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2001
40/12
Pages 2185–2362

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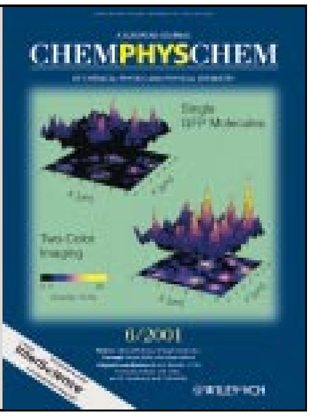
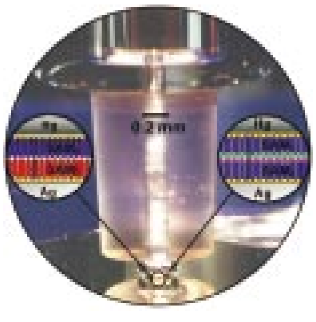
ChemPhysChem* 6/2001 is bound in this issue of *Angewandte Chemie.



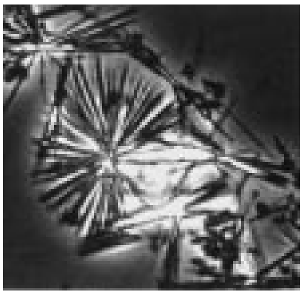
CHEMPHYSCHEM
6/2001

COVER PICTURE

The cover picture shows a Hg-SAM_1//SAM_2-Ag nanojunction, which allows the rapid screening of various self-assembled monolayers (SAMs) for their electronic properties. The setup of this molecular junction, which consists of a mercury electrode with SAM_1 (top) and a silver-coated silicon wafer with SAM_2 (bottom), is simple and allows the rapid screening of various functionalized monolayers. In the picture an interfacial reflection (mirror image) of the mercury drop in the lower silver surface is observed. In this test-bed the electronic properties of various aromatic and terminally functionalized SAMs were determined and correlated with the molecular structure of the respective SAM. Further details on this nanojunction are reported by M. A. Rampi, G. M. Whitesides et al. on p. 2316 ff.



Not just the tiresome first step towards an X-ray structure analysis: There is far more to the crystallization of proteins these days. Protein crystals (see picture) can be easily produced in a stable form and their chemical and physical properties make them interesting and useful for a whole range of disciplines. They are used as industrial catalysts and for enantioselective chromatography. Possible new areas of application are, for example, the purification and formulation of biopharmaceuticals.



Angew. Chem. **2001**, *113*, 2262 – 2281

A. L. Margolin,*
M. A. Navia* .... 2204 – 2222

Protein Crystals as Novel Catalytic Materials

Keywords: biotransformations · drug research · enzyme catalysis · medicinal chemistry · protein crystals

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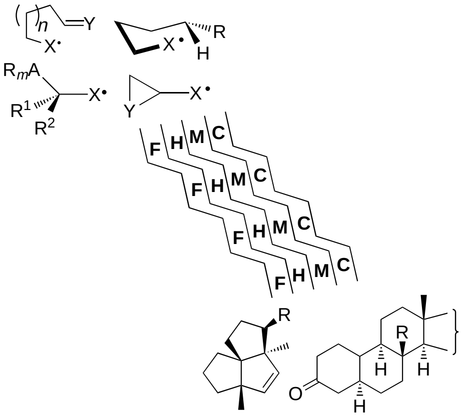
Medium-ring cycles and polycycles (see scheme) are two of the most important target structures that can be formed with the aid of unimolecular cascades of radical rearrangements. In addition to a plethora of spectacular syntheses, a convenient system for classifying free-radical cascades is presented, which is based on the mechanisms of the individual reaction steps: **F** = fragmentation, **H** = H migration, **M** = 1,2-group migration, **C** = cyclization.



Angew. Chem. **2001**, *113*, 2282 – 2307

A. J. McCarroll,
J. C. Walton* .... 2224 – 2248

Programming Organic Molecules: Design and Management of Organic Syntheses through Free-Radical Cascade Processes

Keywords: cyclizations · domino reactions · radical reactions · rearrangements · synthetic methods

VIPs

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

The Reaction Mechanism of the Enzyme-Catalyzed Central Cleavage of *β,β*-Carotene to Retinal

M. G. Leuenberger,
C. Engeloch-Jarret,
W.-D. Woggon*

Activation, Tuning, and Immobilization of Homogeneous Catalysts in an Ionic Liquid/Compressed CO_2 Continuous-Flow System

A. Bösmann, G. Franció,
E. Janssen, M. Solinas,
W. Leitner,* P. Wasserscheid*

Synthetic seco Forms of (–)-Diazonamide A

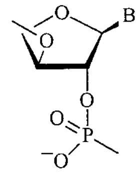
J. Li, X. Chen, A. W. G. Burgett,
P. G. Harran*

Targeting Molecular Recognition: Exploring the Dual Role of Functional Pseudo-Prolines in the Design of SH3 Ligands

G. Tuchscherer,* D. Grell,
Y. Tatsu, P. Durieux,
J. Fernandez-Carneado,
B. Hengst, C. Kardinal, S. Feller*

HIGHLIGHTS

Tracing the origins of life: TNA (see picture) shows base pairing which is similar to that of pentose-based RNA in regard to specificity, strand orientation, and pairing strength. TNA hybridizes with the natural nucleic acids RNA and DNA and is able to form hairpin structures. The potential of TNA as a genetic precursor of RNA is discussed.



Angew. Chem. **2001**, *113*, 2309–2311

P. Herdewijn* 2249–2251

TNA as a Potential Alternative to Natural Nucleic Acids

Keywords: base pairing · DNA structures · nucleic acids · oligonucleotides · threose nucleic acids

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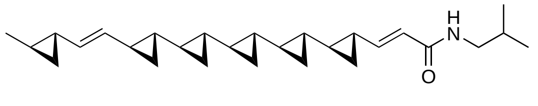
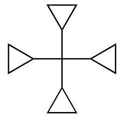
It is amazing what three carbons can do! Nature, industry, and chemists working in academia continue to explore the cyclopropane moiety from various perspectives, among them biological activity, reactivity, and synthetic methodology. Breathtaking multiple cyclopropane ring structures such as **1** and **2** have recently been prepared and represent milestones in the field of small-ring chemistry.



1



2

Angew. Chem. **2001**, *113*, 2312–2314

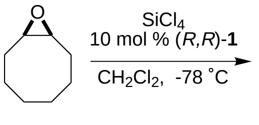
R. Faust* 2251–2253

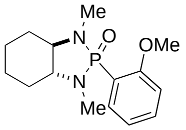
Fascinating Natural and Artificial Cyclopropane Architectures

Keywords: carbocycles · cyclopropanations · natural products · small ring systems · strained molecules

CORRESPONDENCE

The reported ability of chiral phosphonamide 1 to effect the enantioselective opening of *meso* epoxides with silicon tetrachloride has not withstood experimental verification by Denmark's group. Having reexamined the ring-opening of cyclooctene oxide (see scheme), Denmark and co-workers found a serious discrepancy between their results (81–83% recovery of the epoxide and an essentially racemic product) and those reported by Buono et al. (77% yield and >99% *ee*).





(*R*,*R*)-**1**

Angew. Chem. **2001**, *113*, 2315–2316

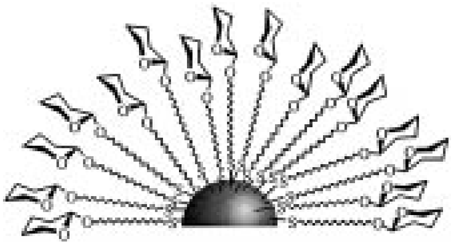
S. E. Denmark,* T. Wynn,
B. G. Jellerichs 2255–2256

Beneficial Effect of *ortho*-Methoxy Groups in the Asymmetric Ring Opening of *meso* Epoxides with Silicon Tetrachloride Catalyzed by Chiral *ortho*-Methoxyphenyldiazaphosphonamide Lewis Bases

Keywords: asymmetric catalysis · correspondence · epoxides · Lewis bases · ring opening

COMMUNICATIONS

Glycosphingolipid clustering and interactions at the cell membrane can be modeled by gold glyconanoparticles prepared with biologically significant oligosaccharides. Such water-soluble gold glyconanoparticles with highly polyvalent carbohydrate displays (see picture, gray hemisphere: gold nanoparticle) have been obtained by a simple and versatile strategy.

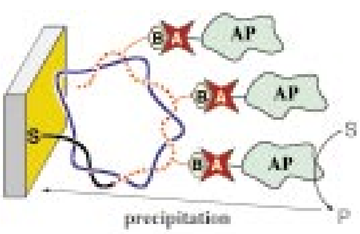


Angew. Chem. **2001**, *113*, 2318–2321

J. M. de la Fuente, A. G. Barrientos,
T. C. Rojas, J. Rojo, J. Cañada,
A. Fernández, S. Penadés* .. 2258–2261

Gold Glyconanoparticles as Water-Soluble Polyvalent Models To Study Carbohydrate Interactions

Keywords: carbohydrates · glycolipids · gold · nanoparticles · self-assembly



Replication, precipitation, and amplification: Polymerase or reverse transcriptase induced replication of DNA/RNA on a transducer (electrode or piezoelectric crystal) leads to the ultrasensitive specific electronic transduction of viral genomes. Biotin tags (B) on the double-stranded assembly provide docking sites for a conjugate between avidin (A) and an alkaline phosphatase (AP). Enzyme biocatalysis of substrate (S) to the insoluble product (P), which precipitates onto the transducer (yellow surface), provides amplification in the analysis of the target DNA.

Angew. Chem. **2001**, *113*, 2321 – 2325

F. Patolsky, A. Lichtenstein, M. Kotler, I. Willner* .... 2261 – 2265

Electronic Transduction of Polymerase or Reverse Transcriptase Induced Replication Processes on Surfaces: Highly Sensitive and Specific Detection of Viral Genomes

Keywords: biosensors · DNA replication · impedance spectroscopy · quartz-crystal microbalance · RNA replication

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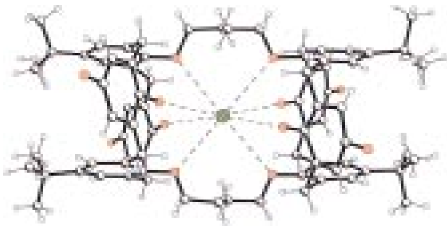

The length of the bridging alkylene chain between two calix[4]diquinone moieties determines the selectivity of the receptors for Group 1 metal ions. These redox-active receptors exhibit remarkable selectivity preferences and substantial electrochemical recognition effects towards Cs^+ and Rb^+ ions. The solid-state crystal structure of the Cs^+ complex of a bis(calix[4]diquinone) derivative is shown (green: Cs^+, red: oxygen).

Angew. Chem. **2001**, *113*, 2325 – 2328

P. R. A. Webber, G. Z. Chen, M. G. B. Drew, P. D. Beer* .. 2265 – 2268

Cesium- and Rubidium-Selective Redox-Active Bis(calix[4]diquinone) Ionophores

Keywords: alkali metals · calixarenes · ionophores · quinones · redox chemistry

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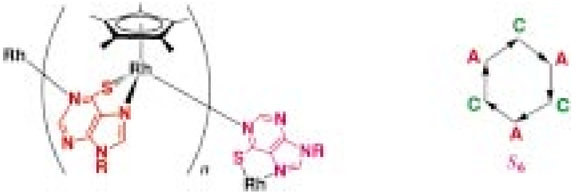
The stereoselective formation of a pseudo-S_6 hexamer resulted from the self-assembling reaction between $[Rh(Cp^*)(H_2O)_3]^{2+}$ and 6-purinethione riboside (see left structure; $Cp^* = C_5Me_5$). The schematic representation (right) shows the direction of the coordination to the S^6 and N(7) donor atoms. C (clockwise) and A (anticlockwise) indicate the chirality of each unit complex.



Angew. Chem. **2001**, *113*, 2328 – 2331

K. Yamanari,* S. Yamamoto, R. Ito, Y. Kushi, A. Fuyuhiro, N. Kubota, T. Fukuo, R. Arakawa ..... 2268 – 2271

Cyclic Hexamer with a Cubic Cavity: Crystal Structure of $[\{Rh(6\text{-Purinethione Ribosido})(Cp^*)\}_6](CF_3SO_3)_6$

Keywords: chirality · nucleosides · rhodium · self-assembly · supramolecular chemistry

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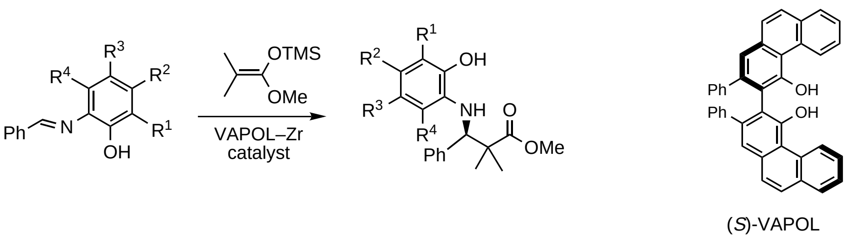
Unusually robust: A remarkably temperature-independent catalyst has been developed for the imino aldol reaction of imines derived from *ortho*-aminophenols (see scheme). This catalyst is prepared from two equivalents of the VAPOL ligand and a zirconium tetraalkoxide. From a consideration of likely intermediates in the catalytic cycle it was deduced that a methyl substituent *ortho* to the phenol (R^1) should enhance induction. This resulted in asymmetric inductions in excess of 98 % *ee* at room temperature as well as at 100°C. TMS = trimethylsilyl.



Angew. Chem. **2001**, *113*, 2331 – 2334

S. Xue, S. Yu, Y. Deng, W. D. Wulff* .... 2271 – 2274

Active Site Design in a Chemzyme: Development of a Highly Asymmetric and Remarkably Temperature-Independent Catalyst for the Imino Aldol Reaction

Keywords: asymmetric catalysis · imino aldol reaction · ligand effects · O ligands · zirconium

A distinct biochemical role of Cu^{2+} as an inhibitor in the aggregation of the peptide Aβ(42) in vitro was revealed by thioflavin T fluorescence assay and atomic force microscopy. The Cu^{2+}–Aβ(42) complex is responsible for the inhibition because it stabilizes the soluble form of Aβ(42) and controls the conformational transition ([Eq. (1)]; $k_i = [A\beta(42)][Cu^{2+}]/[Cu^{2+}-A\beta(42)]$).

$$Cu^{2+}\text{—}A\beta(42) \underset{Cu^{2+}}{\overset{k_i}{\rightleftharpoons}} A\beta(42) \overset{A\beta(42)_i}{\rightleftharpoons} A\beta(42)_{i+1} \qquad (1)$$

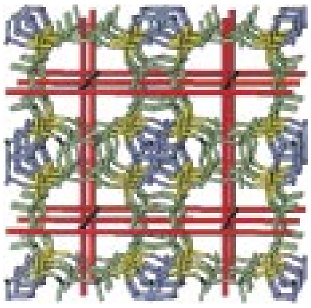
Angew. Chem. **2001**, *113*, 2334–2337

J. Zou, K. Kajita,
N. Sugimoto* 2274–2277

Cu^{2+} Inhibits the Aggregation of Amyloid β-Peptide(1–42) in vitro

Keywords: aggregation · copper · inhibitors · peptides

Subsitution of germanium for silicon in the preparation of the zeolite Beta allows the synthesis and characterization of a third, heretofore predicted, polymorph "C"; a [001] view is shown in the picture. Germanium preferentially occupies positions in double four-membered ring cages, the secondary building units of polymorph C, and favors the formation of polymorph C regardless of which of the eight organic structure-directing agents were used.



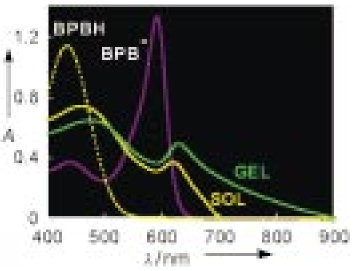
Angew. Chem. **2001**, *113*, 2337–2340

A. Corma,* M. T. Navarro, F. Rey, J. Rius,
S. Valencia 2277–2280

Pure Polymorph C of Zeolite Beta Synthesized by Using Framework Isomorphous Substitution as a Structure-Directing Mechanism

Keywords: germanium · polymorphism · zeolites

Efficient gelation of aqueous fluids by a novel tripodal trischolamide generates chiral hydrophobic pockets in the gel network. A yellow to green color change (see absorbance spectra) in the presence of bromophenol blue (BPBH) indicates the formation of the gel. The bound (anionic) dye (BPB$^-$) shows induced circular dichroism, which is indicative of a chiral environment.



Angew. Chem. **2001**, *113*, 2341–2343

U. Maitra,* S. Mukhopadhyay, A. Sarkar,
P. Rao, S. S. Indi 2281–2283

Hydrophobic Pockets in a Nonpolymeric Aqueous Gel: Observation of such a Gelation Process by Color Change

Keywords: aggregation · gel · hydrophobic effect · materials science · steroids

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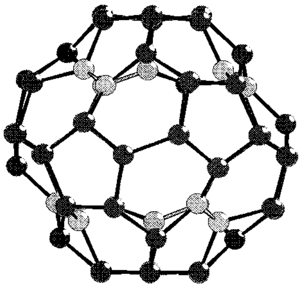
Deflated buckyballs: The single-crystal structure of $C_{60}F_{48} \cdot 2$(mesitylene) revealed the presence of both D_3 and S_6 isomers in the same crystal. C(sp^2)–C(sp^2) bonds (1.30 Å) are much shorter than C(sp^3)–C(sp^3) bonds (1.54–1.63 Å). The C_{60} cage is characterized by concave areas in the regions of six double bonds (see picture). Each double bond is effectively shielded by four F atoms, which accounts for the low reactivity of $C_{60}F_{48}$.



Angew. Chem. **2001**, *113*, 2345–2347

S. I. Troyanov,* P. A. Troshin,
O. V. Boltalina,* I. N. Ioffe, L. N. Sidorov,
E. Kemnitz 2285–2287

Two Isomers of $C_{60}F_{48}$: An Indented Fullerene

Keywords: fluorine · fullerenes · polyaddition · structure elucidation

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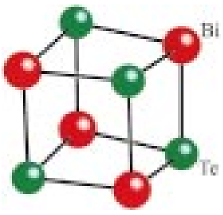
Two valence electrons more than in square-antiprismatic 38-electron clusters such as Bi_8^{2+} or Sn_8^{6-}: This is the reason for the unusual cube-shaped structure of the cation $Bi_4Te_4^{4+}$ (see picture), which is obtained as the chloroaluminate salt from acidic $AlCl_3$/Na[$AlCl_4$] melts.



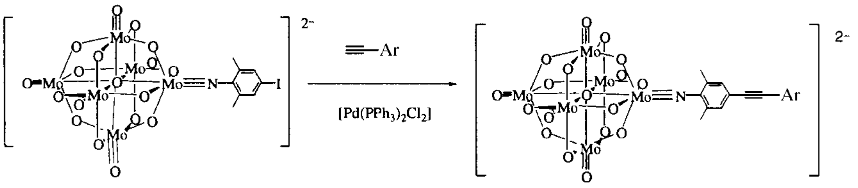
Angew. Chem. **2001**, *113*, 2347–2350

J. Beck,* M. Dolg,
S. Schlüter 2287–2290

$Bi_4Te_4^{4+}$—A Cube-Shaped, Polycationic Main Group Element Cluster

Keywords: ab initio calculations · bismuth · cluster compounds · polycations · tellurium

The Mo$\equiv$N bond is conjugated with the organic segment in the novel molecular organic–inorganic hybrid materials that have been obtained by Pd-catalyzed coupling of an iodo-functionalized hexamolybdate anion and an alkyne (see scheme; Ar = 4-methylphenyl,3-5-di(*tert*-butyl)phenyl). The interaction between the polyoxometalate cluster and the organic conjugated system is particularly apparent from the strong red-shifted absorption in the UV/Vis spectrum.



Angew. Chem. **2001**, *113*, 2353–2356

B. Xu, Y. Wei, C. L. Barnes,
Z. Peng* 2290–2292

Hybrid Molecular Materials Based on Covalently Linked Inorganic Polyoxometalates and Organic Conjugated Systems

Keywords: molybdenum • organic–inorganic hybrids • palladium • polyoxometalates

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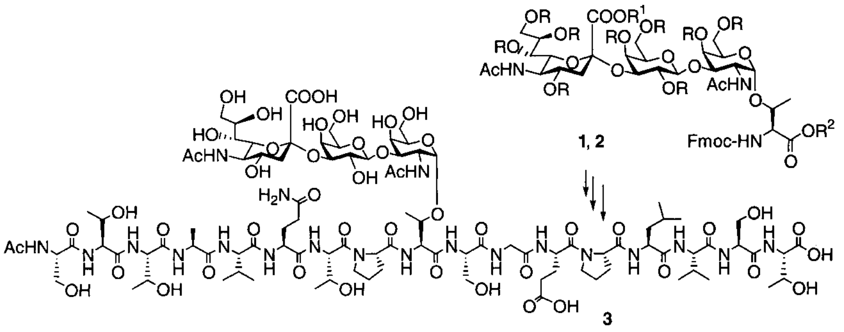
Protection of all functional groups of the carbohydrate portion of the chemoenzymatically synthesized sialyl T threonine ester **1** ($R = R^1 = H$, $R^2 = t$Bu, Fmoc = 9-fluorenylmethoxycarbonyl) and subsequent acidolysis of the *tert*-butyl ester afforded the building block **2** ($R = Ac$, $R^1 = Me$, $R^2 = H$). The latter is a useful tool in the solid-phase synthesis of the N-terminal sequence **3** of the leukemia-associated leukosialin.



Angew. Chem. **2001**, *113*, 2350–2353

N. Bézay, G. Dudziak, A. Liese,
H. Kunz* 2292–2295

Chemoenzymatic-Chemical Synthesis of a (2-3)-Sialyl T Threonine Building Block and Its Application to the Synthesis of the N-Terminal Sequence of Leukemia-Associated Leukosialin (CD 43)

Keywords: amino acids • carbohydrates • chemoenzymatic synthesis • leukosialin • solid-phase synthesis

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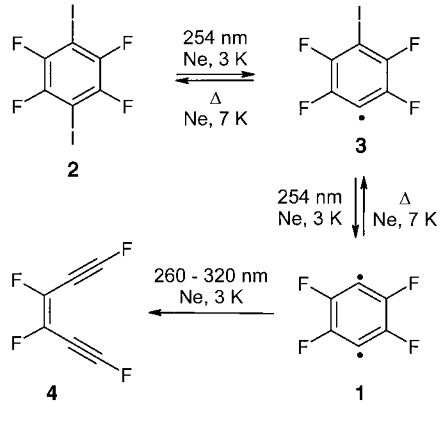
As the first isolated derivative of 1,4-didehydrobenzene, 1,4-didehydro-2,3,5,6-tetrafluorobenzene (**1**) was generated from 1,4-diiodotetrafluorobenzene (**2**) by photolysis at 254 nm in a neon matrix at 3 K. The 4-iodo-2,3,5,6-tetrafluorophenyl radical **3** is formed as an intermediate in this reaction. Both **1** and **3** were characterized by their IR spectra. Compound **1** is photolabile and undergoes a photochemical retro-Bergman reaction to 1,3,4,6-tetrafluorohex-3-ene-1,5-diyne (**4**) upon broad-band UV irradiation (260–320 nm).



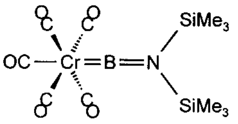
Angew. Chem. **2001**, *113*, 2356–2359

H. H. Wenk, A. Balster, W. Sander,*
D. A. Hrovat, W. T. Borden . 2295–2298

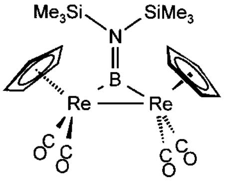
Matrix Isolation of Perfluorinated *p*-Benzyne

Keywords: 1,4-didehydrobenzene • enediynes • IR spectroscopy • matrix isolation

Upon irradiation of [(OC)$_5$W=B=N(SiMe$_3$)$_2$] the complexes **1** and **2** were obtained by intermetallic transfer of BN(SiMe$_3$)$_2$, thus demonstrating the potential of terminal borylene complexes as a source for borylenes at low temperatures and in the condensed phase. Compound **1** is the first structurally authentic chromium complex of boron.



1



2

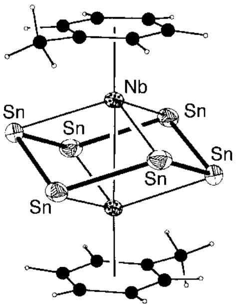
Angew. Chem. **2001**, *113*, 2359–2361

H. Braunschweig,* M. Colling, C. Kollann, H. G. Stammler, B. Neumann 2298–2300

Terminal Borylene Complexes as a Source for the Borylene B–N(SiMe$_3$)$_2$: Alternative Synthesis and Structure of [(OC)$_5$Cr=B=N(SiMe$_3$)$_2$]

Keywords: B ligands · boron · chromium · ligand transfer · rhenium

Sitting in a tin chair: the compound [Nb(η-C$_6$H$_5$Me)$_2$] reacts with the Sn$_9$$^{4-}$ ion in ethylenediamine to give the [(η-C$_6$H$_5$Me)NbSn$_6$Nb(η-C$_6$H$_5$Me)]$^{2-}$ ion, **1**. The complex contains a new Zintl ion, Sn$_6$$^{12-}$, with a chair cyclohexane-like structure and 2c-2e bonds.



1

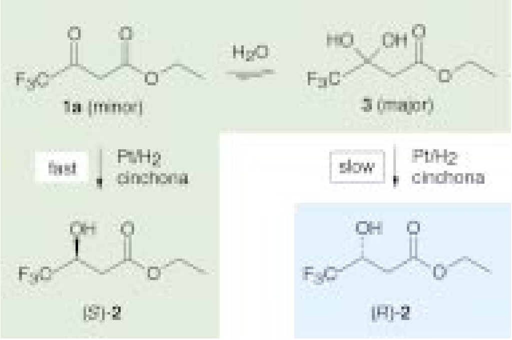
Angew. Chem. **2001**, *113*, 2364–2366

B. Kesanli, J. Fettinger, B. Eichhorn* 2300–2302

The [(η-C$_6$H$_5$Me)NbSn$_6$Nb(η-C$_6$H$_5$Me)]$^{2-}$ Ion: A Complex Containing a Metal-Stabilized Sn$_6$$^{12-}$ Cyclohexane-Like Zintl Ion

Keywords: arenes · cyclohexane structure · niobium · structure elucidation · tin · zintl anions

Two competing reaction pathways, which lead to opposite enantiomers (see scheme), occur in the hydrogenation of **1** over chirally modified platinum, as revealed by catalytic and NMR spectroscopic experiments: the fast reduction of the ketoform **1a** (minor species) and the slow hydrogenolysis of the hydrate **3** (major species).



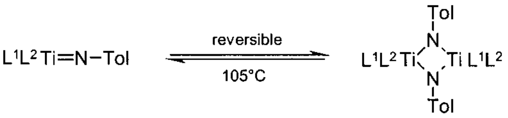
Angew. Chem. **2001**, *113*, 2369–2372

M. von Arx, T. Mallat, A. Baiker* 2302–2305

Inversion of Enantioselectivity during the Platinum-Catalyzed Hydrogenation of an Activated Ketone

Keywords: asymmetric hydrogenation · chiral auxiliaries · heterogeneous catalysis · hydrates · platinum

A complex interplay between the catalyst concentration and the reaction rate exists, as shown by kinetic studies, for the [Cp$_2$TiMe$_2$]-catalyzed intermolecular hydroamination of alkynes. The reason for this is a reversible dimerization of the catalytically active species [Eq. (1)]. L^1, L^2 = Cp (cyclopentadienyl), Tol–NH (Tol = 4-MeC$_6$H$_4$, tolyl).



$$\mathrm{L^1L^2Ti{=}N{-}Tol} \underset{105^\circ\mathrm{C}}{\overset{\text{reversible}}{\rightleftharpoons}} \mathrm{L^1L^2Ti(\mu\text{-}N\text{-}Tol)_2Ti\,L^1L^2} \qquad (1)$$

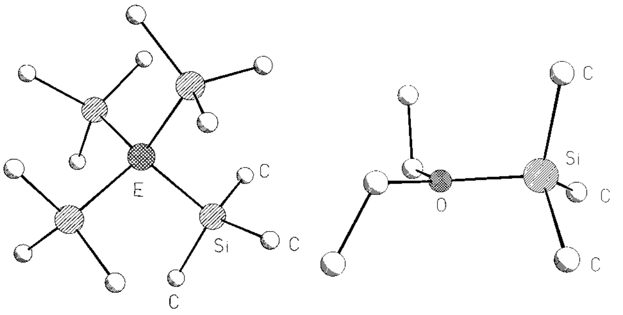
Angew. Chem. **2001**, *113*, 2361–2364

F. Pohlki, S. Doye* 2305–2308

The Mechanism of the [Cp$_2$TiMe$_2$]-Catalyzed Intermolecular Hydroamination of Alkynes

Keywords: alkynes · amination · homogeneous catalysis · metallocenes · titanium

Only strong Lewis acidic, arene-solvated Me_3Si^+ ions react with $E(SiMe_3)_3$ compounds (E = P, As) to give the crystallographically characterized $E(SiMe_3)_4^+$ onium ions **1** (left hand picture), which contain highly negative polarized P and As atoms, respectively. The masked Me_3Si^+ ions in **1** can be easily transferred to Et_2O, to give the first structurally characterized planar silyloxonium ion $[Et_2(Me_3Si)O]^+$ **2** (right hand picture).



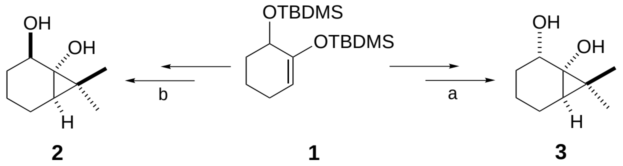
Angew. Chem. **2001**, *113*, 2366–2369

M. Driess,* R. Barmeyer, C. Monsé,
K. Merz 2308–2310

$E(SiMe_3)_4^+$ Ions (E = P, As): Persilylated Phosphonium and Arsonium Ions

Keywords: arsenic · onium ions · phosphonium salts · silicon

The diastereocomplementarity of halo- and alkylcarbenes (paths a and b, respectively) was shown in the cyclopropanation reaction of **1**. The conversion of **1** into 7,7-dimethylbicyclo[4.1.0]heptan-1,2-diols (±)-**2** and (±)-**3** represents an important transformation in a synthetic strategy towards phorbol derivatives. TBDMS = *tert*-butyldimethylsilyl.



Angew. Chem. **2001**, *113*, 2373–2375

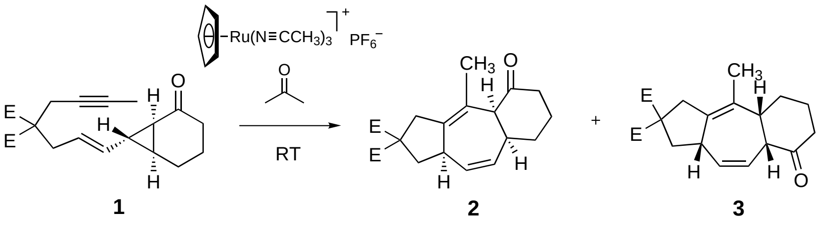
M. G. B. Drew, L. M. Harwood,*
A. J. Macías-Sánchez, R. Scott,
R. M. Thomas, D. Uguen .. 2311–2313

Diastereocontrol in the Synthesis of Models of Rings C and D of Phorbol: Directing Effect of an Ether Substituent on Lithium Carbenoid Mediated Cyclopropanation

Keywords: carbenoids · cyclopropanations · diastereoselectivity · enol ethers · synthetic methods

---

Efficient access to tricyclic compounds such as **2** and **3**, which contain a seven-membered ring, is provided by the ruthenium-catalyzed intramolecular [5+2] cycloaddition of a 1,2,3-trisubstituted cyclopropyl enyne such as **1**. Improved regioselectivity is observed when $In(OTf)_3$ is used as the cocatalyst. (No cocatalyst: **2**:**3** 6:1; cat. $In(OTf)_3$ (10%): **2**:**3** > 20:1; Tf = trifluoromethanesulfonyl).



Angew. Chem. **2001**, *113*, 2375–2378

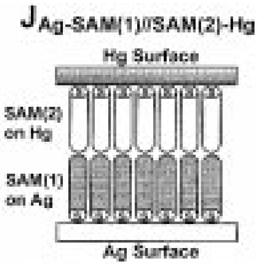
B. M. Trost,* H. C. Shen ... 2313–2316

Constructing Tricyclic Compounds Containing a Seven-Membered Ring by Ruthenium-Catalyzed Intramolecular [5+2] Cycloaddition

Keywords: cycloaddition · diastereoselectivity · enynes · homogeneous catalysis · ruthenium

A convenient experimental system is described, with which electron transport through structurally well-defined, 2–5 nm-thick, organic films can be examined. Two types of junction J have been studied in which self-assembled monolayers (SAMs, for example, SAM(1) formed on Ag from aliphatic and aromatic thiols, and SAM(2), formed on Hg from hexadecanethiol) are in contact through either van der Waals interactions (see picture) or through covalent, hydrogen, or ionic bonds.

Angew. Chem. **2001**, *113*, 2378–2382



R. E. Holmlin, R. F. Ismagilov, R. Haag, V. Mujica, M. A. Ratner, M. A. Rampi,* G. M. Whitesides* 2316–2320

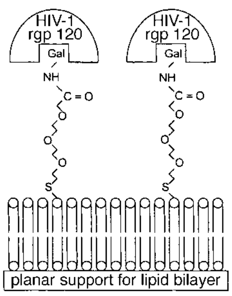
Correlating Electron Transport and Molecular Structure in Organic Thin Films

Keywords: electron transfer · monolayers · self assembly · thin films

---

A critical spacer arm length necessary to promote efficient binding of the HIV-1 surface glycoprotein rgp120 to several synthetic galactosyl-conjugated lipids, reconstituted into planar lipid bilayers, was identified (see figure). This should aid the design of anti-HIV-1 agents based on membrane-tethered, carbohydrate-based receptors for gp120.

Angew. Chem. **2001**, *113*, 2382–2384



Y. Gu, R. LaBell, D. F. O'Brien,* S. S. Saavedra* 2320–2322

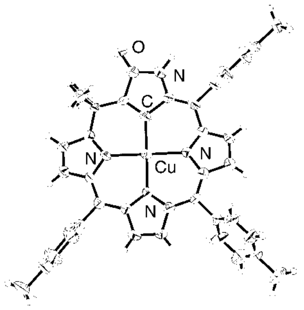
Quantitative Studies of Binding between Synthetic Galactosyl Ceramide Analogues and HIV-1 Gp120 at Planar Membrane Surfaces

Keywords: fluorescence spectroscopy · glycoproteins · HIV · sphingolipids · structure–activity relationships

---

Rare organometallic complexes can be stabilized by using an N-confused system as a carbon ligand. A stable organocopper(II) compound of N-confused calix[4]phyrin has been characterized by X-ray crystallography (see picture). Complete π conjugation was found not to be a prerequisite for the formation of the metal–carbon bond.

Angew. Chem. **2001**, *113*, 2385–2387



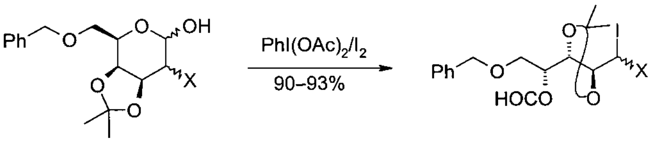
H. Furuta,* T. Ishizuka, A. Osuka,* Y. Uwatoko, Y. Ishikawa* .. 2323–2325

Metal Complexes of an N-Confused Calix[4]phyrin Derivative—The First X-ray Structure of an Organometallic Compound of Divalent Copper

Keywords: C ligands · copper · macrocycles · nickel · porphyrinoids

---

One less carbon atom is found in 1-halo-1-iodo compounds obtained by C1–C2 radical fragmentation of carbohydrate 1,2-halohydrins. This fragmentation is achieved via the anomeric alkoxy radicals of the halohydrins, formed upon reaction with (diacetoxyiodo)benzene and iodine [Eq. (1); X = Cl, Br, I].



(1)

Angew. Chem. **2001**, *113*, 2388–2390

C. C. González, A. R. Kennedy, E. I. León, C. Riesco-Fagundo, E. Suárez* 2326–2328

Fragmentation of Carbohydrate Anomeric Alkoxy Radicals: A New Synthesis of Chiral 1-Halo-1-iodo Compounds

Keywords: carbohydrates · chirality · halides · iodine · radical reactions

Two micellar states are possible for a novel PPO–PDEA diblock copolymer synthesized by atom-transfer radical polymerization. Subtle variation of the solution pH value and temperature is all that is needed to form both conventional micelles (with the PDEA block in the core) and reverse micelles (with the PPO block in the core) in aqueous media (shown schematically). DEA = 2-(diethylamino)ethyl methacrylate, PO = propylene oxide.

Angew. Chem. **2001**, *113*, 2390–2393

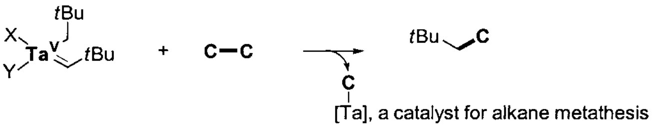
S. Liu, N. C. Billingham,
S. P. Armes* 2328–2331

A Schizophrenic Water-Soluble Diblock Copolymer

Keywords: copolymerizations · micelles · polymerizations · polymers · self-assembly

---

C–C activation of unactivated alkanes on a silica-supported neopentyl neopentylidene Ta^V complex [Eq. (1)] affords the alkane cross-metathesis products tBuCH$_2$R and an alkane-metathesis catalyst. Since the activity and product distributions are similar to those obtained with a silica-supported Ta^{III} hydride, these results are a first step in understanding alkane σ-bond metathesis on metal hydrides.



(1)

Angew. Chem. **2001**, *113*, 2393–2396

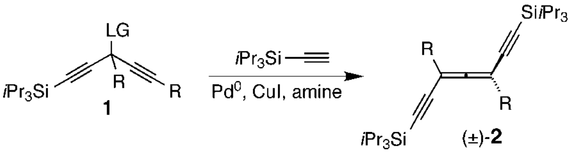
C. Copéret, O. Maury, J. Thivolle-Cazat,*
J.-M. Basset* 2331–2334

σ-Bond Metathesis of Alkanes on a Silica-Supported Tantalum(v) Alkyl Alkylidene Complex: First Evidence for Alkane Cross-Metathesis

Keywords: C–C activation · C–C coupling · metathesis · tantalum

---

Regioselective Pd^0-catalyzed cross-coupling of bispropargylic precursors **1** with silyl-protected alkynes gave rise to the first 1,3-diethynylallenes **2** [Eq. (1), LG = leaving group]. In enantiomerically pure form, these novel carbon-rich modules could provide access—by oxidative oligomerization—to a fascinating new class of helical oligomers and polymers.



(1)

Angew. Chem. **2001**, *113*, 2396–2399

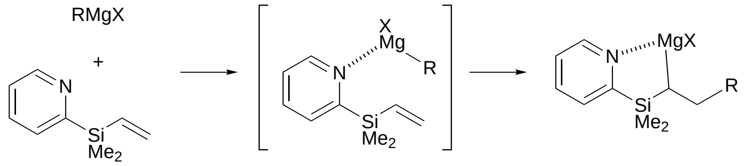
R. C. Livingston, L. R. Cox, V. Gramlich,
F. Diederich* 2334–2337

1,3-Diethynylallenes: New Modules for Three-Dimensional Acetylenic Scaffolding

Keywords: alkynes · allenes · cross-coupling · oligomerization · synthetic methods

---

Facile addition of primary alkyl Grignard reagents to vinylsilanes has been realized for the first time by exploiting the directing effect of a 2-pyridyl group on silicon [Eq. (1)]. Three-component coupling reactions of a Grignard reagent, the vinylsilane, and an electrophile, followed by oxidative removal of the 2-pyridyldimethylsilyl group with H_2O_2 furnishes various secondary alcohols in excellent overall yields.



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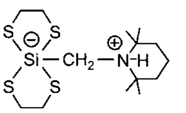
Angew. Chem. **2001**, *113*, 2399–2401

K. Itami, K. Mitsudo,
J.-i. Yoshida* 2337–2339

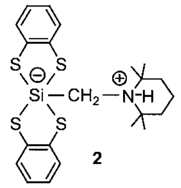
Directed Intermolecular Carbomagnesation across Vinylsilanes: 2-PyMe$_2$Si Group as a Removable Directing Group

Keywords: alcohols · magnesium · multicomponent reactions · silicon · synthetic methods

The zwitterionic compounds 1 and 2 are the first pentacoordinate silicates with covalent SiS_4C skeletons. They were characterized by crystal-structure analyses and NMR spectroscopic studies. Although pentacoordination of silicon is usually favored by ligand atoms of high electronegativity, the structural data of both **1** and **2** are consistent with the presence of five covalent bonds to the silicon atom.



1



2

Angew. Chem. **2001**, *113*, 2401–2403

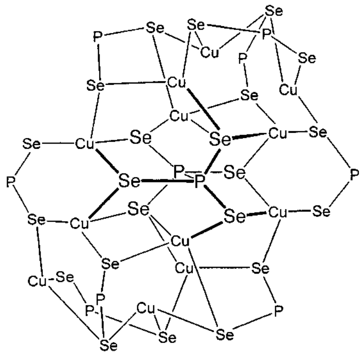
R. Tacke,* M. Mallak,
R. Willeke 2339–2341

Pentacoordination of Silicon by Four Covalent Si–S Bonds and One Covalent Si–C Bond

Keywords: chelates • hypervalent compounds • silicon • S ligands • zwitterions

---

The coexistence of P^{4+} and P^{5+} in one complex and the presence of an ethane-like hexaselenodiphosphato ligand, $P_2Se_6^{4-}$, are the novel features of the title compounds (see structure, in which R = Et or *i*Pr; OR groups omitted for clarity). The coordination mode of $P_2Se_6^{4-}$ in these dodecanuclear copper species is unprecedented and has not even been identified in any mixed ligands containing Group 15/16 elements.



Angew. Chem. **2001**, *113*, 2404–2406

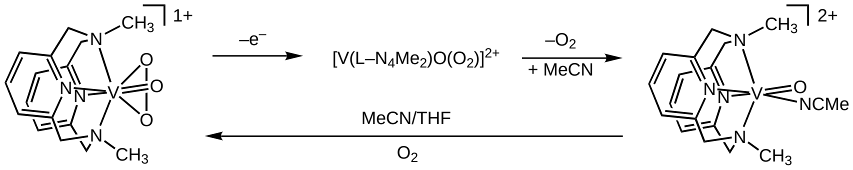
C. W. Liu,* H.-C. Chen, J.-C. Wang,
T.-C. Keng 2342–2344

$[Cu_{12}(P_2Se_6)\{Se_2P(OR)_2\}_8]$: Discrete Copper Clusters Containing an Ethane-Like Hexaselenodiphosphate(IV)

Keywords: cluster compounds • coordination modes • copper • phosphorus • selenium

---

A missing link: A superoxovanadium(V) complex is the first reaction intermediate in the oxidative conversion of a peroxovanadium(V) complex into a vanadyl(IV) complex and molecular oxygen (see scheme). The superoxo species appears also to play an essential role in the formation of the peroxovanadium(V) complex from the vanadyl(IV) complex and molecular oxygen.



Angew. Chem. **2001**, *113*, 2406–2410

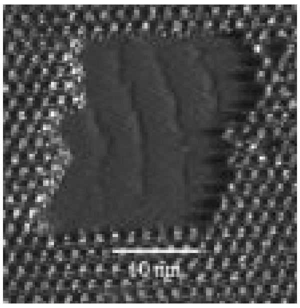
H. Kelm, H.-J. Krüger* 2344–2348

A Superoxovanadium(V) Complex Linking the Peroxide and Dioxygen Chemistry of Vanadium

Keywords: oxidation • oxygen • peroxides • radicals • vanadium

---

Two "face-on" phases and one "edge-on" lamellar phase comprised of self-assembled structures of phthalocyanines have been visualized by scanning tunneling microscopy (STM) at the gel–graphite interface. The switching between the phases can be stimulated with the microscope tip with a resolution on the molecular scale. The STM image shows the manipulated area consisting of π–π stacked phthalocyanines forming the lamellar phase, which is embedded in a hexagonally packed "face-on" phase.



Angew. Chem. **2001**, *113*, 2410–2412

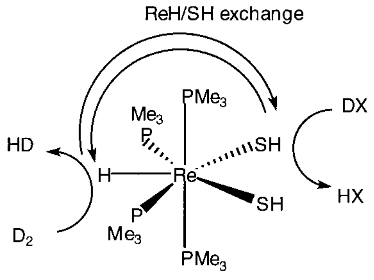
P. Samorí, H. Engelkamp, P. de Witte,
A. E. Rowan, R. J. M. Nolte,
J. P. Rabe* 2348–2350

Self-Assembly and Manipulation of Crown Ether Phthalocyanines at the Gel–Graphite Interface

Keywords: crown compounds • nanostructures • phthalocyanines • scanning tunneling microscopy • self-assembly

Not a poison! In contrast to the high reactivity of **1**, the corresponding trihydride $[ReH_3(PMe_3)_4]$ is kinetically inert. Thus, the usual view that sulfur poisons catalysts is clearly inappropriate in this case. The catalytic properties of **1** result from its difunctional nature with both protic (SH) and hydridic (ReH) sites; these sites communicate by an intramolecular exchange process (see scheme; X = OMe, SH).

Angew. Chem. **2001**, *113*, 2413–2415



1

D. E. Schwarz, J. A. Dopke,
T. B. Rauchfuss,*
S. R. Wilson 2351–2353

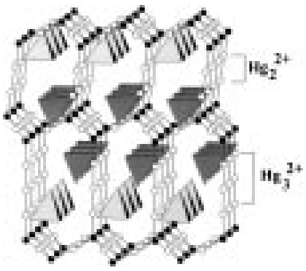
$[ReH(SH)_2(PMe_3)_4]$: A Catalyst for Fundamental Transformations Involving H_2 and H_2S

Keywords: homogeneous catalysis · hydrodesulfurization · hydrogen · P ligands · rhenium · sulfur

---

Pyramids in a mercury tunnel (see picture): Hg_3^{2+} and Hg_2^{2+} units form the tunnel walls of the novel inorganic supramolecular compound $[Hg_{11}As_4](GaBr_4)_4$. This is the first three-dimensional framework that incorporates the subvalent mercury cluster Hg_3^{2+} as a structural unit. Each of the two types of tunnel that extend along the *b* axis of the unit cell contains two columns of $GaBr_4^-$ ions.

Angew. Chem. **2001**, *113*, 2415–2416



A. V. Olenev,
A. V. Shevelkov* 2353–2354

The Hg_3^{2+} Group as a Framework Unit in a Host–Guest Compound: $[Hg_{11}As_4](GaBr_4)_4$

Keywords: host–guest systems · mercury · solid-state structures · subvalent compounds

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

* Author to whom correspondence should be addressed

The cover picture was prepared by Rainer Haag, University of Freiburg, Germany.

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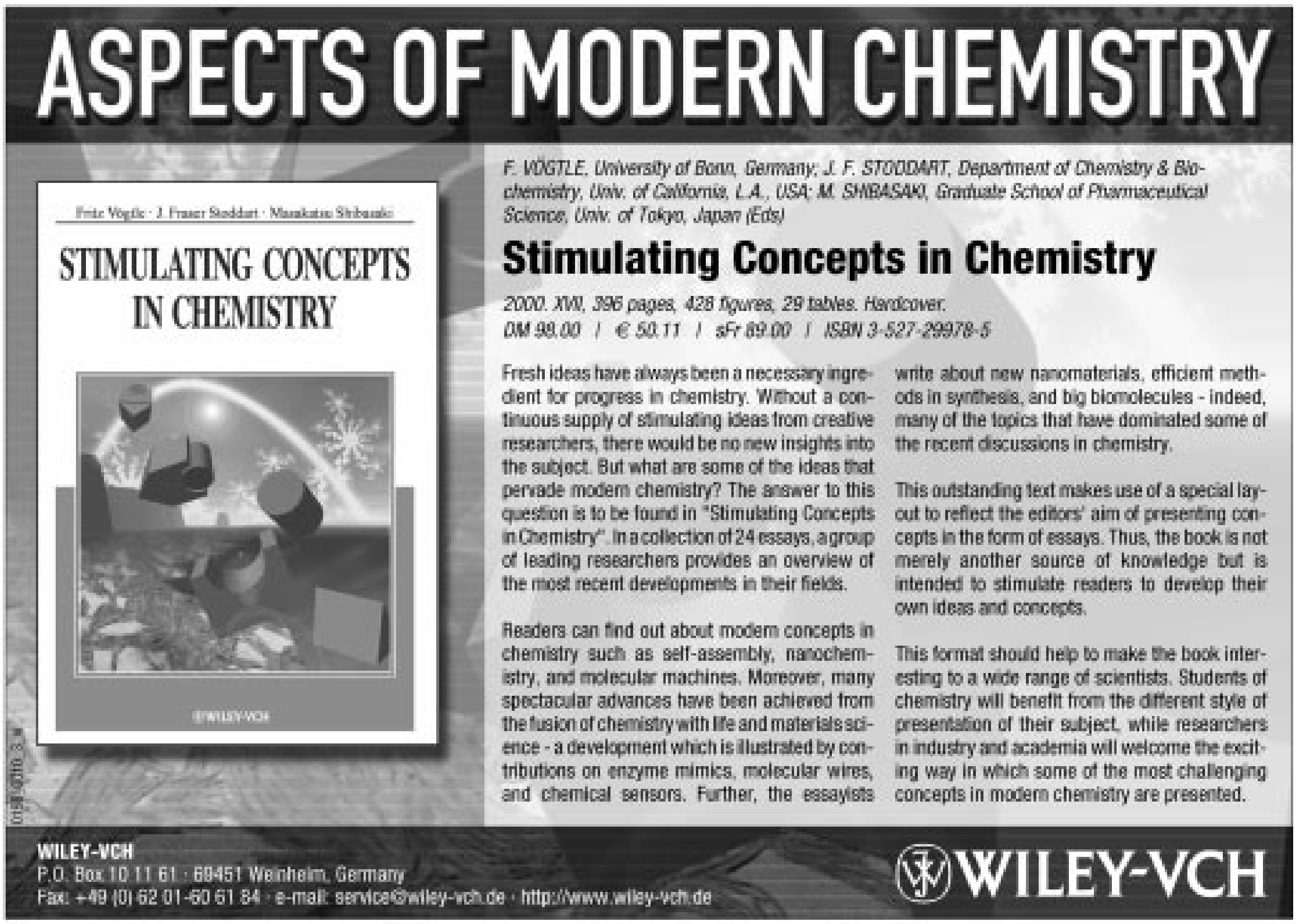

ASPECTS OF MODERN CHEMISTRY

F. VÖGTLE, University of Bonn, Germany; J. F. STODDART, Department of Chemistry & Biochemistry, Univ. of California, L.A., USA; M. SHIBASAKI, Graduate School of Pharmaceutical Science, Univ. of Tokyo, Japan (Eds)

Stimulating Concepts in Chemistry

2000. XVII, 396 pages, 428 figures, 29 tables. Hardcover.
DM 98.00 / € 50.11 / sFr 89.00 / ISBN 3-527-29978-5

Fresh ideas have always been a necessary ingredient for progress in chemistry. Without a continuous supply of stimulating ideas from creative researchers, there would be no new insights into the subject. But what are some of the ideas that pervade modern chemistry? The answer to this question is to be found in "Stimulating Concepts in Chemistry". In a collection of 24 essays, a group of leading researchers provides an overview of the most recent developments in their fields.

Readers can find out about modern concepts in chemistry such as self-assembly, nanochemistry, and molecular machines. Moreover, many spectacular advances have been achieved from the fusion of chemistry with life and materials science - a development which is illustrated by contributions on enzyme mimics, molecular wires, and chemical sensors. Further, the essayists write about new nanomaterials, efficient methods in synthesis, and big biomolecules - indeed, many of the topics that have dominated some of the recent discussions in chemistry.

This outstanding text makes use of a special layout to reflect the editors' aim of presenting concepts in the form of essays. Thus, the book is not merely another source of knowledge but is intended to stimulate readers to develop their own ideas and concepts.

This format should help to make the book interesting to a wide range of scientists. Students of chemistry will benefit from the different style of presentation of their subject, while researchers in industry and academia will welcome the exciting way in which some of the most challenging concepts in modern chemistry are presented.

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