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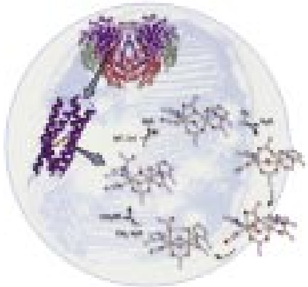
Pages 2725–2934

COVER PICTURE

The cover picture shows in the background the whole cell of a methanotrophic bacterium on which are superimposed components of methane monooxygenase (the structure of the hydroxylase component (top), one of the two four-helix bundles that house the catalytic diiron centers (left)) and a schematic diagram of the catalytic cycle by which the enzyme converts dioxygen and methane into methanol and water. More about this unusual enzyme system is reported by Lippard et al. on p. 2782 ff.

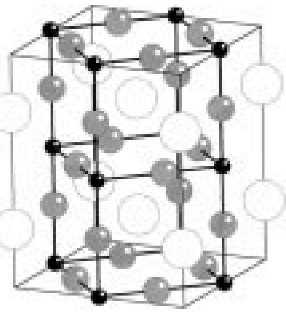


REVIEWS

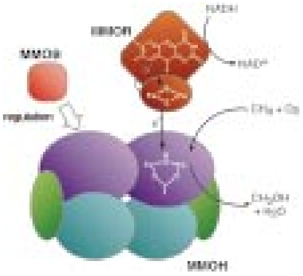
Contents

Theoretical considerations and chemical reasoning lead us to claim that Ag–F bonding in Ag^{III} and Ag^{II} fluorides is substantially covalent, and in this way will resemble Cu–O bonding in Cu^{II} and Cu^{III} oxides. The prospect is that if appropriately modified, such high oxidation-state silver fluorides (for example, $CsAgF_3$ (shown here), made by Hoppe and co-workers) might be superconducting.

Angew. Chem. **2001**, *113*, 2816–2859



Keywords: conducting materials · electronic structure · fluorides · silver · superconductors



An extraordinary enzyme system for studying the fundamental chemistry of both dioxygen and C–H activation as well as for investigating the regulatory mechanism employed by a multicomponent oxygenase is the soluble methane monooxygenase system. The enzyme comprises three protein components (see picture). Activation of dioxygen occurs at a non-heme carboxylate-bridged diiron center in the α subunit of the hydroxylase protein MMOH, and results in spectroscopically characterized high-valent intermediates capable of oxidizing a wide variety of hydrocarbon substrates. MMOR provides the electrons for this reaction after oxidizing NADH to NAD$^+$, while a third protein, MMOB, serves several regulatory functions.

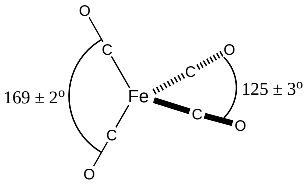
Angew. Chem. **2001**, *113*, 2860–2888

M. Merkx, D. A. Kopp, M. H. Sazinsky, J. L. Blazyk, J. Müller, S. J. Lippard* 2782–2807

Dioxygen Activation and Methane Hydroxylation by Soluble Methane Monooxygenase: A Tale of Two Irons and Three Proteins

Keywords: bioinorganic chemistry · C–H activation · O–O activation · oxidoreductases · oxygenation

HIGHLIGHTS



The structure of the singlet state ($^1A_1$) of [Fe(CO)$_4$] in the gas phase (see picture) has been determined by a combination of laser photochemistry of [Fe(CO)$_5$] and electron diffraction imaging. The ground state of [Fe(CO)$_4$] is known to be a triplet species ($^3B_2$), and this is the species detected in picosecond time-resolved IR experiments with [Fe(CO)$_5$] in solution. This is an appropriate moment to survey the state of knowledge on [Fe(CO)$_4$], beginning from the first low-temperature matrix experiments.

Angew. Chem. **2001**, *113*, 2893–2895

M. Poliakoff,* J. J. Turner* .. 2809–2812

The Structure of [Fe(CO)$_4$]—An Important New Chapter in a Long-Running Story

Keywords: femtochemistry · iron tetracarbonyl · IR spectroscopy · laser spectroscopy · matrix isolation · photochemistry

VIPs

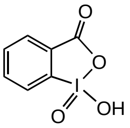
The following communications are “Very Important Papers” in the opinion of two referees. They will be published shortly. Short summaries of these articles can be found on the *Angewandte Chemie* homepage at the address http://www.angewandte.com

Synthesis of the C1–C13 Fragment of Kendomycin: Atropisomerism around a C-Aryl Glycosidic Bond	H. J. Martin, M. Drescher, H. Kählig, S. Schneider, J. Mulzer*
[NdI$_2$(thf)$_5$]: The First Crystallographically Authenticated Divalent Neodymium Complex	M. N. Bochkarev*, I. L. Fedushkin, S. Dechert, A. A. Fagin, H. Schumann*
From Split-Pool Libraries to Spatially Addressable Microarrays and Its Application to Functional Proteomic Profiling	N. Winssinger, J. L. Harris, B. J. Backes, P. G. Schultz*
High Turnover Numbers for Catalytic Selective Epoxidation of Alkenes with 1 atm Molecular Oxygen	Y. Nishiyama, Y. Nakagawa, N. Mizuno*
Zero-Strain Intercalation Cathode for Rechargeable Li-Ion Cell	J. Cho, Y. J. Kim, T.-J. Kim, B. Park*

1433-7851/01/4015-2728 $ 17.50+.50/0

A single-electron transfer (SET) is the key step in new reactions using the hypervalent iodine compound 2-iodoxybenzoic acid (IBX) **1** as a reagent. Efficient oxidations of alcohols, oxidation of the benzylic position, or introduction of α,β-double bonds into carbonyl compounds are other new applications of this reagent.

Angew. Chem. **2001**, *113*, 2889–2892



1 (IBX)

T. Wirth* 2812–2814

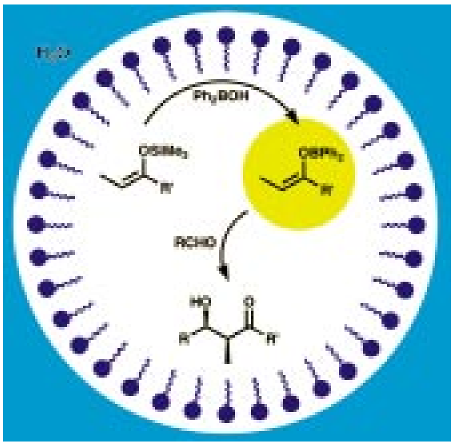
IBX—New Reactions with an Old Reagent

Keywords: hypervalent compounds · iodine reagents · oxidation · radicals

COMMUNICATIONS

Use of boron enolates in water! Boron enolates can be generated and used for aldol reactions in water by using a catalytic amount of Ph_2BOH (see scheme). This is the first example of a catalytic use of a boron source in stereoselective aldol reactions mediated by boron enolates. The mechanism of the reaction is discussed.

Angew. Chem. **2001**, *113*, 2897–2900



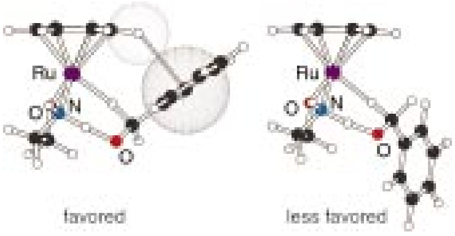
Y. Mori, K. Manabe,
S. Kobayashi* 2815–2818

Catalytic Use of a Boron Source for Boron Enolate Mediated Stereoselective Aldol Reactions in Water

Keywords: aldehydes · aldol reaction · boron · diastereoselectivity

The through-space CH/π attraction between the η^6-arene ligand on Ru and the carbonyl aryl substituent (see transition states in picture) plays a key role in the enantioselective transfer hydrogenation of aromatic carbonyl compounds with 2-propanol or formic acid, catalyzed by chiral η^6-arene–Ru^{II} complexes.

Angew. Chem. **2001**, *113*, 2900–2903



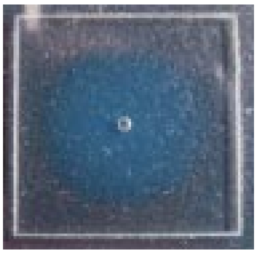
M. Yamakawa, I. Yamada,
R. Noyori* 2818–2821

CH/π Attraction: The Origin of Enantioselectivity in Transfer Hydrogenation of Aromatic Carbonyl Compounds Catalyzed by Chiral η^6-Arene-Ruthenium(II) Complexes

Keywords: asymmetric synthesis · CH/π interactions · density functional calculations · hydrogenation · ruthenium

Graft polymerization of photofunctional core–shell polymer microspheres of polystyrene-block-poly(4-vinylpyridine) in methyl methacrylate locks the microspheres in a body-centered cubic arrangement and yields a polymeric superstructure that exhibits a blue color tone (see picture). Similar optical properties are also observed in a diblock polymer with a lamellar morphology.

Angew. Chem. **2001**, *113*, 2903–2906



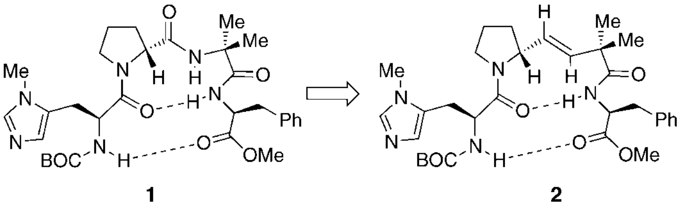
K. Ishizu,* S. Shiratori,*
T. Hosokawa* 2821–2824

Architecture of Polymeric Superstructures: Self-Color Tone Films Constructed by Mesoscopically Ordered Cubic Lattices

Keywords: polymerization · polymers · structure elucidation · thin films

1433-7851/01/4015-2729 $ 17.50+.50/0

Olefinic analogues of effective peptide-based catalysts for the kinetic resolution of functionalized racemic secondary alcohols have been synthesized. The isosteric replacement of the peptide amide bond in **1** with an (*E*)-alkene to form **2** has enabled the evaluation of the kinetic role of particular amides within these catalysts.



Angew. Chem. **2001**, *113*, 2906–2909

M. M. Vasbinder, E. R. Jarvo,
S. J. Miller* 2824–2827

Incorporation of Peptide Isosteres into Enantioselective Peptide-Based Catalysts as Mechanistic Probes

Keywords: asymmetric catalysis · kinetic resolution · peptidomimetics · reaction mechanisms

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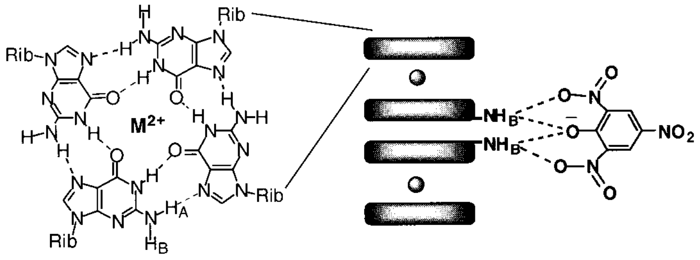
G-Quartets can bind anions as well as cations: Solid-state and solution data indicate that self-assembled ion-pair receptors are formed from 16 guanosine monomers, 2 divalent cations, and 4 picrate anions. Hydrogen-bonding, ion–dipole, and base-stacking interactions combine to give a tubular complex with a cation-loaded interior. An array of hydrogen-bond donors on the receptor's surface then enables anion coordination (see schematic representation, shaded rectangles = G-quartets, shaded circles = cations).



Angew. Chem. **2001**, *113*, 2909–2913

X. Shi, J. C. Fettinger,
J. T. Davis* 2827–2831

Ion-Pair Recognition by Nucleoside Self-Assembly: Guanosine Hexadecamers Bind Cations and Anions

Keywords: ion pairs · nucleosides · receptors · self-assembly · supramolecular chemistry

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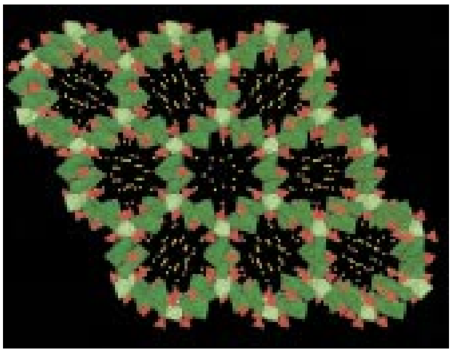
Nanoporosity, good thermal stability, antiferromagnetic ordering, and hydrogenation with basic catalytic character are four important properties of the large-pore (24MR), zeolitic nickel(II) phosphate, VSB-5 ($Ni_{20}[(OH)_{12}(H_2O)_6][(HPO_4)_8(PO_4)_4]\cdot 12H_2O$), which has been prepared under alkaline hydrothermal conditions. The structure of VSB-5 is depicted: NiO_6 octahedra: green; PO_4 tetrahedra: red.



Angew. Chem. **2001**, *113*, 2913–2916

N. Guillou, Q. Gao, P. M. Forster,
J.-S. Chang, M. Nogues, S.-E. Park,*
G. Férey,* A. K. Cheetham* 2831–2834

Nickel(II) Phosphate VSB-5: A Magnetic Nanoporous Hydrogenation Catalyst with 24-Ring Tunnels

Keywords: heterogeneous catalysis · hydrogenation · microporous materials · nickel · P ligands · zeolites

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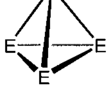
Not only fullerenes but also inorganic cage molecules can be highly spherical aromatic. The molecular allotropes **1** (E = N, P, As, Sb, Bi) of the Group V elements and a variety of Zintl anions are even double spherical aromatic and obey the $2(N+1)^2$ rule, since both their σ and π shells are completely filled. This is reflected by a pronounced diatropic character.



1

Angew. Chem. **2001**, *113*, 2916–2920

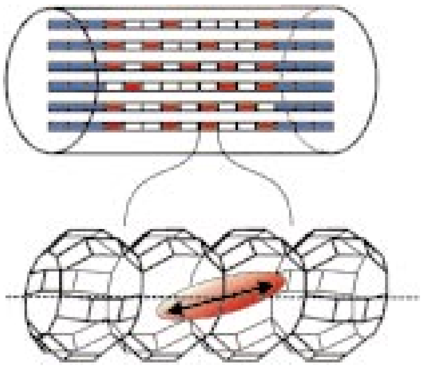
A. Hirsch,* Z. Chen, H. Jiao 2834–2838

Spherical Aromaticity of Inorganic Cage Molecules

Keywords: aromaticity · cluster compounds · electronic structure · ring current · zintl anions

In a radiationless process, electronic excitation energy can be transported in the photonic antennae presented herein from the borders to the center of cylindrical zeolite L crystals (ca. 2 μm). These antennae are formed by supramolecular organization (see schematic representation) of a cationic and a neutral dye in the parallel channels of the crystal. The rectangles symbolize adsorption sites, for which the red ones are filled with red-emitting dyes and blue ones with blue-emitting dyes.

Angew. Chem. **2001**, *113*, 2921 – 2924



M. Pauchard, S. Huber,
R. Méallet-Renault, H. Maas, R. Pansu,
G. Calzaferri* .... 2839 – 2842

Time- and Space-Resolved Luminescence of a Photonic Dye – Zeolite Antenna

Keywords: dyes/pigments · energy transfer · fluorescence spectroscopy · zeolites

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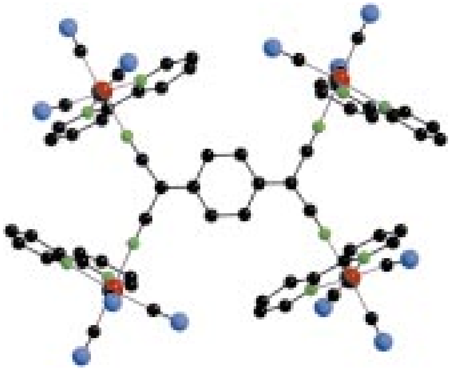
Innocent behavior of a typical non-innocent ligand has been observed for the first structurally characterized discrete metal complex with tetranucleating TCNQ. The coordination of four $[Re(CO)_3(bpy)]^+$ units (see picture: C: black, N: green, O: blue, Re: red) facilitates the reduction of the already excellent π-acceptor molecule TCNQ by a further 0.74 V! TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane, bpy = 2,2′-bipyridine.

Angew. Chem. **2001**, *113*, 2927 – 2930



H. Hartmann, W. Kaim,* I. Hartenbach,
T. Schleid, M. Wanner,
J. Fiedler .... 2842 – 2844

A Fully Characterized Complex Ion with Unreduced TCNQ as Fourfold Bridging Ligand: $[(\mu_4\text{-TCNQ})\{fac\text{-}Re(CO)_3(bpy)\}_4]^{4+}$

Keywords: electrochemistry · N ligands · rhenium · tetranuclear complexes

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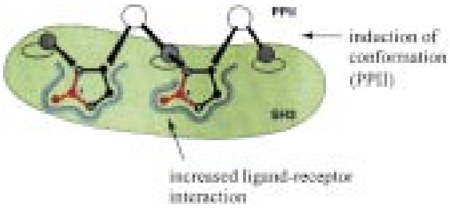
Pseudoprolines (ΨPro) have been developed as tools for inducing bioactive conformations that allow for optimal spatial complementation in protein – protein interactions. This dual function of ΨPro was explored for tuning proline-rich peptides as potent ligands for SH3 domains (see picture).

Angew. Chem. **2001**, *113*, 2930 – 2934



G. Tuchscherer,* D. Grell, Y. Tatsu,
P. Durieux, J. Fernandez-Carneado,
B. Hengst, C. Kardinal,
S. Feller* .... 2844 – 2848

Targeting Molecular Recognition: Exploring the Dual Role of Functional Pseudoprolines in the Design of SH3 Ligands

Keywords: helical structures · ligand design · molecular recognition · protein – ligand interactions · pseudoprolines

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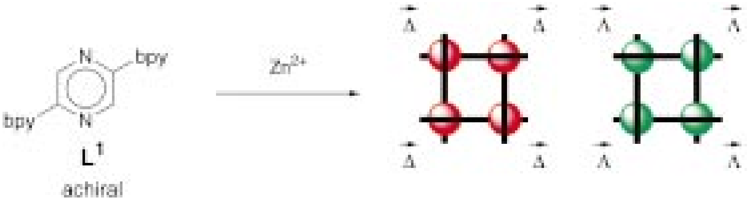
Squaring the cycle: Ligand L^1 has been developed for the fabrication of chiral molecular squares (see scheme), which can also be considered as circular helicates. By using a chirally modified ligand, one of the two forms of the complex can be generated selectively. bpy = 2,2′-bipyridin-6-yl.



Angew. Chem. **2001**, *113*, 2924 – 2927

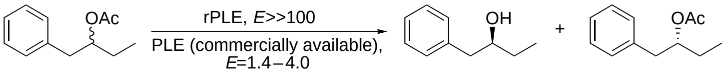
T. Bark, M. Düggeli, H. Stoeckli-Evans,
A. von Zelewsky* .... 2848 – 2851

Designed Molecules for Self-Assembly: The Controlled Formation of Two Chiral Self-Assembled Polynuclear Species with Predetermined Configuration

Keywords: diastereoselectivity · ligand design · pyrazine · self-assembly · zinc

1433-7851/01/4015-2731 $ 17.50+.50/0

Stable product quality without the interfering influences of other isoenzymes and hydrolases is possible through the application of recombinant pig liver esterase (rPLE), for which functional expression has now been achieved for the first time. In the hydrolysis of 1-phenyl-2-butyl acetate rPLE leads to substantially higher enantioselectivity than commercial PLE preparations (see scheme).



Angew. Chem. **2001**, *113*, 2934–2936

By Overexpression in the Yeast *Pichia pastoris* to Enhanced Enantioselectivity: New Aspects in the Application of Pig Liver Esterase

Keywords: enzyme catalysis • gene expression • hydrolases • kinetic resolution • pig liver esterase

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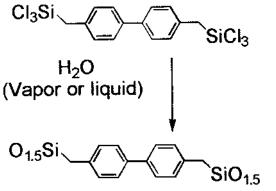
Mild solid/gas or solid/liquid reactions can be used to prepare crystalline organosilicates, a class of silica-based hybrid materials, from the corresponding solid chlorosilanes (see picture). Hydrolysis and polycondensation in the solid state lead to the formation of the highly anisotropic organosilicates.



Angew. Chem. **2001**, *113*, 2946–2948

Hydrolysis/Polycondensation in the Solid State: Access to Crystalline Silica-Based Hybrid Materials

Keywords: anisotropy • hybrid materials • materials science • silicates • solid-state reactions

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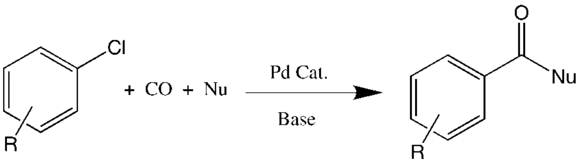
The right ligand enables the efficient carbonylation of unactivated chloroarenes. A general synthesis of benzoic acid derivatives is possible with the palladium–ferrocenylphosphane catalysts (see scheme).



Angew. Chem. **2001**, *113*, 2940–2943

A More Efficient Catalyst for the Carbonylation of Chloroarenes

Keywords: aryl chlorides • carbonylation • C–C bond formation • homogeneous catalysis • palladium

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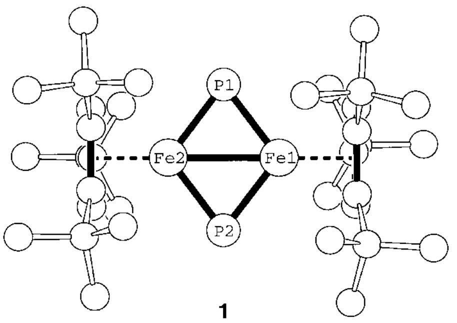
The short thermolysis of the butterfly molecule $[\{Cp'''(OC)_2Fe\}_2P_4]$ affords, besides $[Cp'''FeP_5]$ and $[\{Cp'''Fe\}_2P_4]$, the diphosphadiferratetrahedrane $[\{Cp'''Fe\}_2(\mu\text{-}CO)(\mu\text{-}\eta^2{:}\eta^2\text{-}P_2)]$ with a Fe–Fe double bond in 18 % yield. The P_2 building block was split photochemically into two μ-P ligands with elimination of CO. In the resulting dinuclear complex **1**, the ^{31}P NMR signal is shifted to extremely low field ($\delta = 1406.9$), and the rhombic Fe_2P_2 four-membered ring is almost orthogonal to the eclipsed Cp‴ five-membered rings (see picture); $Cp''' = tBu_3C_5H_2$.



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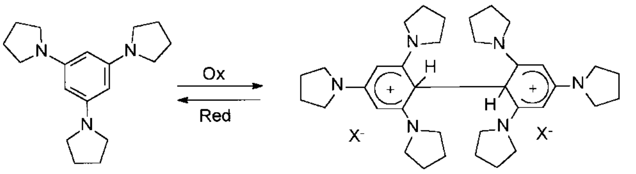
Angew. Chem. **2001**, *113*, 2944–2945

Synthesis, Structure, and Reactivity of a Diphosphadiferratetrahedrane with a Fe–Fe Double Bond

Keywords: iron • phosphorus • P ligands

1,3,5-tripyrrolidinobenzene is the first example of an aromatic amine that forms σ dimers during oxidation/reduction cycles [Eq. (1); $X^- = ClO_4^-$], and thus turns out to be an efficient molecular switch. Surprisingly, such σ dimers are relatively stable intermediates during the formation of conjugated oligomers and polymers.



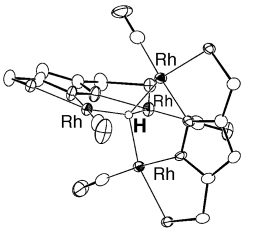
(1)

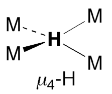
Angew. Chem. **2001**, *113*, 2936–2940

Evidence for σ Dimerization During Anodic Redox Switching of 1,3,5-Tripyrrolidinobenzene: A New Molecular Switch

Keywords: cyclic voltammetry • dimerization • electrochemistry • molecular machines • radical ions

Metal–metal bonds are not essential for multiply bridging hydride ligands. A tetranuclear μ_4-hydride complex $[(\mu_4\text{-H})Rh_4(PNNP)_2(CO)_4]^+$ (PNNP = 3,5-bis(diphenylphosphanylmethyl)pyrazolate), in which the quadruply bridging hydrido ligand holds the four isolated metal centers together to form a tetrahedral metal array, has been prepared and characterized by spectroscopic methods and single-crystal X-ray diffraction (see picture).





Angew. Chem. **2001**, *113*, 2951–2953

S. Tanaka, M. Akita* 2865–2867

$[(\mu_4\text{-H})Rh_4(PNNP)_2(CO)_4]^+$: A Novel Hydride Bridging Mode

Keywords: cluster compounds • hydride ligands • N,P ligands • rhodium • silanes

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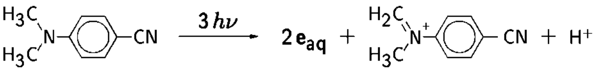
Startling facts are often revealed by the quantitative investigation of a reaction thought to be understood. The photoionization of dimethylaminobenzonitrile, which was previously regarded as biphotonic, was found to occur by the successive absorption of *three* photons, and to produce *two* electrons per starting molecule [Eq. (1)]. The explanation is an intervening rapid chemical reaction: deprotonation followed by intramolecular charge transfer.



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Angew. Chem. **2001**, *113*, 2948–2951

M. Goez,* V. Zubarev 2867–2869

Double Photoionization of Dimethylaminobenzonitrile in Solution: A Three-Quantum Process with Intervening Chemical Step

Keywords: charge transfer • kinetics • laser chemistry • photochemistry • solvated electrons

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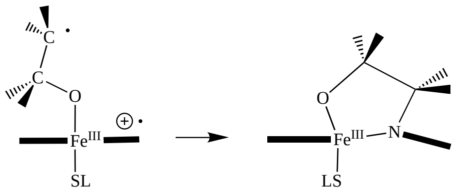
The suicidal complex ^{4}2, which inactivates cytochrome P450 during olefin epoxidation, was shown by density functional calculations to be formed from the same high-spin intermediate (^{4}**1**-III) that leads to stereochemical scrambling.



^{4}**1**-III ^{4}**2**

Angew. Chem. **2001**, *113*, 2955–2958

S. P. de Visser, F. Ogliaro, S. Shaik* 2871–2874

How Does Ethene Inactivate Cytochrome P450 En Route to Its Epoxidation? A Density Functional Study

Keywords: cytochromes • density functional calculations • electronic structure • enzymes

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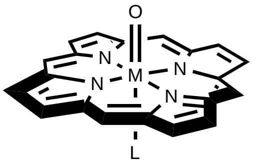
Chameleon states: the ruthenium and iron metalloporphyrin analogues of compound I of cytochrome P450 (**1**; L = thiolate) possess low-lying states that change their electronic structure with solvent polarization. The ground state of the ruthenium complex is a low-spin electrophilic state, whereas the ground state of the iron complex is triradicaloid.



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Angew. Chem. **2001**, *113*, 2958–2962

F. Ogliaro, S. P. de Visser, J. T. Groves,* S. Shaik* 2874–2878

Chameleon States: High-Valent Metal–Oxo Species of Cytochrome P450 and Its Ruthenium Analogue

Keywords: cytochromes • density functional calculations • electronic structure • metalloporphyrin • ruthenium

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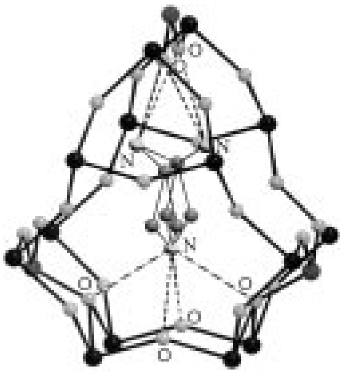
Eight- and six-ring channels built from NbO_6 octahedra and SiO_4 or GeO_4 tetrahedra, respectively, are contained in the structures of the first organically templated niobium silicate and germanate open-framework structures. The organic template (piperazine) occupies a well-defined position at the intersection of the channels (see picture).



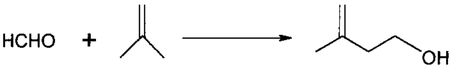
Angew. Chem. **2001**, *113*, 2963–2965

R. J. Francis,* A. J. Jacobson 2879–2881

The First Organically Templated Open-Framework Niobium Silicate and Germanate Phases: Low-Temperature Hydrothermal Syntheses of $[(C_4N_2H_{11})Nb_3SiO_{10}]$ (NSH-1) and $[(C_4N_2H_{11})Nb_3GeO_{10}]$ (NGH-1)

Keywords: germanium • hydrothermal synthesis • niobium • silicates • template synthesis

Resistance to leaching and re-usability are characteristic of the novel heterogeneous Lewis acid catalyst that was prepared by anchoring tin(IV) chloride on silica grafted with tetraalkylammonium or pyridinium chloride groups. The catalyst displays high activity and selectivity in the synthesis of 3-methyl-3-buten-1-ol by the Prins condensation of isobutene with formaldehyde [Eq. (1)].



(1)

Angew. Chem. **2001**, *113*, 2965–2968

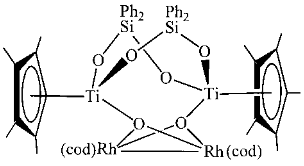
T. M. Jyothi, M. L. Kaliya,
M. V. Landau* 2881–2884

A Lewis Acid Catalyst Anchored on Silica Grafted with Quaternary Alkylammonium Chloride Moieties

Keywords: heterogeneous catalysis · Prins reaction · supported catalysts · tin

---

Rhodium supported on titania–silica is modeled by **1**, which was obtained from [{Cp*TiMe(μ-O_2SiPh_2)}$_2$] (**2**) and [{Rh(OH)(cod)}$_2$]. Complex **2** and its triply bridged derivative [Cp*Ti(μ-O_2SiPh_2)$_3$TiCp*] (**3**) can be envisaged as molecular models of titania–silica systems. Compounds **1**–**3** could potentially provide insights into the nature of the catalytically active sites in these systems; cod = 1,5-cyclooctadiene, Cp* = η^5-C_5Me_5.



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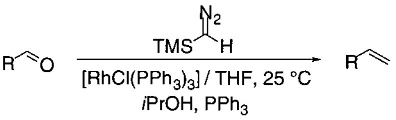
Angew. Chem. **2001**, *113*, 2968–2971

R. Fandos,* A. Otero,* A. Rodríguez,
M. J. Ruiz, P. Terreros 2884–2887

Molecular Models of Titania–Silica Systems and a Late Transition Metal Complex Grafted Thereon

Keywords: bridging ligands · O ligands · rhodium · titanium

A variety of terminal alkenes are produced in excellent yields by the rhodium(I)-catalyzed methylenation of aldehydes using $TMSCHN_2$ and PPh_3 [Eq. (1)]. These mild reaction conditions allowed the conversion of enolizable substrates and the chemoselective methylenation of aldehydes over ketones. TMS = trimethylsilyl.



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Angew. Chem. **2001**, *113*, 2971–2974

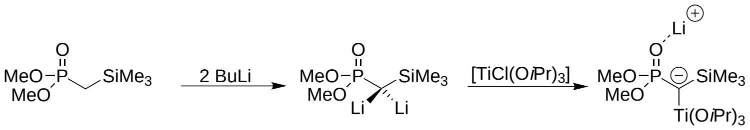
H. Lebel,* V. Paquet,
C. Proulx 2887–2890

Methylenation of Aldehydes: Transition Metal Catalyzed Formation of Salt-Free Phosphorus Ylides

Keywords: aldehydes · alkenes · diazo compounds · olefinations · rhodium

---

The titanium-stabilized lithium carbanion 1 represents a new class of organodimetallic compounds that are easily accessible by a dilithiation–transmetalation sequence [Eq. (1)]. The X-ray structure of **1** revealed an aggregate consisting of two titanated lithium phosphonate units and two molecules of LiCl as the aggregation nucleus. Density functional calculations on a model system showed excellent agreement with the solid-state structure and suggest a configurational stability comparable to those of lithium phosphonates.



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(1)

Angew. Chem. **2001**, *113*, 2974–2977

J. F. K. Müller,* K. J. Kulicke,
M. Neuburger, M. Spichty . 2890–2893

Carbanions Substituted by Transition Metals: Synthesis, Structure, and Configurational Restrictions of a Lithium Titanium Phosphonate

Keywords: anions · density functional calculations · lithium · phosphonate ligands · titanium

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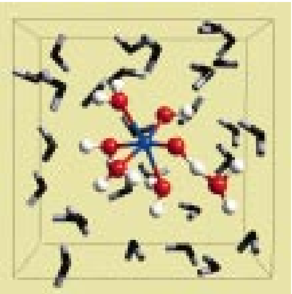
The spontaneous formation of the contested ferryl ion is evident in ab initio molecular dynamics calculations on the Fe^{II}/H_2O_2 system in aqueous solution (Fenton reagents). Not only is the ferryl ion preferred over the hydroxyl radical as the active oxidative species, but the solvent water molecules play a crucial role in the mechanism. The picture shows the unit cell containing the iron complex surrounded by solvent water molecules 1.8 ps after the start of the simulation, when the ferryl ion is being formed (blue: iron, red: oxygen, white: hydrogen).



Angew. Chem. **2001**, *113*, 2977–2979

B. Ensing, F. Buda, P. Blöchl,
E. J. Baerends* 2893–2895

Chemical Involvement of Solvent Water Molecules in Elementary Steps of the Fenton Oxidation Reaction

Keywords: ab initio calculations · Fenton reaction · oxidation · peroxides · solvent effects

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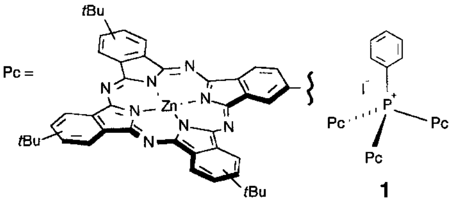

At least three phthalocyanine units can be incorporated into phosphonium salts to give compounds such as **1**, following unprecedented exchange reactions between phthalocyanine moieties bound to a palladium center and phenyl groups bound to the coordinated phosphane. Preliminary second-order nonlinear optics studies of the phthalocyanine–phosphonium salts have been carried out.

Angew. Chem. **2001**, *113*, 2979–2982

G. de la Torre, A. Gouloumis, P. Vázquez, T. Torres* 2895–2898

Insights into the Aryl–Aryl Exchange between Palladium and Phosphane Ligands in Pd^{II} Complexes: Preparation of Phthalocyanine-Containing Phosphonium Salts

Keywords: aryl–aryl exchange • nonlinear optics • palladium • phthalocyanines • P ligands

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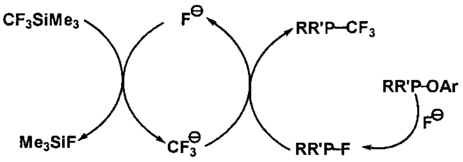


A new way of forming P–C bonds: Catalytic amounts of F$^-$ ions facilitate the reaction of P^{III}–F compounds with CF_3SiMe_3 to give P^{III}–CF_3 compounds (see scheme). These compounds can also be obtained in a one-pot procedure from P^{III}–OAr precursors (also shown).

Angew. Chem. **2001**, *113*, 2982–2984

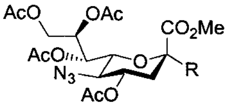
I. Tworowska, W. Dąbkowski, J. Michalski* 2898–2900

Synthesis of Tri- and Tetracoordinate Phosphorus Compounds Containing a PCF_3 Group by Nucleophilic Trifluoromethylation of the Corresponding PF Compounds

Keywords: fluorine • nucleophilic substitution • phosphorus • trifluoromethylation

---

5-Azido sialyl donors with *O*-acetyl protecting groups are useful α-selective glycosylation reagents, especially for primary hydroxyl groups as acceptors. This is shown with a variety of reactions using **1** as a sialyl donor. It was also possible to synthesize NeuAcα(2→9)NeuAc as a thioglycoside donor for use in subsequent glycosylations.



1, R = STol, $OP(OEt)_2$

Angew. Chem. **2001**, *113*, 2984–2987

C.-S. Yu, K. Niikura, C.-C. Lin,* C.-H. Wong* 2900–2903

The Thioglycoside and Glycosyl Phosphite of 5-Azido Sialic Acid: Excellent Donors for the α-Glycosylation of Primary Hydroxyl Groups

Keywords: α-sialylation • glycosylation • sialic acids • sialyl phosphites • thiosialosides

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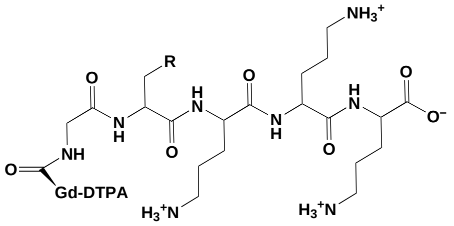


Clinically relevant relaxivity enhancement of a magnetic resonance imaging (MRI) contrast agent has been achieved by using prodrug Gd^{3+} complexes (see picture, DTPA = diethylenetriaminepentaaceto). Enzymatic cleavage of lysine residues from the prodrug exposes a group that has a high affinity to human serum albumin and promotes enhanced relaxivity, thus enabling the detection of targets at submicromolar concentrations.

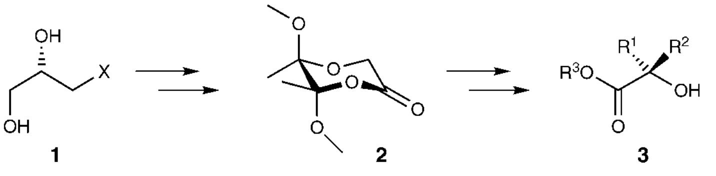
Angew. Chem. **2001**, *113*, 2987–2990

A. L. Nivorozhkin, A. F. Kolodziej, P. Caravan, M. T. Greenfield, R. B. Lauffer, T. J. McMurry* 2903–2906

Enzyme-Activated Gd^{3+} Magnetic Resonance Imaging Contrast Agents with a Prominent Receptor-Induced Magnetization Enhancement

Keywords: chelates • inhibitors • lanthanides • MRI • peptides

According to a chiral memory protocol, a chiral glycolic acid equivalent, the butane-2,3-diacetal-desymmetrized glycolate **2**, is obtained from chiral 3-halopropane-1,2-diols **1**. Compound **2** is a new and effective building block for the synthesis of mono- and dialkylated α-hydroxy acids **3**, which constitute a biologically and pharmacologically important structural motif.



Angew. Chem. **2001**, *113*, 2990–2993

E. Díez, D. J. Dixon,
S. V. Ley* 2906–2909

Butane-2,3-Diacetal-Desymmetrized Glycolic Acid—A New Building Block for the Stereoselective Synthesis of Enantiopure α-Hydroxy Acids

Keywords: alkylation • α-hydroxy acids • asymmetric synthesis • chiral memory • diastereoselectivity

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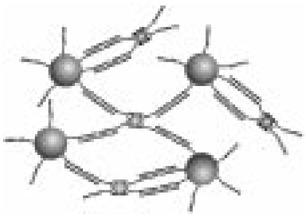
DNA hybridization enables the three-dimensional assembly of Au nanoparticles and streptavidin (see picture). The high-density DNA-modified Au nanoparticles were stable to nonspecific binding of streptavidin. Structural and melting investigations on the assemblies showed their formation was reversible.



Angew. Chem. **2001**, *113*, 2993–2996

S.-J. Park, A. A. Lazarides, C. A. Mirkin,*
R. L. Letsinger* 2909–2912

Directed Assembly of Periodic Materials from Protein and Oligonucleotide-Modified Nanoparticle Building Blocks

Keywords: DNA structures • nanostructures • oligonucleotides • proteins • small-angle X-ray scattering

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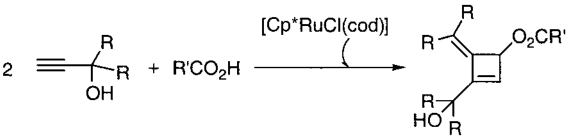
The precatalyst [Cp*RuCl(cod)] promotes the head-to-head cyclodimerization of propargylic alcohols and the formation of novel alkylidene cyclobutenes (see scheme; $Cp^* = C_5Me_5$, cod = 1,5-cyclooctadiene) by addition of carboxylic acid to the Ru(η^4-cyclobutadiene) intermediate and dehydration.



Angew. Chem. **2001**, *113*, 2996–2999

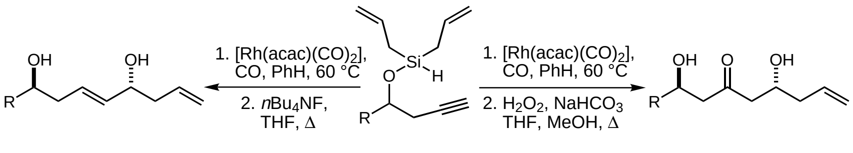
J. Le Paih, S. Dérien, C. Bruneau,
B. Demerseman, L. Toupet,
P. H. Dixneuf* 2912–2915

Ruthenium-Catalyzed One-Step Transformation of Propargylic Alcohols into Alkylidene Cyclobutenes: X-ray Characterization of an Ru(η^3-cyclobutenyl) Intermediate

Keywords: alkynes • cyclobutenes • homogeneous catalysis • ruthenium

---

Two new C–C bonds as well as a remote stereocenter are formed in the title reaction. With remarkable efficiency, this new reaction provides, through remote 1,5-asymmetric induction, *anti*-1,5 diols that are useful synthons for polyol synthesis (see scheme; Hacac = acetylacetone).



Angew. Chem. **2001**, *113*, 2999–3001

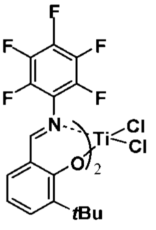
S. J. O'Malley,
J. L. Leighton* 2915–2917

Tandem Intramolecular Alkyne Silylformylation–Allylsilylation: A Case of Remote 1,5-Asymmetric Induction

Keywords: allylation • asymmetric induction • carbonylation • domino reactions • silylformylation

---

The presence of fluorine atoms in the ligand transforms titanium–salicylidene complex (see picture) into an effective catalyst for the living polymerization of ethylene. The catalyst displays very high activities (maximum turnover frequency 24300 $\text{min}^{-1}\text{atm}^{-1}$) and creates high molecular weight polyethylene ($M_n > 400000$) with extremely narrow polydispersities ($M_w/M_n < 1.20$) at very high polymerization temperatures (25–50°C).



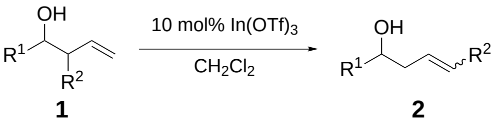
Angew. Chem. **2001**, *113*, 3002–3004

J. Saito, M. Mitani, J. Mohri, Y. Yoshida, S. Matsui, S. Ishii, S. Kojoh, N. Kashiwa,
T. Fujita* 2918–2920

Living Polymerization of Ethylene with a Titanium Complex Containing Two Phenoxy-Imine Chelate Ligands

Keywords: fluorine • homogeneous catalysis • polymerization • polymers • titanium

A retro-ene reaction that generates the parent aldehyde and a sigmatropic rearrangement are involved in the In(OTf)$_3$-catalyzed conversion of homoallylic alcohols **1** into the thermodynamically favored regioisomers **2**. This method can be used for the stereocontrolled synthesis of linear homoallylic 22α-sterols from their readily accessible branched 22β isomers.



Angew. Chem. **2001**, *113*, 3005 – 3006

T.-P. Loh,* K.-T. Tan,
Q.-Y. Hu .... 2921 – 2922

The First In(OTf)$_3$-Catalyzed Conversion of Kinetically Formed Homoallylic Alcohols into the Thermodynamically Preferred Regioisomers: Application to the Synthesis of 22α-Sterols

Keywords: ene reaction • indium • retro reactions • sigmatropic rearrangement

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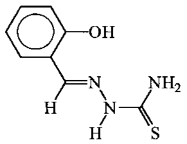
From two to five: A mononuclear Ru complex of salicylaldehyde thiosemicarbazone (H$_3$saltsc, **1**), in which only two of the coordination sites of **1** participate in bonding ([Ru(bpy)$_2$(H$_2$saltsc)]ClO$_4$), could be used to synthesize the cyclic complex cation [{Ru(bpy)$_2$(saltsc)}$_4$Ni$_4$]$^{4+}$ (bpy = 2,2′-bipyridine). Its formation demonstrates that the Ru complex can act as an N,N,O donor ligand for the construction of polynuclear complexes.



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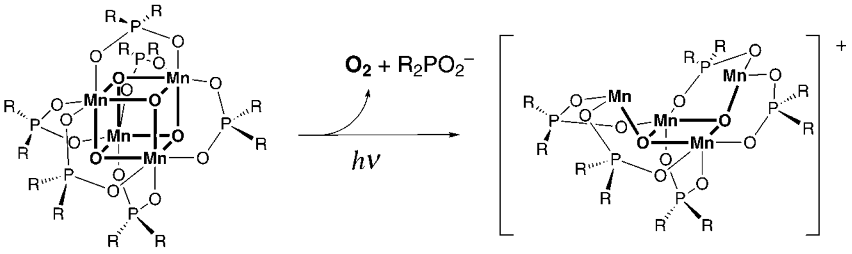
Angew. Chem. **2001**, *113*, 3007 – 3009

I. Pal, F. Basuli, T. C. W. Mak,
S. Bhattacharya* .... 2923 – 2925

Synthesis, Structure, and Properties of a Novel Heterooctametallic Complex Containing a Cyclic Ru$_4$Ni$_4$ Core

Keywords: nickel • N,O ligands • ruthenium • S ligands

Cores for thought! A new [Mn$_4$O$_4$]$^{6+}$ “cubane” core complex (L$_6$Mn$_4$O$_4$) with six facially bridging phosphinate chelate ligands (L$^-$ = (MePh)$_2$PO$_2^-$) was synthesized. Photo-excitation releases molecular O$_2$ by intramolecular coupling of two core oxygen atoms and selective rearrangement to a [Mn$_4$O$_2$]$^{6+}$ “butterfly” core ([L$_5$Mn$_4$O$_2$]$^+$; see scheme). Thus the Mn$_4$O$_4$ cubane core exhibits unique reactivity in O$_2$ evolution which may account for its presence in the photosynthetic enzyme.



Angew. Chem. **2001**, *113*, 3009 – 3012

M. Yagi, K. V. Wolf, P. J. Baesjou,
S. L. Bernasek,
G. C. Dismukes* .... 2925 – 2928

Selective Photoproduction of O$_2$ from the Mn$_4$O$_4$ Cubane Core: A Structural and Functional Model for the Photosynthetic Water-Oxidizing Complex

Keywords: cluster compounds • manganese • oxygen • photosynthesis • water oxidation

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

* Author to whom correspondence should be addressed

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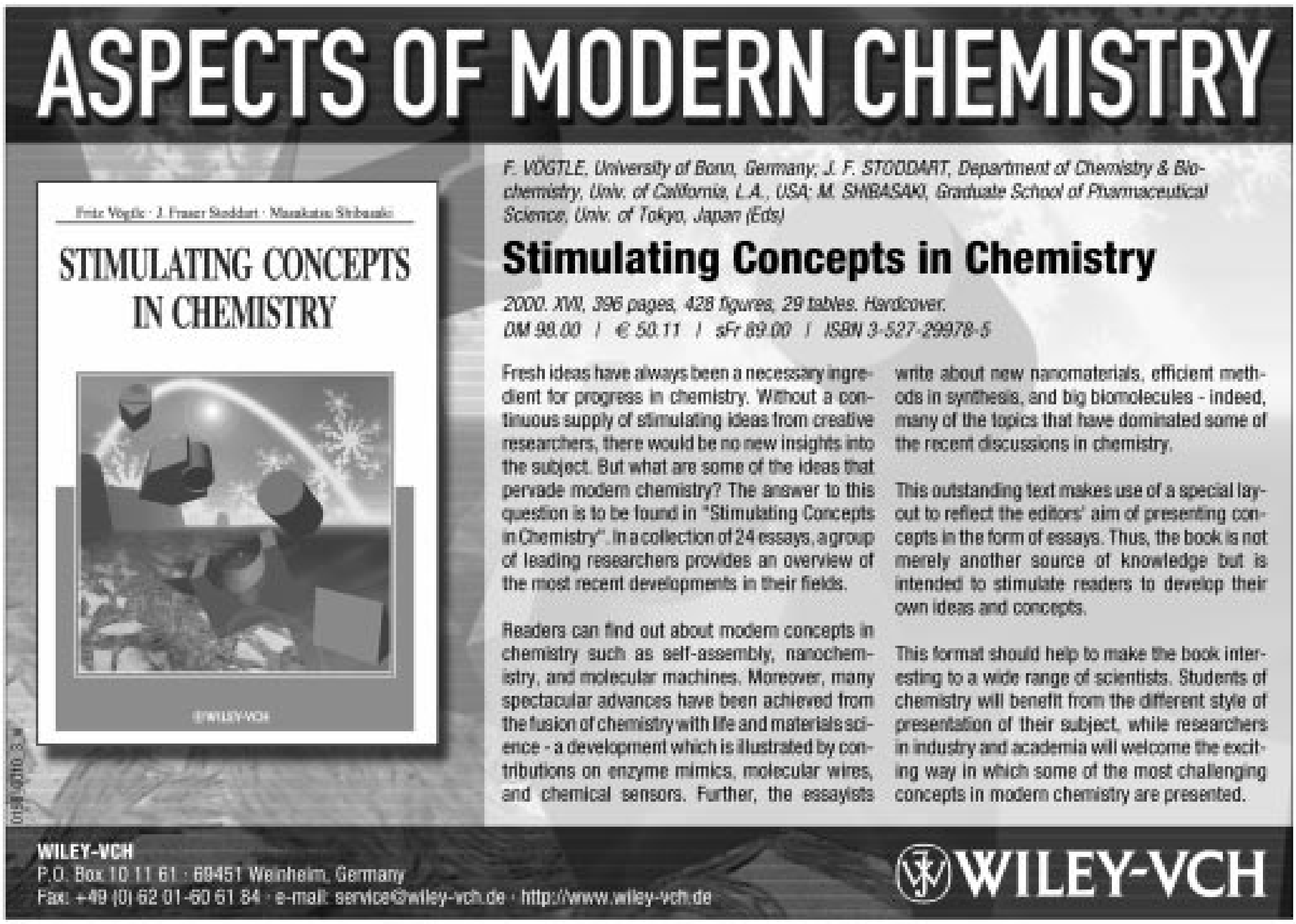

ASPECTS OF MODERN CHEMISTRY

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.

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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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