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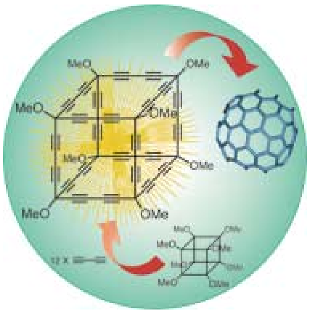
Pages 4155–4354

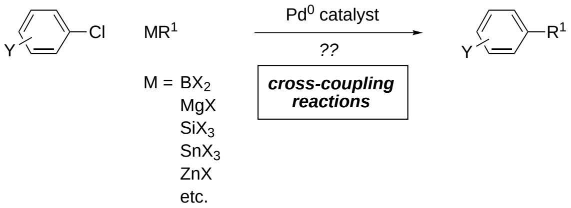
COVER PICTURE

The cover picture shows the first expanded cubane with a C_{56} core. Formally derived by insertion of buta-1,3-diynediyl moieties into all 12 C–C single bonds of octamethoxycubane, its synthesis actually proceeds by the formation of corners, edges, and faces as key building blocks and intermediates. The expanded cubane is highly strained and explodes upon scraping. Under conditions of Fourier-transform ion-cyclotron-resonance mass spectrometry it rearranges into fullerenes, which, in the positive-ion mode, undergo fullerene coalescence reactions. Full details are described by Diederich et al. on p. 4339 ff.



REVIEW

Their relatively low cost and wide availability can make aryl chlorides more attractive substrates for coupling reactions than the corresponding bromides or iodides. Although scattered examples of couplings of aryl chlorides had been reported earlier, for most processes it was not until the last few years that comparatively general and mild methods were described (see scheme for a general reaction). This article furnishes an overview both of the pioneering early developments and the exciting recent discoveries in this area.



Angew. Chem. **2002**, *114*, 4350–4386

A. F. Littke, G. C. Fu* 4176–4211

Palladium-Catalyzed Coupling Reactions of Aryl Chlorides

Keywords: catalysis · cross-coupling · ligand effects · palladium · synthetic methods

ESSAY

Concerned skepticism about the direction “his” science had taken dominated the last 30 years of the life of the biochemist Erwin Chargaff, who died on June 20 this year at the age of almost 97. This obituary is an eloquent account of the life of this faciscinating person who never forgot his European roots in spite of spending more than two thirds of his life in America.

Angew. Chem. **2002**, *114*, 4387 – 4390

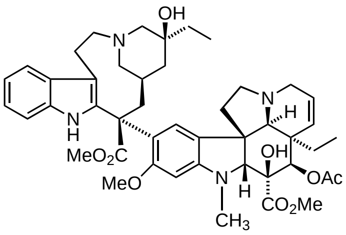
L. Jaenicke* .... 4213 – 4216

The Torch of Erwin Chargaff and the Fire of Heraklitus Devour Their Children

Keywords: Chargaff, Erwin • history of chemistry • nucleic acids

HIGHLIGHTS

More than 40 years after the isolation of vinblastine (**1**), and after considerable synthetic effort, Fukuyama et al. have now successfully completed the first de novo synthesis of this bisindole alkaloid and tumor therapeutic agent. Thus, not only should the synthesis of analogues and potentially more active compounds be possible, but the methods developed during the course of the synthesis should also expand the repertoire of the synthetic chemist.



1

Angew. Chem. **2002**, *114*, 4391 – 4393

C. Schneider* .... 4217 – 4219

First De Novo Synthesis of the Bisindole Alkaloid Vinblastine

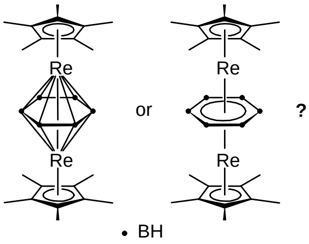
Keywords: alkaloids • asymmetric synthesis • radical reactions • total synthesis • vinblastine

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

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
Porphyrazines as Molecular Scaffolds: Periphery–Core Spin Coupling Between Metal Ions of a Schiff Base Porphyrazine	M. Zhao, C. Stern, A. G. M. Barrett,* B. M. Hoffman*
Beyond the Icosahedron: The First 13-Vertex Carborane	A. Burke, D. Ellis, B. T. Giles, B. E. Hodson, S. A. Macgregor, G. M. Rosair, A. J. Welch*
Topomerization of a Distorted-Rhomboid Tetraborane(4) and its Hydroboration to a Pentaborane(7)	C. Präsang, M. Hofmann, G. Geiseler, W. Massa, A. Berndt*
A New Diversity-Oriented Synthesis of α-Amino Acid Derivatives by a Silyltelluride-Mediated Radical Coupling Reaction of Imines and Isonitriles	S. Yamago,* H. Miyazoe, T. Nakayama, M. Miyoshi, J. Yoshida
Facile Solid-State Synthesis of Highly Conducting Poly(ethylenedioxythiophene)	H. Meng, D. F. Perepichka, F. Wudl*

Cluster or triple-decker—that is the question! The recently described electron-deficient metallaboranes $[\{(C_5Me_5)Re\}_2B_nH_n]$ ($n = 6-10$; see scheme) conform neither to the Wade-Mingos' rules for clusters nor to the 18-valence-electron rule as applied to triple-decker sandwich complexes. Does this mean that these rules are no longer valid?



Angew. Chem. **2002**, *114*, 4394 – 4397

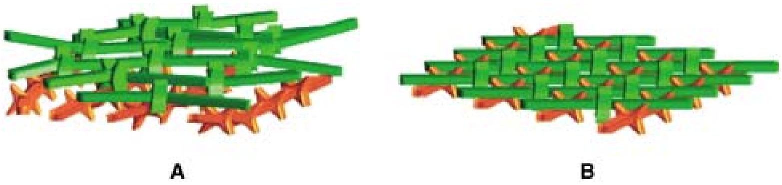
H. Wadepohl* .... 4220 – 4223

Hypoelectronic Dimetallaboranes

Keywords: cluster compounds · electron-counting rules · isolobal relationships · metallaboranes · triple-decker sandwich complexes

COMMUNICATIONS

Chiral network: Poly(phenylacetylene) chains were derivatized with chiral side chains and bulky pentiptycene groups to give interlocking optically active aggregates (see figure; **A** forms initially and the aggregate then tightens to form **B**) in both solution and solid state. The resultant grid is a stable organization with high optical activity, high quantum yields, and superior detection limits for trinitrotoluene.



Angew. Chem. **2002**, *114*, 4399 – 4404

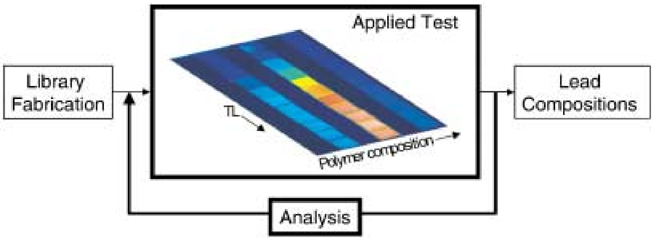
S. Zahn, T. M. Swager* ..... 4225 – 4230

Three-Dimensional Electronic Delocalization in Chiral Conjugated Polymers

Keywords: circular dichroism · fluorescence spectroscopy · materials science · polymers · supramolecular chemistry

---

A new general high-throughput screening approach is described that incorporates performance testing of materials arrays at multiple levels (see scheme; TL = test level). This approach is essential when intrinsic properties of materials do not provide knowledge about their long-term performance. The approach is illustrated by fluorescence screening of polymer compositions for their weathering, providing materials ranking up to 800 times faster than by traditional methods.



Angew. Chem. **2002**, *114*, 4404 – 4407

R. A. Potyrailo,*
J. E. Pickett .... 4230 – 4233

High-Throughput Multilevel Performance Screening of Advanced Materials

Keywords: analytical methods · combinatorial chemistry · high-throughput screening · materials science

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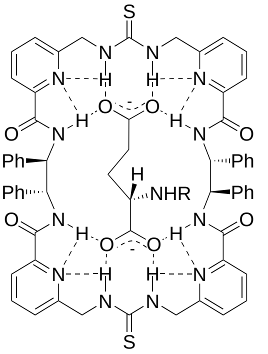
Solvation of the macrocycle by polar solvents leads to strong binding of an *N*-protected excitatory amino acid neurotransmitter. A 1:1 complex forms highly enantioselectively between the macrocycle and *N*-Boc-L-glutamate (as the dicarboxylate anion, see picture) in CH_3CN and DMSO (with a larger entropic driving force for binding), but no binding occurs in the less competitive solvent $CDCl_3$.



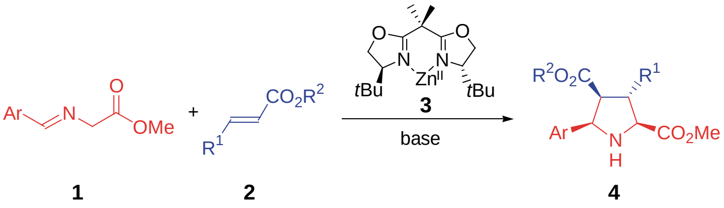
Angew. Chem. **2002**, *114*, 4407 – 4409

S. Rossi, G. M. Kyne, D. L. Turner,
N. J. Wells, J. D. Kilburn* ... 4233 – 4236

A Highly Enantioselective Receptor for *N*-Protected Glutamate and Anomalous Solvent-Dependent Binding Properties

Keywords: amino acids · enantioselectivity · glutamate · receptors · solvent effects

Highly substituted pyrrolidines 4 are formed in a highly diastereo- and enantioselective 1,3-dipolar cycloaddition reaction of azomethine ylides with electron-deficient alkenes **2**. The azomethine ylides are generated from glycinates **1** catalyzed by a chiral zinc(II) bisoxazoline catalyst **3**.



Angew. Chem. **2002**, *114*, 4410 – 4412

A. S. Gothelf, K. V. Gothelf, R. G. Hazell, K. A. Jørgensen* . . . . 4236 – 4238

Catalytic Asymmetric 1,3-Dipolar Cycloaddition Reactions of Azomethine Ylides—A Simple Approach to Optically Active Highly Functionalized Proline Derivatives

Keywords: asymmetric catalysis · cycloaddition · nitrogen heterocycles · ylide · zinc

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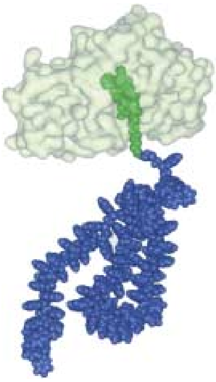
Controlled modification of horseradish peroxidase with an apolar polymer chain (see figure) by cofactor reconstitution leads to giant amphiphiles, which form vesicular aggregates in aqueous solution.



Angew. Chem. **2002**, *114*, 4413 – 4415

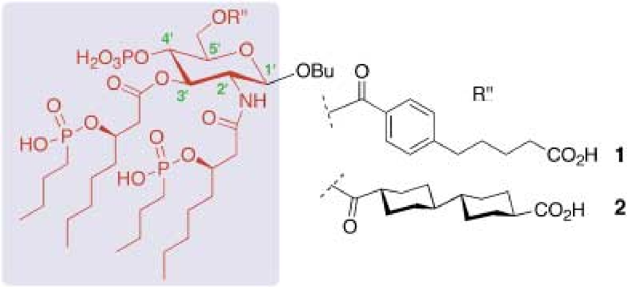
M. J. Boerakker, J. M. Hannink, P. H. H. Bomans, P. M. Frederik, R. J. M. Nolte,* E. M. Meijer, N. A. J. M. Sommerdijk* . . . . 4239 – 4241

Giant Amphiphiles by Cofactor Reconstitution

Keywords: aggregation · amphiphiles · enzyme catalysis · enzymes · polymers

---

Septic shock may be treated by this new immunomodulatory approach: Active immunization of mice (three strains) with synthetic lipid X bisphosphonate glycoconjugates **1** and **2** resulted in significant protection (up to 94 %) against a sublethal challenge of lipid A (from *E. coli* serotype *O111:B4*).



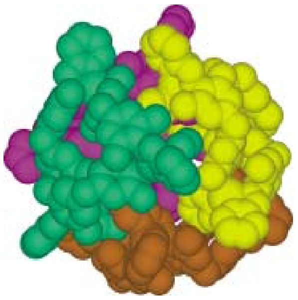
Angew. Chem. **2002**, *114*, 4415 – 4418

L. H. Jones, L. J. Altobell III, M. T. MacDonald, N. A. Boyle, P. Wentworth, Jr.,* R. A. Lerner, K. D. Janda* . . . . 4241 – 4244

Active Immunization with a Glycolipid Transition State Analogue Protects against Endotoxic Shock

Keywords: endotoxicosis · glycoconjugates · immunochemistry · lipid A

Bowls to balls: Triangular bowl-shaped copper(I) circular helicates based on pyridylimine ligands are assembled by mixing readily available reagents. The bowl-shaped topography of the triangles controls the supramolecular aggregation of four of these units into a chiral tetrameric ball-shaped structure (see picture) held together by face – edge (CH ··· π) π interactions and CH ··· F interactions.



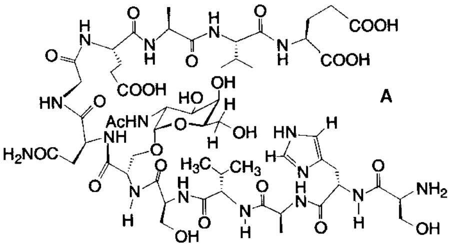
Angew. Chem. **2002**, *114*, 4418 – 4421

L. J. Childs, N. W. Alcock, M. J. Hannon* . . . . 4244 – 4247

Assembly of a Nanoscale Chiral Ball through Supramolecular Aggregation of Bowl-Shaped Triangular Helicates

Keywords: copper · helical structures · nanostructures · self-assembly · supramolecular chemistry

The conformation in water of synthetic (glyco)peptides from the recognition domain of E-cadherin determines how they interact with transformed keratinocytes. Among a peptide, a cycloglycopeptide, and a linear glycopeptide with identical sequences, only the glycopeptide with the preferred conformation **A** can induce cell differentiation.



Angew. Chem. **2002**, *114*, 4423–4426

J. Habermann, K. Stüber, T. Skripko,
T. Reipen, R. Wieser,
H. Kunz* 4249–4252

Induction of Cell Differentiation in Transformed Keratinocytes by Synthetic (Glyco)peptides from the Homophilic Recognition Domain of E-Cadherin

Keywords: cell differentiation · cycloglycopeptides · E-cadherin · glycopeptides · solid-phase synthesis

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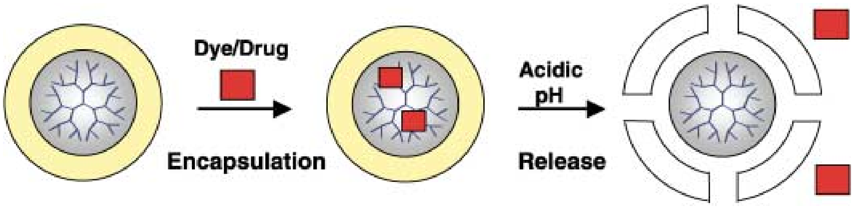
A simple and efficient concept has been developed for the synthesis of pH-responsive molecular nanocarriers based on commercially available hyperbranched polymers. These dendritic core-shell architectures can encapsulate, transport, and selectively release polar guest molecules in an acidic environment (pH 3–6, see scheme). The observed release properties render these molecular nanocarriers promising candidates for controlled drug and gene delivery.



Angew. Chem. **2002**, *114*, 4426–4431

M. Krämer, J.-F. Stumbé, H. Türk,
S. Krause, A. Komp, L. Delineau,
S. Prokhorova, H. Kautz,
R. Haag* 4252–4256

pH-Responsive Molecular Nanocarriers Based on Dendritic Core-Shell Architectures

Keywords: dendrimers · drug delivery · micelles · polymers · supramolecular chemistry

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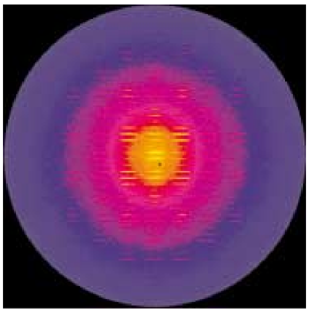
Two in one: Only the combination of the analysis of diffuse X-ray scattering (see picture) and high-resolution electron microscopy reveals that the structure of $Tb_{13}Br_{18}B_3$ consists of discrete clusters as well as chains of condensed clusters.



Angew. Chem. **2002**, *114*, 4431–4433

O. Oeckler, L. Kienle, H. Mattausch,
A. Simon* 4257–4259

$Ln_{13}Br_{18}B_3$ (Ln = Gd, Tb)—A Compound Containing a Combination of Discrete and Condensed Clusters

Keywords: boron · cluster compounds · electron microscopy · lanthanides · solid-state structures

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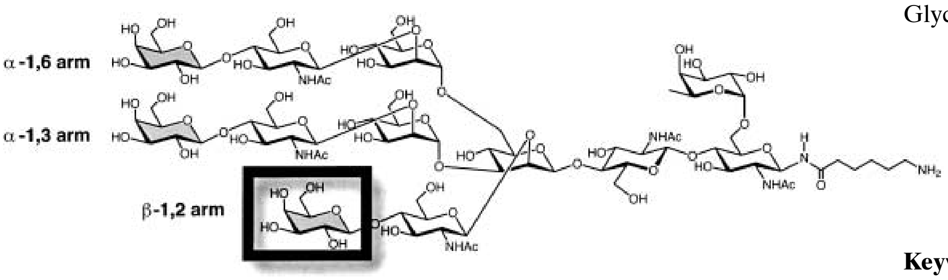
Three arms carry more than two: By the total synthesis of the entire oligosaccharide, the proposed structure of the LEC14 antigen from a CHO cell line was confirmed. Surprisingly, enzymatic galactosylation of LEC14 gave the shown compound, which has a novel three-armed structural motif.



Angew. Chem. **2002**, *114*, 4434–4437

I. Prahl, C. Unverzagt* 4259–4262

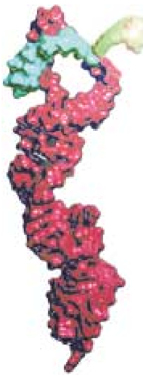
Enzymatic Elongation of the LEC14 Antigen Generates a β-1,2 Arm on *N*-Glycans

Keywords: glycans · glycosides · glycosylation · oligosaccharides · total synthesis

1433-7851/02/4122-4161 $ 20.00+.50/0

By fusing an aptamer to a ribozyme, an aptazyme was constructed (see picture) which sensitively and specifically detects the presence of HIV-1 reverse transcriptase (RT). The fusion construct not only serves as a biosensor, but is also well suited for screening lead structures binding to the primer/template binding site of HIV-1 RT.

Angew. Chem. **2002**, *114*, 4440 – 4444



J. S. Hartig, M. Famulok* ... 4263 – 4266

Reporter Ribozymes for Real-Time Analysis of Domain-Specific Interactions in Biomolecules: HIV-1 Reverse Transcriptase and the Primer – Template Complex

Keywords: hammerhead ribozyme • proteins • reverse transcriptase • ribozymes • RNA • RNA – protein interactions

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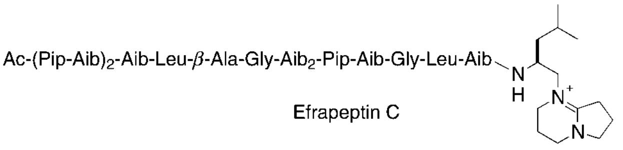
Synthetically challenging, the efrapeptins are a class of peptide antibiotics rich in α,α-dialkylated amino acids. Efrapeptin C (see picture) was synthesized for the first time by a combination of solution-phase and solid-phase peptide synthesis steps with segment condensations.



Efrapeptin C

Angew. Chem. **2002**, *114*, 4438 – 4440

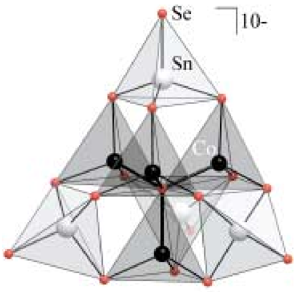
M. Jost, J.-C. Greie, N. Stemmer,
S. D. Wilking, K. Altendorf,
N. Sewald* .... 4267 – 4269

The First Total Synthesis of Efrapeptin C

Keywords: α-aminoisobutyric acid • efrapeptins • peptides • solid-phase synthesis • total synthesis

---

A water and methanol mixture permits the transfer of the tin – chalcogen substructure of chalcogenostannate anions into the coordination sphere of transition-metal ions without decomposition. The reaction of $K_4[SnSe_4]$ with $[Co(en)_3]Cl_3$ yields compound **1**, which contains highly charged, purely inorganic ternary anions.



1

Angew. Chem. **2002**, *114*, 4444 – 4447

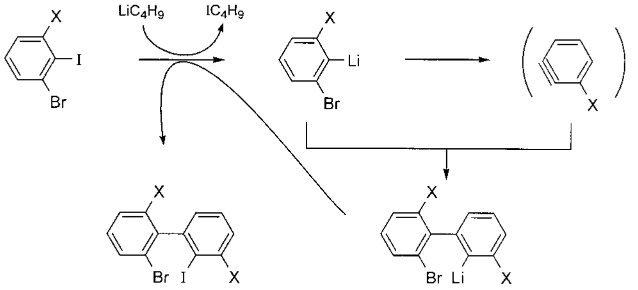
C. Zimmermann, M. Melullis,
S. Dehnen* .... 4269 – 4272

Reactivity of Chalcogenostannate Salts: Unusual Synthesis and Structure of a Compound Containing Ternary Cluster Anions $[Co_4(\mu_4\text{-}Se)(SnSe_4)_4]^{10-}$

Keywords: chalcogens • cluster compounds • cobalt • density functional calculations • stannates • structure elucidation

---

1,2-Didehydroarenes (“arynes”) mediate as extremely reactive, short-lived intermediates in selective aryl – aryl coupling processes to form biaryls with unprecedented substituent patterns (see scheme, X = H, F, Cl). Possible applications include the synthesis of novel ligands for asymmetric catalysis.



Angew. Chem. **2002**, *114*, 4447 – 4450

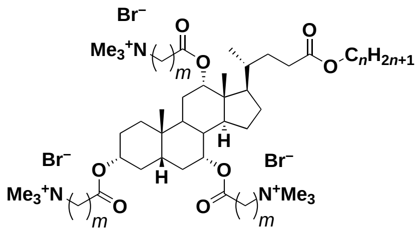
F. Leroux, M. Schlosser* .... 4272 – 4274

The “Aryne” Route to Biaryls Featuring Uncommon Substituent Patterns

Keywords: aryl – aryl coupling • arynes • atropisomerism • biaryls • lithium reagents

Charged trident: A new facial amphiphile (see structure) based on cholic acid and with a permanent ionic character was prepared. The aggregation of this three-headed surfactant into small micelles and its inhibitory effect on bacterial growth are presented.

Angew. Chem. **2002**, *114*, 4451 – 4453



H. M. Willemen, L. C. P. M. de Smet,
A. Koudijs, M. C. A. Stuart,
I. G. A. M. Heikamp-de Jong,
A. T. M. Marcelis,*
E. J. R. Sudhölter .... 4275 – 4277

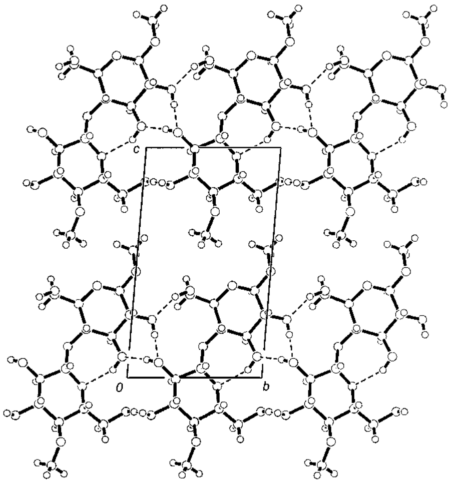
Micelle Formation and Antimicrobial Activity of Cholic Acid Derivatives with Three Permanent Ionic Head Groups

Keywords: amphiphiles · antibiotics · cholic acid · micelles · self-assembly

---

A parallel arrangement of molecules (see figure) that can be compared to the proposed models of native cellulose I is found in crystals of triclinic methyl 4-*O*-methyl-β-D-glucopyranosyl-(1-4)-β-D-glucopyranoside. This cellobiose derivative crystallizes in the triclinic space group *P*1 and the monoclinic space group $P2_1$.

Angew. Chem. **2002**, *114*, 4453 – 4457



A. Rencurosi, J. Röhrling, J. Pauli,
A. Potthast, C. Jäger, S. Pérez, P. Kosma,
A. Imberty* .... 4277 – 4281

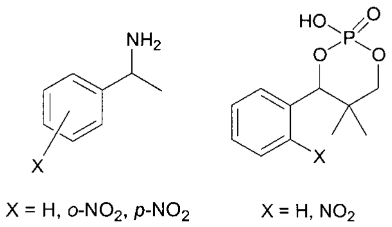
Polymorphism in the Crystal Structure of the Cellulose Fragment Analogue Methyl 4-*O*-Methyl-β-D-Glucopyranosyl-(1-4)-β-D-Glucopyranoside

Keywords: carbohydrates · cellobiose · cellulose · polymorphism

---

Not double Dutch! The resolution of racemates with families of structurally related resolving agents (see examples depicted) is termed Dutch Resolution. Certain family members are regularly not incorporated; these turn out to be nucleation inhibitors. This leads to a simplified, two-component resolution procedure with a high chance of initial success.

Angew. Chem. **2002**, *114*, 4457 – 4462



J. W. Nieuwenhuijzen,
R. F. P. Grimbergen, C. Koopman,
R. M. Kellogg,* T. R. Vries,* K. Pouwer,
E. van Echten, B. Kaptein, L. A. Hulshof,
Q. B. Broxterman* .... 4281 – 4286

The Role of Nucleation Inhibition in Optical Resolutions with Families of Resolving Agents

Keywords: chiral resolution · chirality · combinatorial chemistry

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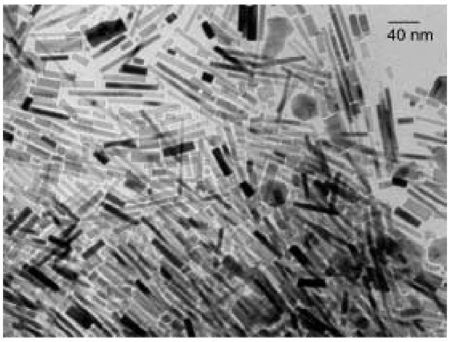
The shape of things to come: Nanospheres, thermodynamically stable nanorods, and nanowires are selectively produced in solution from $[Co(\eta^3\text{-}C_8H_{13})(\eta^4\text{-}C_8H_{12})]$ in the presence of oleic acid and various amines. The aspect ratio of the nanorods is controlled by the length of the alkyl chain of the amine. Nanorods with approximate dimensions of 9 × 40 nm (see Figure) are ferromagnetic at room temperature.

Angew. Chem. **2002**, *114*, 4462 – 4465

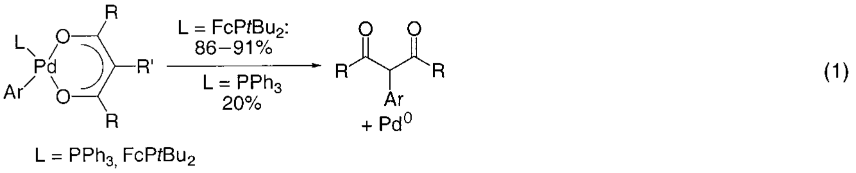


F. Dumestre, B. Chaudret,* C. Amiens,
M.-C. Fromen, M.-J. Casanove,
P. Renaud, P. Zurcher .... 4286 – 4289

Shape Control of Thermodynamically Stable Cobalt Nanorods through Organometallic Chemistry

Keywords: cobalt · magnetic properties · nanostructures · organometallic synthesis · self-assembly

Steric hindrance of the ancillary phosphane ligand triggers reductive elimination from aryl palladium complexes of typically unreactive ligands derived from 1,3-dicarbonyl anions [Eq. (1); $FcPtBu_2$ = di-*tert*-butylphosphanylferrocene]. This reaction is the product-forming step of the recently developed palladium-catalyzed malonate arylations.



Angew. Chem. **2002**, *114*, 4465–4467

J. P. Wolkowski,
J. F. Hartwig* 4289–4291

Generation of Reactivity from Typically Stable Ligands: C–C Bond-Forming Reductive Elimination from Aryl Palladium(II) Complexes of Malonate Anions

Keywords: arylation · C–C coupling · elimination · malonate · palladium

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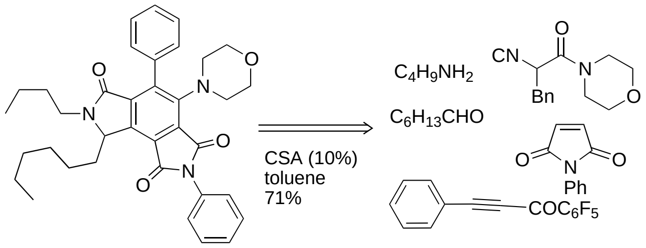
Seven functional groups are involved in a highly ordered five-component domino process, which leads to a biologically relevant polyheterocycle. In this one-pot transformation, the formation of seven chemical bonds provides a hexasubstituted benzene core (see scheme; CSA = camphorsulfonic acid).



Angew. Chem. **2002**, *114*, 4467–4470

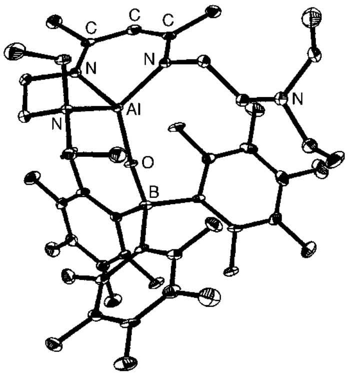
P. Janvier, H. Bienaymé,
J. Zhu* 4291–4294

A Five-Component Synthesis of Hexasubstituted Benzene

Keywords: cycloaddition · domino reactions · heterocycles · multicomponent reactions · synthetic methods

---

Stabilization of the presumed Al–O double bond in $LAlO \cdot B(C_6F_5)_3$, the simplest member of the alumoxane series, was achieved by the strong Lewis acid $B(C_6F_5)_3$. $LAlO \cdot B(C_6F_5)_3$ was synthesized by hydrolysis of $LAlMe_2$ with $H_2O \cdot B(C_6F_5)_3$ and characterized by X-ray structure analysis (see picture) L = $Et_2NCH_2CH_2NC(Me)CHC(Me)NCH_2CH_2NEt_2$.



Angew. Chem. **2002**, *114*, 4470–4472

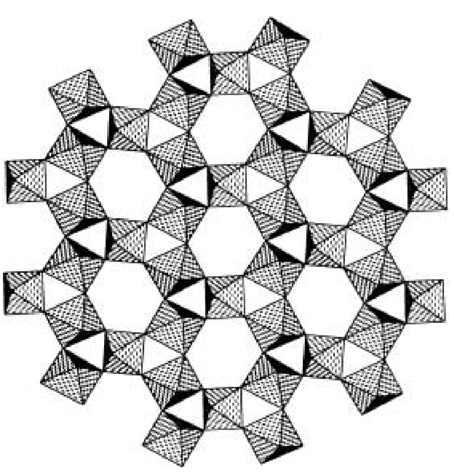
D. Neculai, H. W. Roesky,*
A. M. Neculai, J. Magull, B. Walfort,
D. Stalke 4294–4296

Formation and Characterization of the First Monoalumoxane, $LAlO \cdot B(C_6F_5)_3$

Keywords: aluminum · Lewis acids · monoalumoxane · multiple bonds

---

A perfect Kagomé lattice is displayed by the mixed-valent layered structure of $[HN(CH_2)_6NH][Fe^{III}Fe^{II}_2F_6(SO_4)_2] \cdot [H_3O]$ (see picture), in which 100% of the iron sites are occupied. The complex exhibits unusual magnetic properties; both magnetic frustration and ferrimagnetic behavior are observed.



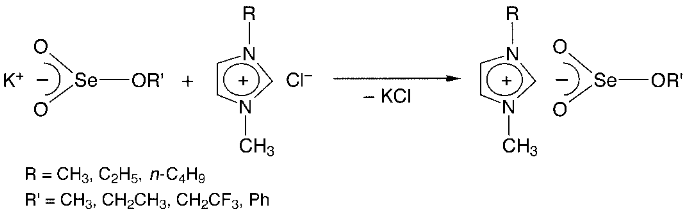
Angew. Chem. **2002**, *114*, 4473–4476

G. Paul, A. Choudhury,
E. V. Sampathkumaran,
C. N. R. Rao* 4297–4300

Organically Templated Mixed-Valent Iron Sulfates Possessing Kagomé and Other Types of Layered Networks

Keywords: hydrothermal synthesis · iron · Kagomé lattice · layered structures · magnetic properties

Highly active catalysts for the carbonylation of a variety of substrate materials have been prepared in the form of selenium-containing ionic liquids. Products from the reactions of [$KSeO_2(OCH_3)$] and 1-alkyl-3-methylimidazolium chlorides (see scheme) exhibit surprisingly high activity for the oxidative carbonylation of aniline, even at temperatures as low as 40 °C.



Angew. Chem. **2002**, *114*, 4476 – 4479

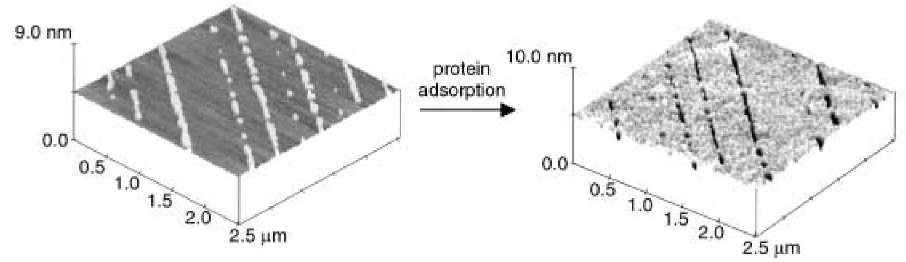
H. S. Kim,* Y. J. Kim, H. Lee, K. Y. Park, C. Lee, C. S. Chin .... 4300 – 4303

Ionic Liquids Containing Anionic Selenium Species: Applications for the Oxidative Carbonylation of Aniline

Keywords: carbonylation • cyclic voltammetry • homogeneous catalysis • ionic liquids • selenium

---

Selective adsorption of human serum albumin and human γ globulin to the liquidlike phase of chemically homogeneous, mixed phospholipid monolayers supported on a solid surface gives rise to arrays of linear 150 – 200-nm-wide grooves (see images). The protein-covered areas could be metallized by the adsorption of Au nanoparticles.



Angew. Chem. **2002**, *114*, 4479 – 4482

P. Moraille, A. Badia* ...... 4303 – 4306

Spatially Directed Protein Adsorption by Using a Novel, Nanoscale Surface Template

Keywords: adsorption • monolayers • nanostructures • phospholipids • proteins

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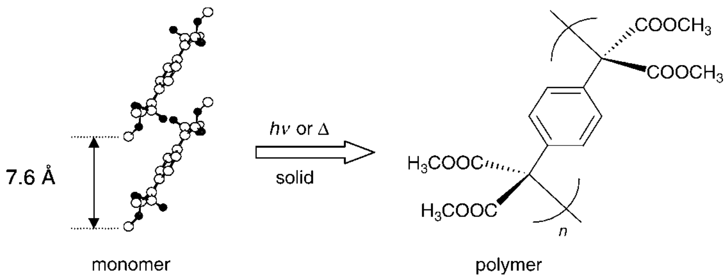
The difference in the crystal-packing mode of a monomer can significantly affect its polymerization reactivity. Synthesis of 7,7,8,8-tetrakis(methoxycarbonyl)quinodimethane (**1**) afforded two polymorphs: prisms (**1a**), and needles (**1b**). The former, **1a**, polymerized topochemically under thermal polymerization and photopolymerization (see scheme) but **1b** did not.



Angew. Chem. **2002**, *114*, 4482 – 4485

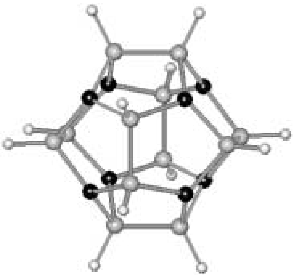
T. Itoh,* S. Nomura, T. Uno, M. Kubo, K. Sada, M. Miyata* .... 4306 – 4309

Topochemical Polymerization of 7,7,8,8-Tetrakis(methoxycarbonyl)quinodimethane

Keywords: polymerization • polymorphism • quinodimethanes • topochemistry

1433-7851/02/4122-4165 $ 20.00+.50/0

The $2(N+1)^2$ electron-counting rule for spherical aromaticity can also be applied to spherical homoaromatic systems: The adamantane-, cubane-, and dodecahedrane-based species containing two or eight delocalized electrons were designed by bridging the sp^2 carbon atoms of highly symmetrical (T_d, T_h) carbon polyhedrane units. Their aromatic character was demonstrated by the highly negative nucleus-independent chemical shift (NICS) values at the cage centers, for example $C_{20}H_{12}$ (see picture) has an NICS value of −36.4 ppm.



Angew. Chem. **2002**, *114*, 4485–4488

Z. Chen, H. Jiao, A. Hirsch,*
P. von Ragué Schleyer* 4309–4312

Spherical Homoaromaticity

Keywords: aromaticity • cage compounds • electron-counting rules • NICS • spherical homoaromaticity

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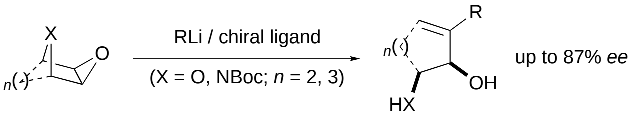
Enantioselective generation and intermolecular trapping of a lithium carbenoid occurs in the reaction of epoxides of 2,5-dihydrofuran, 2,5-dihydropyrrole, and oxa- and aza-bicyclo[*n*.2.1]alkenes ($n = 2, 3$) with organolithium compounds in the presence of external chiral ligands. This methodology leads to the synthesis of important unsaturated diol and amino alcohol functionality (see scheme; *tert*-butoxycarbonyl).



Angew. Chem. **2002**, *114*, 4489–4492

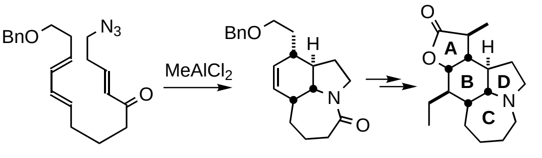
D. M. Hodgson,* C. R. Maxwell,
T. J. Miles, E. Paruch, M. A. H. Stent,
I. R. Matthews, F. X. Wilson,
J. Witherington 4313–4316

Enantioselective Alkylative Double Ring Opening of Epoxides: Synthesis of Enantioenriched Unsaturated Diols and Amino Alcohols

Keywords: alkenes • amino alcohols • diols • enantioselectivity • epoxides

---

Four stereocenters and three rings are established in one step in a new formal synthesis of (±)-stenine (see scheme). This key reaction cascade consists of an intramolecular Diels–Alder reaction followed by an intramolecular Schmidt reaction. The resulting tricyclic intermediate was readily transformed into a known intermediate en route to stenine, thus completing the formal synthesis.



(±)-stenine

Angew. Chem. **2002**, *114*, 4492–4494

J. E. Golden, J. Aubé* 4316–4318

A Combined Intramolecular Diels–Alder/Intramolecular Schmidt Reaction: Formal Synthesis of (±)-Stenine

Keywords: Diels–Alder reaction • domino reactions • lactams • natural products • ring expansion

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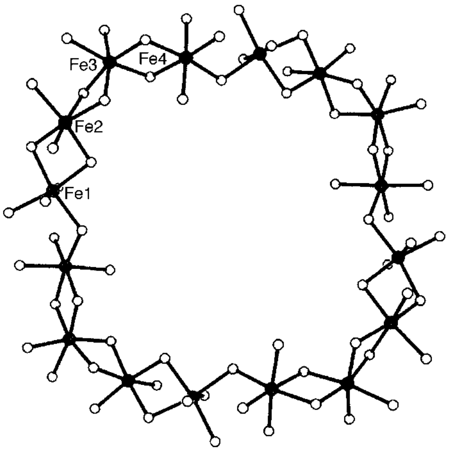
Wheels of iron: The synthesis, structure, and initial magnetic properties of two new ferric wheels are reported; these are the first examples of unsupported octametallic and hexadecametallic (see picture) iron wheels.



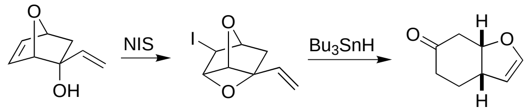
Angew. Chem. **2002**, *114*, 4494–4497

L. F. Jones, A. Batsanov, E. K. Brechin,*
D. Collison,* M. Helliwell, T. Mallah,
E. J. L. McInnes, S. Piligkos . 4318–4321

Octametallic and Hexadecametallic Ferric Wheels

Keywords: cluster compounds • EPR spectroscopy • iron • magnetic properties • metal–metal interactions

A radical alternative to the anionic oxy-Cope rearrangement is reported (e.g., see scheme; NIS = *N*-iodosuccinimide). In contrast to the sigmatropic rearrangement, this nonconcerted fragmentation–cyclization process is independent of the stereochemistry of the starting material.



Angew. Chem. **2002**, *114*, 4497–4499

R. Chuard, A. Giraud,
P. Renaud* 4321–4323

A Radical Alternative to the Anionic Oxy-Cope Rearrangement

Keywords: domino reactions · radical reactions · sigmatropic rearrangement

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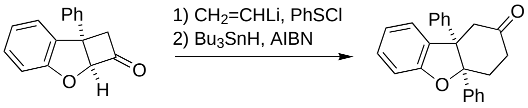
The two-carbon ring expansion of cycloalkanones is now possible in a two-step procedure. This procedure is based on an unusual cascade reaction that consists of a [2,3]-sigmatropic rearrangement (Mislow–Braverman–Evans rearrangement) of an allylic sulfoxide followed by a radical fragmentation–cyclization process (see scheme; AIBN = azobisisobutyronitrile).



Angew. Chem. **2002**, *114*, 4499–4501

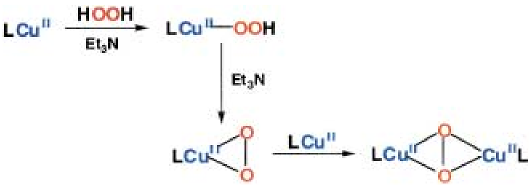
R. Chuard, A. Giraud,
P. Renaud* 4323–4325

Allyl Sulfoxides as Precursors for Radical Two-Carbon Ring Expansion of Cyclobutanones

Keywords: ketones · radical reactions · ring expansion · sigmatropic rearrangement · sulfoxides

---

A mononuclear (η^2-peroxo)copper(II) complex is observed in the reaction of H_2O_2 and a copper(II) complex supported by a tridentate pyridylethylamine ligand (see scheme). The formation of this unprecedented intermediate species can be followed at −90 °C by EPR and UV/Vis absorption spectroscopy.



Angew. Chem. **2002**, *114*, 4501–4504

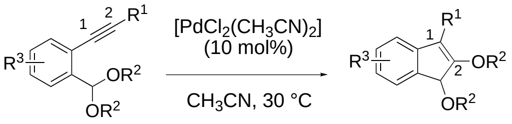
T. Osako, S. Nagatomo, Y. Tachi,
T. Kitagawa, S. Itoh* 4325–4328

Low-Temperature Stopped-Flow Studies on the Reactions of Copper(II) Complexes and H_2O_2: The First Detection of a Mononuclear Copper(II)–Peroxo Intermediate

Keywords: copper · kinetics · ligand effects · peroxides · stopped-flow studies

---

Activated ethers: The shown reaction of the dialkylacetals **1** gave the carboalkoxylation products **2** in high to moderate yields. Mechanistic investigation revealed that the reaction proceeded through the addition of an acetal C–O bond to the C–C triple bond, followed by an unprecedented rearrangement of an alkynyl group substituent.



1 **2**

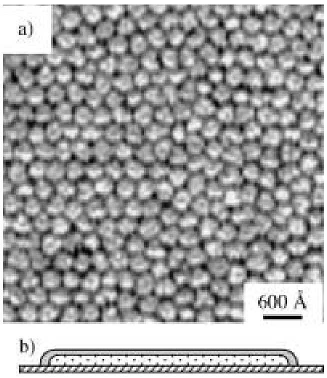
Angew. Chem. **2002**, *114*, 4504–4507

I. Nakamura, G. B. Bajracharya,
Y. Mizushima,
Y. Yamamoto* 4328–4331

Indenol Ether Formation from Aryl Alkynes Bearing *ortho*-Acetals: An Unprecedented Rearrangement in Palladium-Catalyzed Carboalkoxylation

Keywords: acetals · alkynes · palladium · rearrangement · synthetic methods

A small nonpolar amphiphile, namely, the semifluorinated alkane $C_8F_{17}C_{16}H_{33}$, forms monodisperse surface micelles [ca. 300 Å in diameter; see AFM image (a)] in which the fluorinated segments point outwards and the hydrocarbon segments inwards. A disklike model (b) allows the micelle size to be predicted from the lengths of the fluorinated and hydrocarbon segments of such molecules.



Angew. Chem. **2002**, *114*, 4507 – 4510

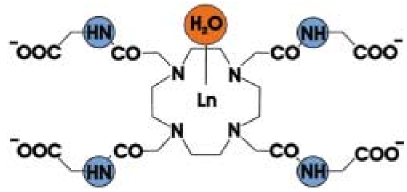
M. Maaloum, P. Muller,
M. P. Krafft* .... 4331 – 4334

Monodisperse Surface Micelles of Nonpolar Amphiphiles in Langmuir Monolayers

Keywords: amphiphiles · micelles · monolayers · self-assembly · semifluorinated alkanes

---

Attractive alternatives to conventional contrast agents for magnetic resonance imaging applications are the paramagnetic chemical exchange saturation transfer (CEST) agents based on saturation transfer (ST) to the solvent water resonance. The ratio of ST effects obtained upon irradiating Ln-coordinated water and amide protons in [Ln(dotamGly)] (dotam = 1,4,7,10-tetrakis(carbamoylmethyl)-1,4,7,10-tetrazacyclododecane; see picture) complexes is pH dependent and concentration independent.



Angew. Chem. **2002**, *114*, 4510 – 4512

S. Aime,* D. Delli Castelli,
E. Terreno .... 4334 – 4336

Novel pH-Reporter MRI Contrast Agents

Keywords: imaging agents · lanthanides · NMR spectroscopy · pH sensors · saturation transfer

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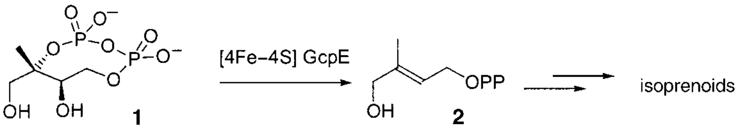
One of the last bottlenecks in the elucidation of the methylerythritol phosphate pathway for isoprenoid biosynthesis has been solved. A [4Fe – 4S] cluster is the prosthetic group of the GcpE protein from *E. coli*. This enzyme is involved in the conversion of **1** into **2**, through two successive one-electron transfers.



Angew. Chem. **2002**, *114*, 4513 – 4515

M. Seemann, B. T. S. Bui, M. Wolff,
D. Tritsch, N. Campos, A. Boronat,
A. Marquet, M. Rohmer* ... 4337 – 4339

Isoprenoid Biosynthesis through the Methylerythritol Phosphate Pathway: The (*E*)-4-Hydroxy-3-methylbut-2-enyl Diphosphate Synthase (GcpE) is a [4Fe – 4S] Protein

Keywords: biosynthesis · electron transfer · enzymes · isoprenoids

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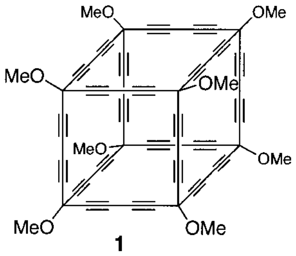
Formal insertion of buta-1,3-diynediyl moieties into all twelve C–C single bonds of octamethoxycubane gives the explosive expanded cubane **1**. Fourier-transform ion-cyclotron-resonance (FT-ICR) mass spectrometric studies show that **1** readily loses its eight MeO groups and subsequently rearranges into fullerene ions. In the positive ion mode, these ions undergo fullerene coalescence reactions.



1

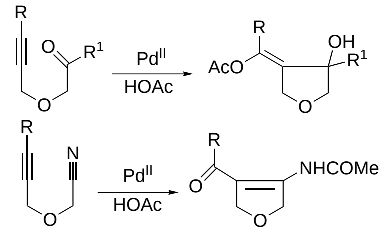
Angew. Chem. **2002**, *114*, 4515 – 4519

P. Manini, W. Amrein, V. Gramlich,
F. Diederich* .... 4339 – 4343

Expanded Cubane: Synthesis of a Cage Compound with a C_{56} Core by Acetylenic Scaffolding and Gas-Phase Transformations into Fullerenes

Keywords: alkynes · cage compounds · cubanes · fullerenes · mass spectrometry

The insertion of carbonyl or nitrile units into a carbon–palladium bond has been achieved under mild reaction conditions (see scheme). The Pd^{II}-catalyzed system, which does not require organometallic reagents, redox systems, or additives to obtain a high yield of cyclized product, is effective with a wide variety of functionalized alkyne compounds.



Angew. Chem. **2002**, *114*, 4519–4521

L. Zhao, X. Lu* 4343–4345

Pd^{II}-Catalyzed Cyclization of Alkynes Containing Aldehyde, Ketone, or Nitrile Groups Initiated by the Acetoxypalladation of Alkynes

Keywords: carbonyl ligands · insertion · nitrile group · N ligands · palladium

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

* Author to whom correspondence should be addressed

Accelerated publications

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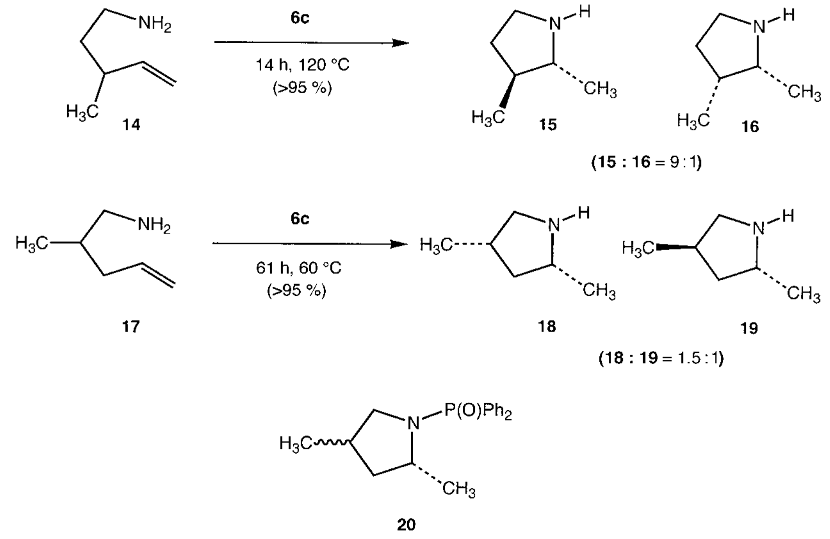
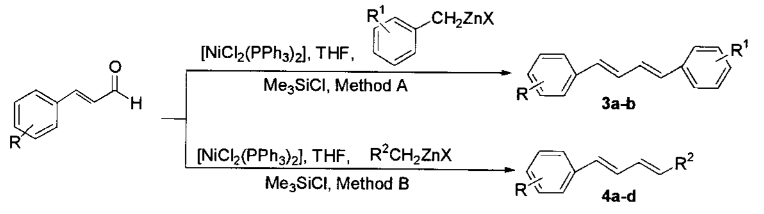
CORRIGENDA

In the Review by **A. Schnepf** and **H. Schnöckel** in Issue 19, **2002**, pp. 3533–3552, two formulas were accidentally swapped in Section 4.4.2. The cluster $[Ga_{10}R_6]^-$ (R = Si*t*Bu) should be number **23** and the cluster $[Ga_{10}R_6]$ (R = $Si(SiMe_3)_3$) should be number **22**.

In the Communication by **Y. K. Kim** and **T. Livinghouse** in Issue 19, **2002**, pp. 3645–3647, the incorrect complex number was printed above the reaction arrows in Scheme 4: **6f** should be replaced by **6c**. The editorial team apologizes for this error.



In the Communication by **J.-X. Wang et al.** in Issue 15, **2002**, pp. 2757–2760 the lower section of Scheme 1 should have appeared as follows:



In addition, the compounds labeled **1**–**8** in Scheme 2 are distinct from any other numbered species in either the main text, the Experimental Section, or the Supporting Information.