenknecht* ....... 2978–2980

A Model Nucleoside for Electron Injection into DNA: 5-Pyrenyl-2′-Deoxyribose

**Keywords:** charge transfer · cross-coupling · electron transfer · nucleosides · protonation

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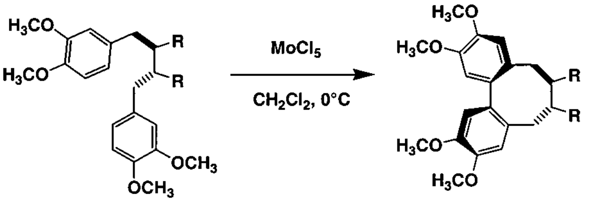
**Avoiding six-membered rings**: The oxidative coupling reaction of electron-rich 1,4-diarylbutanes with molybdenum pentachloride as the sole reagent leads to the exclusive formation of eight-membered ring systems (see scheme).



*Angew. Chem.* **2002**, *114*, 3103–3104

B. Kramer, A. Averhoff,
S. R. Waldvogel* ........... 2981–2982

Highly Selective Formation of Eight-Membered-Ring Systems by Oxidative Cyclization with Molybdenum Pentachloride—An Environmentally Friendly and Inexpensive Access to 2,2′-Cyclolignans

**Keywords:** biaryl compounds · C–C coupling · cyclization · molybdenum · natural products

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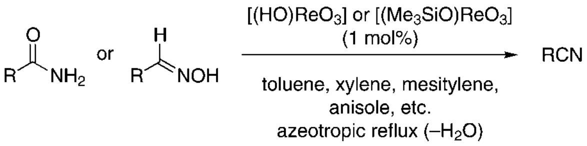
**An economical and environmentally benign process** for the preparation of nitriles by the dehydration of primary amides and aldoximes is catalyzed by rhenium(VII) oxo complexes such as perrhenic acid and trimethylsilylperrhenate (see scheme). The reaction proceeds at azeotropic reflux (with the removal of water) under essentially neutral conditions.



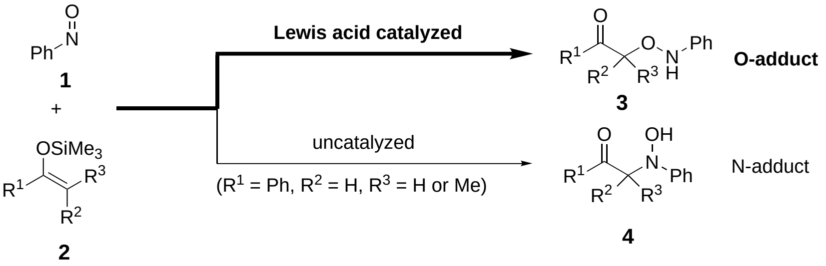
*Angew. Chem.* **2002**, *114*, 3109–3112

K. Ishihara, Y. Furuya,
H. Yamamoto* ............. 2983–2986

Rhenium(VII) Oxo Complexes as Extremely Active Catalysts in the Dehydration of Primary Amides and Aldoximes to Nitriles

**Keywords:** dehydration · green chemistry · homogeneous catalysis · nitriles · rhenium

**Not N-adduct but O-adduct** is formed in the Lewis acid catalyzed nucleophilic addition of silyl enol ethers **2** to the N=O bond of nitrosobenzene (**1**). Various Lewis acids (e.g. alkylsilyl triflates) efficiently catalyze the formation of the aminooxy ketone (O-adduct **3**) rather than of the hydroxyamino ketone (N-adduct **4**), which is the product of the uncatalyzed reaction.



*Angew. Chem.* **2002**, *114*, 3112–3114

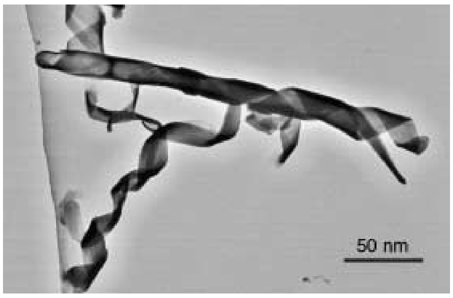
N. Momiyama,
H. Yamamoto* ............ 2986–2988

Lewis Acid Promoted, O-Selective, Nucleophilic Addition of Silyl Enol Ethers to N=O bonds

**Keywords:** Lewis acids · nitroso compounds · nucleophilic addition · silyl enol ethers · synthetic methods

---

**A lamellar hybrid mesostructure** containing polymerizable diacetylinic groups is coassembled in the in situ synthesis of silica by acid hydrolysis and condensation of tetraethylorthosilicate (TEOS) in the presence of 1,2-bis(10,12-tricosadiyonyl)-*sn*-glycero-3-phosphatidylcholine ($DC_{8,9}PC$) lipid molecules. This mesostructure is subsequently twisted into high aspect-ratio tubules and ribbons with helical architecture (see picture). Interactions between the silica and lipid headgroups promote diacetylenic polymerization under conditions at which the unmineralized lipid microstructures show little or no activity.



*Angew. Chem.* **2002**, *114*, 3114–3117

A. M. Seddon, H. M. Patel, S. L. Burkett,
S. Mann* ................. 2988–2991

Chiral Templating of Silica–Lipid Lamellar Mesophase with Helical Tubular Architecture

**Keywords:** mesoporous materials · nanotubes · silica · surfactants · template synthesis

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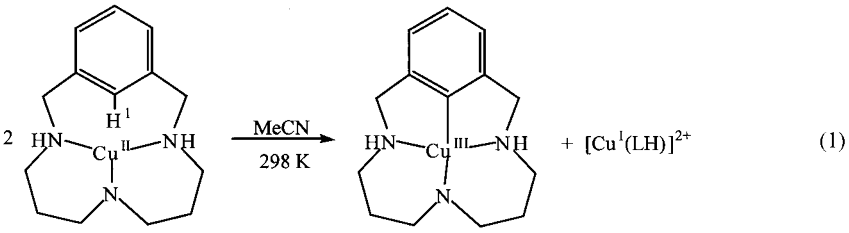
**Simple triazamacrocyclic ligands** react with copper(II) salts under mild conditions to give the products of intramolecular aryl C–H activation and metal disproportionation [Eq. (1)]. The novel organometallic $Cu^{III}$ complexes thus formed are stable under protic conditions.



*Angew. Chem.* **2002**, *114*, 3117–3120

X. Ribas, D. A. Jackson, B. Donnadieu,
J. Mahía, T. Parella, R. Xifra,
B. Hedman,* K. O. Hodgson,*
A. Llobet,* T. D. P. Stack* .. 2991–2994

Aryl C–H Activation by $Cu^{II}$ To Form an Organometallic Aryl–$Cu^{III}$ Species: A Novel Twist on Copper Disproportionation

**Keywords:** C–H activation · copper · macrocyclic ligands · X-ray absorption

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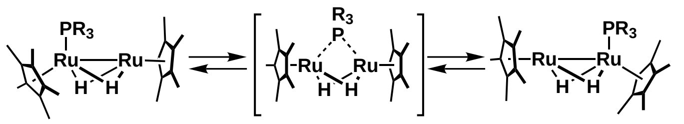
**On the move!** Novel diruthenium dihydrido $[\{(\eta^5\text{-}C_5Me_5)Ru\}_2(PR_3)(\mu\text{-}H)_2]$ complexes, which were synthesized in the reaction of $[\{(\eta^5\text{-}C_5Me_5)Ru\}_2(\mu\text{-}H)_4]$ with a phosphorus ligand containing no aryl substituents, undergo intramolecular migration of the phosphorus ligand between the two ruthenium centers (see scheme). Support for this result is derived from variable temperature NMR spectroscopic studies and preliminary DFT calculations.



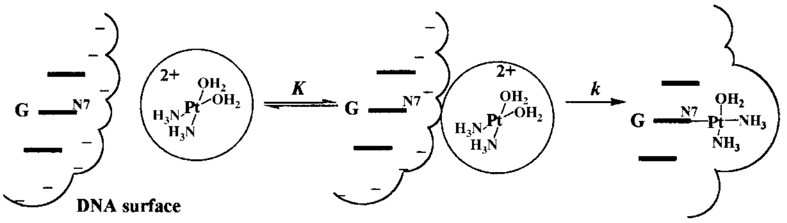
*Angew. Chem.* **2002**, *114*, 3120–3123

Y. Ohki, H. Suzuki* ........ 2994–2997

Migration of a Phosphane Ligand between the Two Metal Centers in Diruthenium Hydrido Complexes

**Keywords:** hydride ligands · P ligands · reaction mechanisms · ruthenium

**The main factor** determining the sequence-selective binding of platinum complexes to DNA is the accessibility of the N7 atom of guanine (G). The rate constants observed for the reactions of *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ with DNA G residues in various sequences can be accounted for by a mathematical formula compatible with the kinetic model shown in the scheme, where the association constant *K* is determined by the molecular electrostatic potential and the rate constant *k* by the accessible area of the N7 van der Waals sphere.



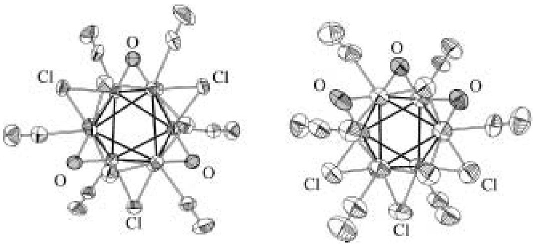
*Angew. Chem.* **2002**, *114*, 3124–3127

V. Monjardet-Bas,
M.-A. Elizondo-Riojas,* J.-C. Chottard,
J. Kozelka* ................ 2998–3001

A Combined Effect of Molecular Electrostatic Potential and N7 Accessibility Explains Sequence-Dependent Binding of *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ to DNA Duplexes

**Keywords:** DNA complexes • electrostatic interactions • kinetics • platinum • sequence selectivity

**The distribution of the oxygen atoms varies** in the two isomers of the $[Nb_6Cl_9O_3(CN)_6]^{5-}$ ion found in the title compounds (both isomers are shown). This difference in the inner ligand sphere in turn leads to variations in the structure and physical properties of the cluster oxyhalides.



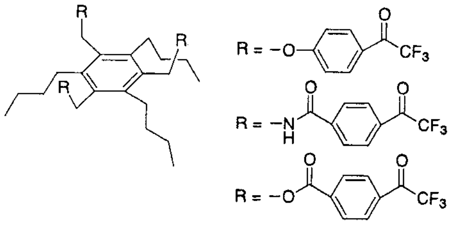
*Angew. Chem.* **2002**, *114*, 3128–3130

N. G. Naumov,* S. Cordier,
C. Perrin .................. 3002–3004

Two $[Nb_6Cl_9O_3(CN)_6]^{5-}$ Isomer Anions in Two $Nb_6$ Cluster Oxyhalides: $Cs_5[Nb_6Cl_9O_3(CN)_6]\cdot 4H_2O$ and $(Me_4N)_5[Nb_6Cl_9O_3(CN)_6]\cdot 5H_2O$

**Keywords:** cluster compounds • cyanides • isomers • niobium • solid-state structures

**Selective sensors**: Trifluoroacetophenone derivatives were synthesized with a hexasubstituted benzene ring as a preorganized spacer (see scheme) and their characteristics as ionophores were examined for use in ion-selective electrodes. The electrode membranes based on these neutral carriers combined with a cationic additive showed a monoanionic Nernstian response to underivatized phenylalanine, with excellent selectivity towards other essential amino acids and inorganic anions.



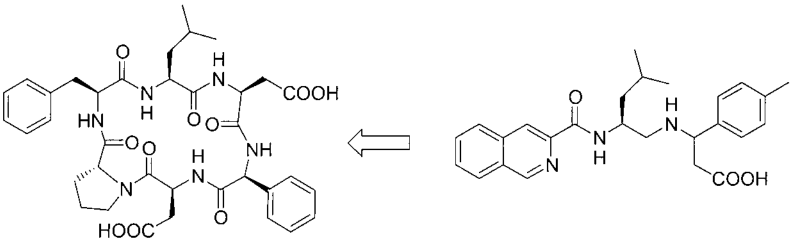
*Angew. Chem.* **2002**, *114*, 3131–3133

S.-i. Sasaki, A. Hashizume, D. Citterio,
E. Fujii, K. Suzuki* ......... 3005–3007

Trifluoroacetophenone Derivatives as Amino Acid Selective Ionophores for the Potentiometric Determination of Phenylalanine

**Keywords:** amino acids • ionophores • molecular recognition • sensors

**Non-peptidic compounds** (e.g. **2**) derived from cyclic peptides such as **1** are able to inhibit the α4β7-integrin/MAdCAM-1 interaction. 3-Amino arylpropionic acids are valuable dipeptide mimetics. MAdCAM-1 = mucosal addressin cell-adhesion molecule 1.



**1** **2**

*Angew. Chem.* **2002**, *114*, 3133–3137

D. Gottschling, J. Boer, A. Schuster,
B. Holzmann, H. Kessler* .. 3007–3011

Combinatorial and Rational Strategies To Develop Nonpeptidic α4β7-Integrin Antagonists from Cyclic Peptides

**Keywords:** drug research • inhibitors • integrins • peptidomimetics • medicinal chemistry

**In how many different ways can carbon and iodine combine to form a stable molecule?** Here is a new possibility: the first reported iodocumulene. Tetraiodobutatriene ($C_4I_4$; see picture) is formed spontaneously and in good yield from diiodobutadiyne ($C_4I_2$). In solution, however, $C_4I_4$ disproportionates to give hexaiodobutadiene ($C_4I_6$) and unknown carbon-rich by-products.

*Angew. Chem.* **2002**, *114*, 3137 – 3140

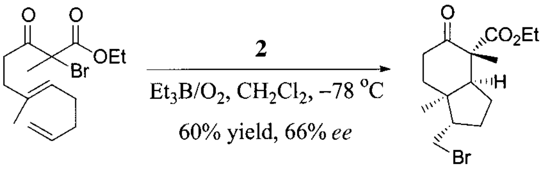
J. A. Webb, P.-H. Liu, O. L. Malkina, N. S. Goroff* .............. 3011 – 3014

Tetraiodobutatriene: A New Cumulenic Carbon Iodide

**Keywords:** addition • alkynes • carbon • cumulenes • iodine

---

**Various polycyclic ring skeletons** (e.g. **3**) are formed from unsaturated $\alpha$-bromo $\beta$-keto esters (e.g. **1**) in a Lewis acid catalyzed atom-transfer tandem radical-cyclization reaction in moderate to good yields and with excellent stereoselectivities. Furthermore, in the presence of chiral complexes such as [Yb(Ph-pybox)(OTf)$_3$] (**2**), the enantioselective cyclization gave up to 84% *ee*. OTf = trifluoromethanesulfonate, pybox = 2,6-bis(2-oxazolin-2-yl)pyridine.



**1** **3**

*Angew. Chem.* **2002**, *114*, 3140 – 3143

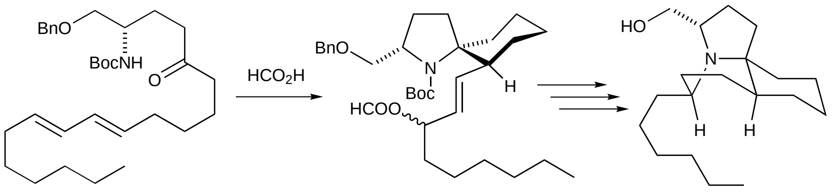
D. Yang,* S. Gu, Y.-L. Yan, H.-W. Zhao, N.-Y. Zhu ................. 3014 – 3017

Atom-Transfer Tandem Radical Cyclization Reactions Promoted by Lewis Acids

**Keywords:** cyclization • enantioselectivity • Lewis acids • radicals • synthetic methods

---

**A short synthesis**: The naturally occurring (−)-lepadiformine ((−)-**3**) was prepared in nine steps in 31.4% overall yield. The key step involved the formation of **2** by the spirocyclization of the *N*-acyliminium ion generated from **1**. Furthermore, HPLC analysis of the synthetic material and the natural product established the absolute configuration of **3** as 3*S*,5*R*,7a*S*,11a*S*. Bn = benzyl, Boc = *tert*-butoxycarbonyl.



**1** **2** (–)-**3**

*Angew. Chem.* **2002**, *114*, 3143 – 3146

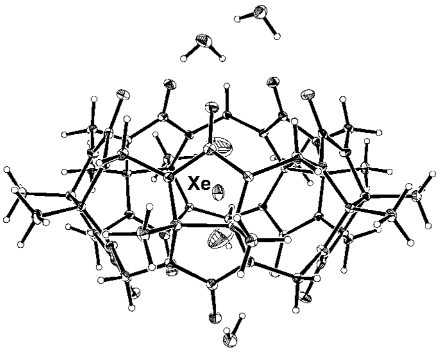
H. Abe, S. Aoyagi, C. Kibayashi* ............. 3017 – 3020

Total Synthesis of the Natural Enantiomer of (−)-Lepadiformine and Determination of Its Absolute Stereochemistry

**Keywords:** configuration determination • natural products • spiro compounds • total synthesis

---

**Miniature gas jars with lids**: Salt-free decamethylcucurbit[5]uril (MeCuc5) powder, absorbs $N_2$, $O_2$, Ar, $N_2O$, NO, CO, and $CO_2$ selectively at room temperature and desorbs at 110°C, this process can be carried out repeatedly. In contrast, all noble gases from He to Xe were encapsulated inside MeCuc5 in solution and the crystal structures of the gas inclusion complexes were determined (see picture for Xe complex).



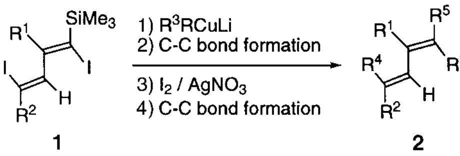
*Angew. Chem.* **2002**, *114*, 3146 – 3149

Y. Miyahara,* K. Abe, T. Inazu .................... 3020 – 3023

“Molecular” Molecular Sieves: Lid-Free Decamethylcucurbit[5]uril Absorbs and Desorbs Gases Selectively

**Keywords:** cage compounds • cucurbiturils • gas encapsulation • host – guest systems • inclusion compounds

**Taking advantage** of the presence of a silyl group at the α position in **1**, carbon–carbon bonds are formed regioselectively by the reaction of **1** with organocuprate compounds. This method is a practical and efficient approach to molecules of type **2** ($R^1$–$R^5$ = alkyl, aryl) with a variety of substitution patterns.



*Angew. Chem.* **2002**, *114*, 3149–3151

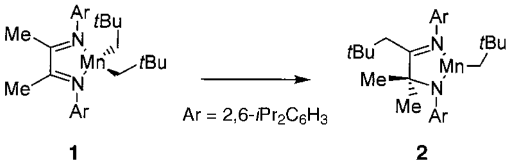
R. Nakajima, C. Delas, Y. Takayama, F. Sato* .................... 3023–3025

Efficient and General Synthetic Approach to Pentasubstituted Conjugated Dienes Using Site-Selective Coupling of Cuprates with 1,4-Diiodo-1,3-alkadienes as the Key Reaction

**Keywords:** C–C coupling • cuprates • dienes • regioselectivity • synthetic methods

---

**Ligand transformations** that depend on the substitution patterns of the diimine ligands occur upon their complexation with $Mn^{II}$ dialkyl complexes. For example the 1,3-migration of the neopentyl unit from Mn to a carbon atom and the 1,2-migration of the methyl in the putative intermediate **1** give the product **2**.



*Angew. Chem.* **2002**, *114*, 3151–3153

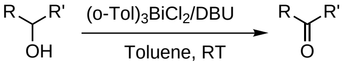
V. Riollet, C. Copéret,* J.-M. Basset, L. Rousset, D. Bouchu, L. Grosvalet, M. Perrin .................. 3025–3027

Reaction of "$[Mn^{II}(CH_2tBu)_2]$" with Bidentate Diimine Ligands: From Simple Base Adducts to C–C Activation of the Ligand

**Keywords:** C–C activation • chelates • manganese • N ligands

---

**High efficiency and chemoselectivity** as well as the facile isolation of the carbonyl products by simple workup procedures characterize a new method of alcohol oxidation. A variety of primary and secondary alcohols are oxidized to aldehydes and ketones by the combined use of tris(2-methylphenyl)bismuth dichloride and 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) under mild conditions [Eq. (1)].



(1)

*Angew. Chem.* **2002**, *114*, 3154–3157

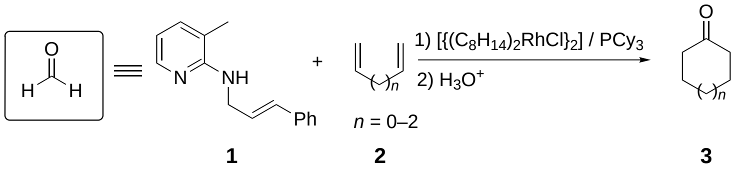
Y. Matano,* H. Nomura .... 3028–3031

Facile Oxidation of Alcohols to Carbonyl Compounds Using a Tris(2-methylphenyl)bismuth Dichloride–DBU Binary System

**Keywords:** alcohols • bismuth • carbonyl compounds • oxidation • substituent effects

---

**Formaldehyde in disguise**: The allylic amine **1** is used as a masked form of formaldehyde in the rhodium-catalyzed cyclization of dienes **2**. The reaction provides access to various cycloalkanones **3** through chelation-assisted C–H- and C–C-bond activation.



*Angew. Chem.* **2002**, *114*, 3157–3159

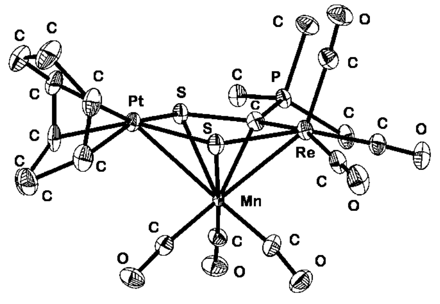
D.-Y. Lee, I.-J. Kim, C.-H. Jun* ................. 3031–3033

Synthesis of Cycloalkanones from Dienes and Allylamines through C–H and C–C Bond Activation Catalyzed by a Rhodium(I) Complex

**Keywords:** C–C activation • C–H activation • cyclization • dienes • rhodium

---

**A new ring for cymantrene**: the five-membered ring of the new cymantrene analogue shown in the picture contains two sulfur atoms, two different transition-metal atoms (Re and Pt), and only one carbon atom and forms a π complex with a $\{Mn(CO)_3\}$ unit.



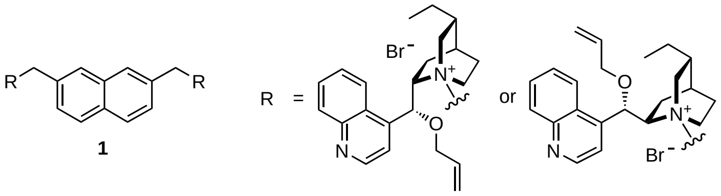
*Angew. Chem.* **2002**, *114*, 3160–3162

D. Miguel,* D. Morales, V. Riera, S. García-Granda ........... 3034–3036

An Analogue of Cymantrene $[(\eta^5\text{-}C_5H_5)Mn(CO)_3]$ That Contains a Dimetalladithiacyclopentadienyl ring

**Keywords:** cluster compounds • isolobal relationships • manganese • metallacycles • platinum • rhenium

**A new class of naphthalene-based dimeric cinchona alkaloids 1** are very efficient and practical phase-transfer catalysts in the alkylation of a glycine derivative. The mild reaction conditions and the high catalytic efficiency (high yields and *ee* values) could make these alkaloids practical catalysts in the industrial synthetic process for natural and nonnatural chiral α-amino acids.



*Angew. Chem.* **2002**, *114*, 3162–3164

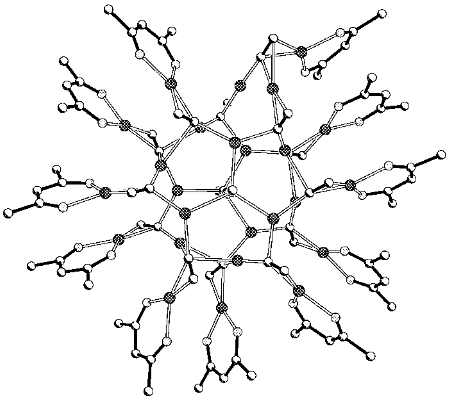
H.-g. Park,* B.-S. Jeong, M.-S. Yoo, J.-H. Lee, M.-k. Park, Y.-J. Lee, M.-J. Kim, S.-s. Jew* .......... 3036–3038

Highly Enantioselective and Practical Cinchona-Derived Phase-Transfer Catalysts for the Synthesis of α-Amino Acids

**Keywords:** alkylation · amino acids · cinchona alkaloids · phase-transfer catalysis · synthetic methods

---

**A remarkably anisotropic structure** is exhibited by [Cu$_{26}$(hfac)$_{11}$(1-pentynyl)$_{15}$] (hfac = hexafluoroacetylacetone), the largest Cu$^{I}$ cluster to have been isolated (see picture). A variety of copper–alkynyl bridging modes are found within the disc-shaped cluster, with all but one of the 26 Cu atoms being located in either of two "layers". Many short Cu$^{I}\cdots$Cu$^{I}$ interactions can be discerned within the cluster.



*Angew. Chem.* **2002**, *114*, 3164–3167

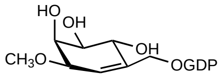
T. C. Higgs,* P. J. Bailey, S. Parsons, P. A. Tasker* .............. 3038–3041

Facile Syntheses of Copper(I) Alkynyl Clusters Stabilized by Hexafluoroacetylacetonate (hfac) Ligands: The Structure of [Cu$_{26}$(hfac)$_{11}$(1-pentynyl)$_{15}$]

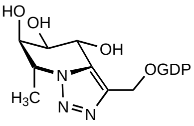
**Keywords:** alkyne ligands · cluster compounds · copper · metal–metal interactions · O ligands

---

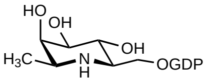
**Mimics of the geometry** or charge of the fucose moiety of GDP-fucose in the transition state of fucosyltransferase-catalyzed reactions, compounds **1**–**3** are good competive inhibitors of *α*-1,3-fucosyltransferases V and VI with $K_i$ values between 6 and 13 μM. GDP = guanosine diphosphate.



**1**



**2**



**3**

*Angew. Chem.* **2002**, *114*, 3167–3170

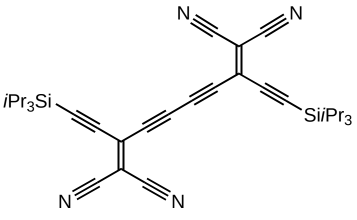
M. L. Mitchell, F. Tian, L. V. Lee, C.-H. Wong* .............. 3041–3044

Synthesis and Evaluation of Transition-State Analogue Inhibitors of *α*-1,3-Fucosyltransferase

**Keywords:** carbocycles · enzymes · inhibitors · transition states · triazoles

---

**Extended π-electron acceptors**, such as **1**, have been constructed by the acetylenic scaffolding of a series of novel cyanoethynylethenes. Electrochemical analysis shows that acceptor strength is a function of π-electron conjugation length, and that a linear correlation exists between the electron affinities (B3LYP, 3-21G) and their first reduction potential.



**1**

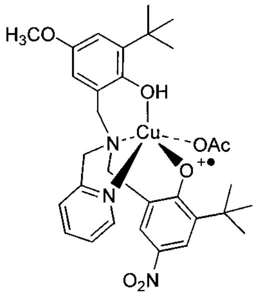
*Angew. Chem.* **2002**, *114*, 3170–3173

N. N. P. Moonen, C. Boudon, J.-P. Gisselbrecht, P. Seiler, M. Gross, F. Diederich* ............. 3044–3047

Cyanoethynylethenes: A Class of Powerful Electron Acceptors for Molecular Scaffolding

**Keywords:** alkynes · conjugation · cyanoethynylethenes · cyclic voltammetry · electron acceptors

**The axial phenol group is protonated** and the equatorial phenoxyl group antiferromagnetically coupled to the cupric center in the complex $[\mathrm{Cu^{II}(LH)(OAc)}]^{\bullet+}$ (see picture), which can be considered as both a structural and functional model of galactose oxidase. This complex reproduces the features of the enzyme chemistry. The phenoxyl radical position (equatorial versus axial) is dictated by protonation.



*Angew. Chem.* **2002**, *114*, 3173–3176

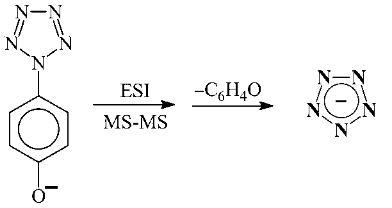
F. Thomas,* G. Gellon,
I. Gautier-Luneau, E. Saint-Aman,
J.-L. Pierre ................ 3047–3050

A Structural and Functional Model of Galactose Oxidase: Control of the One-Electron Oxidized Active Form through Two Differentiated Phenolic Arms in a Tripodal Ligand

**Keywords:** copper · enzyme models · N ligands · oxidation · radicals

---

**The long-sought pentazolate anion, *cyclo*-$N_5^-$**, the isoelectronic polynitrogen counterpart of the cyclopentadienide anion, has been experimentally detected for the first time. Using electrospray ionization mass spectrometry and carefully selected collision voltages, the aryl substituent in the *para*-pentazolylphenolate anion can be removed selectively without breaking the nitrogen–nitrogen bonds of the pentazolate anion (see scheme), thus delineating a synthetic method for the bulk synthesis of $N_5^-$.



*Angew. Chem.* **2002**, *114*, 3177–3180

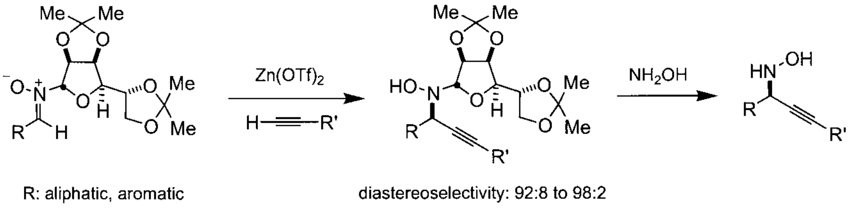
A. Vij,* J. G. Pavlovich, W. W. Wilson,
V. Vij, K. O. Christe* ....... 3051–3054

Experimental Detection of the Pentaazacyclopentadienide (Pentazolate) Anion, *cyclo*-$N_5^-$

**Keywords:** mass spectrometry · nitrogen · pentaazacyclopentadienide anion · pentazolate anion

---

**In situ generation of nucleophilic alkynilides** by using substoichiometric amounts of $Zn(OTf)_2$ (OTf = trifluoromethanesulfonate) followed by removal of the chiral auxiliary enables the direct use of a wide range of terminal acetylenes in the synthesis of optically pure propargylic *N*-hydroxylamines (see scheme).



*Angew. Chem.* **2002**, *114*, 3180–3182

R. Fässler, D. E. Frantz, J. Oetiker,
E. M. Carreira* ............ 3054–3056

First Synthesis of Optically Pure Propargylic *N*-Hydroxylamines by Direct, Highly Diastereoselective Addition of Terminal Alkynes to Nitrones

**Keywords:** acetylides · diastereoselectivity · glycosylnitrones · hydroxylamines · zinc

---

**Room-temperature C–H borylation** using a stoichiometric amount of arenes and bis(pinacolato)diboron ($pin_2B_2$) is efficiently catalyzed by iridium(I) complexes generated from $[\{Ir(OMe)(cod)\}_2]$ (cod = 1,5-cyclooctadiene) and 4,4′-di-*tert*-butyl-2,2′-bipyridine (dtbpy) in hexane, and provides the corresponding arylboronates in excellent yields [Eq. (1)].

$$\underset{(1.0\ \text{equiv})}{\mathrm{pin_2B_2}} + \underset{(2.0\ \text{equiv})}{2\,\mathrm{H{-}Ar}} \xrightarrow[\text{hexane/RT}]{\substack{1/2[\{\mathrm{Ir(OMe)(cod)}\}_2]/\mathrm{dtbpy} \\ (3\ \mathrm{mol\%})}} 2\,\mathrm{pinB{-}Ar} + \mathrm{H_2} \qquad (1)$$

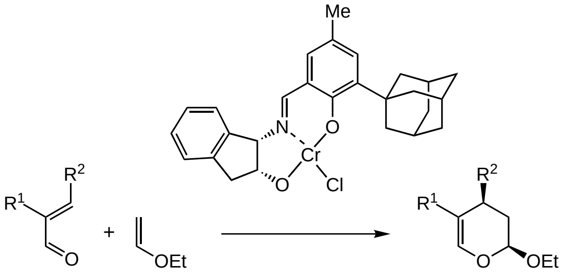
*Angew. Chem.* **2002**, *114*, 3182–3184

T. Ishiyama,* J. Takagi, J. F. Hartwig,
N. Miyaura* ................ 3056–3058

A Stoichiometric Aromatic C–H Borylation Catalyzed by Iridium(I)/2,2′-Bipyridine Complexes at Room Temperature

**Keywords:** arenes · boron · C–H activation · homogeneous catalysis · iridium

**Straightforward access** to useful synthetic intermediates is provided by this new method. Simple, $\alpha,\beta$-unsaturated aldehydes are excellent substrates in the hetero-Diels–Alder reaction with inverse electron demand, catalyzed by $Cr^{III}$–Schiff base complexes (see scheme; $R^1$, $R^2$ = alkyl or aryl) in the presence of 4-Å molecular sieves and no solvent. The resulting dihydropyrans are obtained in high enantio- (89–98% *ee*) and diastereoselectivity (>95% *de*) and yield (40–95%).



*Angew. Chem.* **2002**, *114*, 3185–3187

**Keywords:** asymmetric catalysis · chromium · cycloaddition · dihydropyran · hetero-Diels–Alder

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

Accelerated publications

* Author to whom correspondence should be addressed

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