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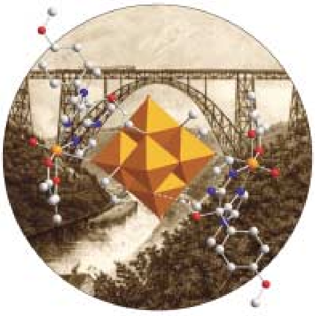
Pages 2423–2618

COVER PICTURE

The cover picture shows a polyhedral representation of a polyoxovanadate core $\{V_6O_{13}(OMe)_6\}^{2-}$, which is linked to two vanadyl moieties. These are coordinated through the N_2O_2 donor set of organic ligands, which additionally stabilize the hexavanadate through two hydrogen bonds. This compound can be considered as “bridging the gap” between polyoxometalates and classic coordination compounds. Fittingly, in the background, is Müngsten railway bridge near Wuppertal, Germany, which links the towns of Remscheid and Solingen. The bridge, which was built in 1897, at a height of 107 m, an arch width of 170 m, and a total length of 500 m was considered an engineering masterpiece of its time in Europe. More about the successful linkage of two important classes of compounds is reported in the communication by M. Piepenbrink, M. U. Triller, N. H. J. Gorman, and B. Krebs on pp. 2523 ff.



REVIEW

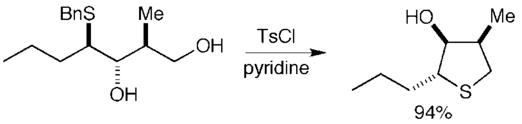
Contents

Since the discovery of the carbon nanotubes in 1991, much effort has been made to find nanotubes and other anisotropic nanomaterials. This interest is caused by the outstanding structural characteristics of such materials that are combined with promising physical and chemical properties. This review focuses on the advances made in oxidic nanotubes, such as vanadium oxide nanotubes (see picture) and nanorods, and highlights the most important synthetic trends.

Angew. Chem. **2002**, *114*, 2554–2571

Keywords: nanomaterials · nanorods · nanotubes · oxides · solvothermal synthesis

Cyclization reactions involving thiiranium and thiolanium ion intermediates lead to highly substituted saturated O, N, and S heterocycles in high yield and with complete stereocontrol (see scheme).



Angew. Chem. **2002**, *114*, 2572–2593

D. J. Fox, D. House,*
S. Warren* 2462–2482

Mechanisms of Sulfanyl (RS) Migrations: Synthesis of Heterocycles

Keywords: cyclization • heterocycles • rearrangement • sulfanyl groups • thiiranium ions

ESSAY

Out of the Blue: The noble colors blue and purple were highly regarded in the past because of their rarity. Thus ancient civilizations invented blue and purple pigments, such as, Egyptian Blue (see amulet shown), Chinese Blue, and Chinese Purple, all of which contain alkaline-earth metals and copper. It is shown how their synthesis may have been developed in ancient times: an understanding of stoichiometry, the control of reaction temperature, and the hypothesis of knowledge transfer are essential.

Angew. Chem. **2002**, *114*, 2595–2600

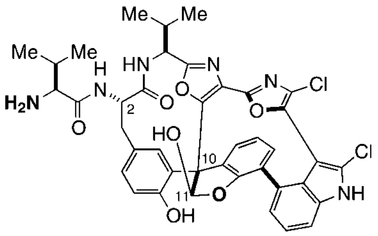
H. Berke* 2483–2487

Chemistry in Ancient Times: The Development of Blue and Purple Pigments

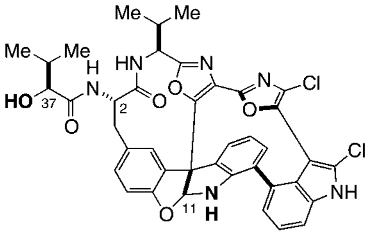
Keywords: alkaline-earth metals • dyes/pigments • history of science

HIGHLIGHTS

Revision of the structure originally proposed for the antimitotic natural product diazonamide A (**2**) was required after the recent synthesis of polycycle (**1**); the total synthesis of **2** still remains elusive. However, there is much to learn from the significant synthetic contributions and innovative strategies developed to date.



1
nominal diazonamide A
1991 assignment



2
(–)-diazonamide A
2001 assignment

Angew. Chem. **2002**, *114*, 2601–2606

T. Ritter, E. M. Carreira* ... 2489–2495

The Diazonamides: The Plot Thickens

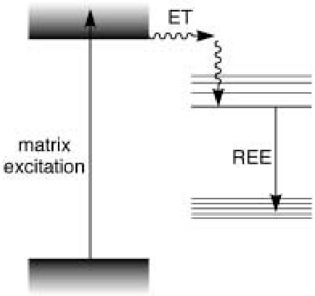
Keywords: antitumor agents • atropisomerism • natural products • structure elucidation • total synthesis

VIPs

The following communications are “Very Important Papers” in the opinion of two referees. They will be published shortly (that marked with a diamond will be published in the next issue). Short summaries of these articles can be found on the *Angewandte Chemie* homepage at the address http://www.angewandte.org

Highly Selective Transport of Organic Compounds by Using Supported Liquid Membranes Based on Ionic Liquids	L. C. Branco, J. G. Crespo, C. A. M. Afonso*	◆
Atom-Transfer Tandem Radical Cyclization Reactions Promoted by Lewis Acids	D. Yang,* S. Gu, H.-W. Zhao, N.-Y. Zhu	
Metallabenzenes and Valence Isomers: Synthesis and Characterization of a Platinabenzene	V. Jacob, T. J. R. Weakley, M. M. Haley*	

Matrix excitation above the band-gap energy enables lanthanide ions in host–guest systems to be sensitized (see scheme; ET = energy transfer; REE = rare earth emission). The enhanced luminescence of the enclosed lanthanide ions gives characteristic linelike emission spectra.



Angew. Chem. **2002**, *114*, 2607–2608

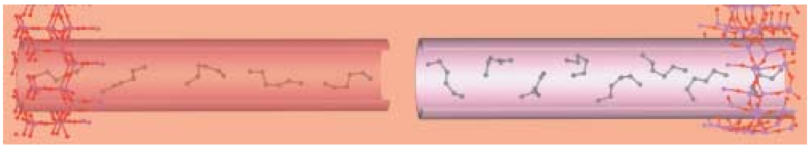
H. Maas, A. Currao,
G. Calzaferri* 2495–2497

Encapsulated Lanthanides as Luminescent Materials

Keywords: energy transfer · glasses · lanthanides · luminescence · zeolites

COMMUNICATIONS

Doing a stretch in zeolites: Usually molecular sieves selectively process and yield the fastest diffusing, least bulky molecule. When sieves were identified that seemed to selectively yield, adsorb, and stabilize isomers with a larger diameter, the term "inverse shape selectivity" was coined. Molecular simulations indicate that these sieves preferentially yield molecules because of entropic effects, which favor those molecules that have the shortest effective length. In narrow zeolite pores linear molecules are stretched whereas in wide pores they can be coiled (see diagram).



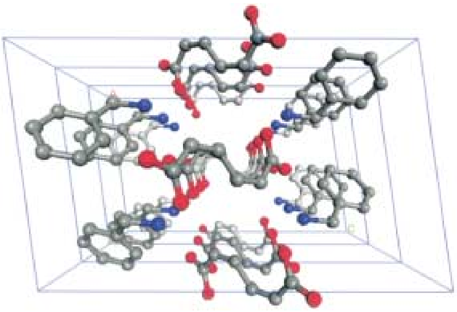
Angew. Chem. **2002**, *114*, 2609–2612

M. Schenk, S. Calero, T. L. M. Maesen,
L. L. van Benthem, M. G. Verbeek,
B. Smit* 2499–2502

Understanding Zeolite Catalysis: Inverse Shape Selectivity Revised

Keywords: alkanes · heterogeneous catalysis · molecular modeling · shape selectivity · zeolites

Stacking made to order: Weak intermolecular interactions such as 2D hydrogen-bonding networks, aromatic-ring stacking, and CH/π or halogen–halogen interactions account for the columnar organization of muconic and sorbic acid derivatives in the crystalline state (see picture). When the stacking distance is close to 5 Å these 1,3-dienes undergo topochemical polymerization upon irradiation.



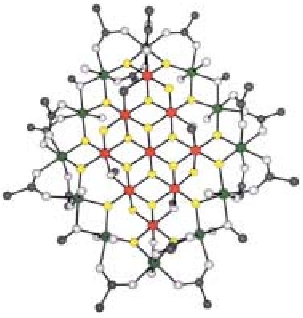
Angew. Chem. **2002**, *114*, 2612–2615

A. Matsumoto,* K. Sada,* K. Tashiro,*
M. Miyata,* T. Tsubouchi, T. Tanaka,
T. Odani, S. Nagahama, T. Tanaka,
K. Inoue, S. Saragai,
S. Nakamoto 2502–2505

Reaction Principles and Crystal Structure Design for the Topochemical Polymerization of 1,3-Dienes

Keywords: crystal engineering · polymerization · solid-state reactions · supramolecular chemistry · topochemistry

Beautiful offspring: Manganese/oxide/carboxylate-cluster chemistry continues to surprise with its rich variety of structural types. Here a new Mn_{21} cluster (see picture Mn^{4+} (red), Mn^{3+} (green)) with a $12\,Mn^{III}9\,Mn^{IV}$ oxidation level and an approximately planar core is reported.



Angew. Chem. **2002**, *114*, 2616–2618

J. T. Brockman, J. C. Huffman,
G. Christou* 2506–2508

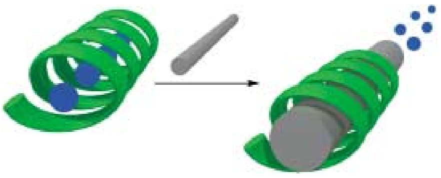
A High Nuclearity, Mixed-Valence Manganese(III,IV) Complex: $[Mn_{21}O_{24}(OMe)_8(O_2CCH_2tBu)_{16}(H_2O)_{10}]$

Keywords: cluster compounds · magnetic properties · manganese · mixed-valent compounds · structure elucidation

A. Star, D. W. Steuerman, J. R. Heath, J. F. Stoddart* 2508–2512

Starched Carbon Nanotubes

Common-or-garden starch can render single-walled carbon nanotubes (SWNTs) readily soluble in water. The secret is to preorganize the linear amylose component in the starch into a helix with iodine prior to bringing the SWNTs on the scene. The SWNTs displace the iodine molecules in a "pea-shooting" type of mechanism (see scheme). After some physical cajoling of the aqueous solution containing the starch–SWNT complex, a fine "bucky paper" is formed. Spitting in the aqueous solution, followed by sitting around for a few hours, also enables equally fine "bucky paper" to be harvested.



Angew. Chem. **2002**, *114*, 2618–2622

Keywords: amylose • hydrophobic interactions • molecular recognition • nanotubes • self-assembly

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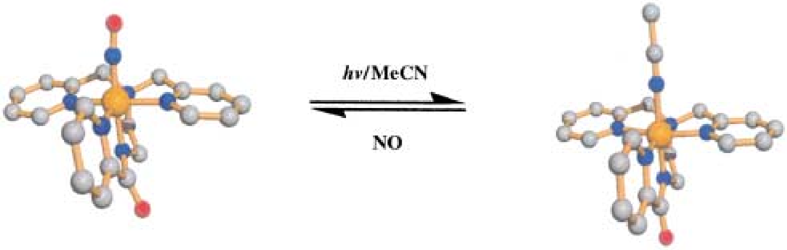
A. K. Patra, R. Afshar, M. M. Olmstead, P. K. Mascharak* 2512–2515

The First Non-Heme Iron(III) Complex with a Ligated Carboxamido Group That Exhibits Photolability of a Bound NO Ligand

Reversible NO binding in acetonitrile is observed in the non-heme Fe^{III} complex $[Fe(PaPy_3)(NO)](ClO_4)_2$ (see scheme). The NO moiety is photolabile, and can dissociate from this complex under very mild conditions. The carboxamido nitrogen donor *trans* to NO appears to play a crucial role in the observed photolability. ($PaPy_3$ = *N*-[*N*,*N*-bis(2-pyridylmethyl)aminoethyl]-2-pyridinecarboxamide).



$[(PaPy_3)Fe(NO)]^{2+}$ $[(PaPy_3)Fe(CH_3CN)]^{2+}$

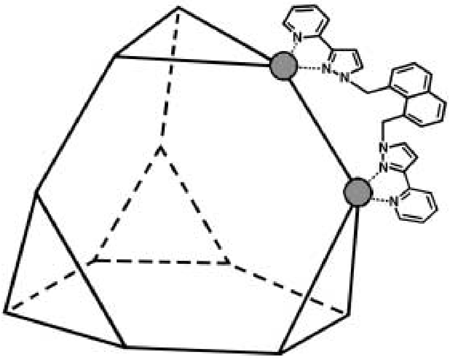
Angew. Chem. **2002**, *114*, 2622–2625

Keywords: iron • nitric oxide • N ligands • photolability

Z. R. Bell, J. C. Jeffery, J. A. McCleverty, M. D. Ward* 2515–2518

Assembly of a Truncated-Tetrahedral Chiral $[M_{12}(\mu\text{-}L)_{18}]^{24+}$ Cage

Instead of the expected tetrahedral M_4L_6 cage, a far more complicated $M_{12}L_{18}$ cage forms when the bridging ligand shown reacts with Co^{II} ions. The dodecanuclear cage has the topology of a tetrahedron in which all four vertices are truncated to reveal triangular faces. A bridging ligand spans each of the 18 edges of the metal cage, and all 12 metal–tris(chelate) centers are homochiral. $[BF_4]^-$ ions are located in the large central cavity and in the two-dimensional cavities at the center of each face.

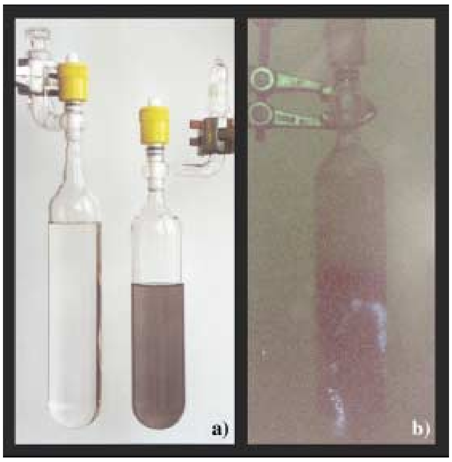


Angew. Chem. **2002**, *114*, 2625–2628

Keywords: cage compounds • host–guest systems • N ligands • self-assembly • supramolecular chemistry

Small flashes (b) occur during the freezing of triethylgallium samples in liquid nitrogen, and on warming from −196°C this is accompanied by decomposition (a). This effect was observed during the determination of the crystal structures of $GaMe_3$ and $GaEt_3$, which both show intermolecular interactions between their electron-deficient gallium atoms and the alkyl groups of neighboring molecules.

Angew. Chem. **2002**, *114*, 2629–2633



N. W. Mitzel,* C. Lustig, R. J. F. Berger,
N. Runeberg 2519–2522

Luminescence Phenomena and Solid-State Structures of Trimethyl- and Triethylgallium

Keywords: ab initio calculations · gallium · luminescence · photochemistry · solid-state structures

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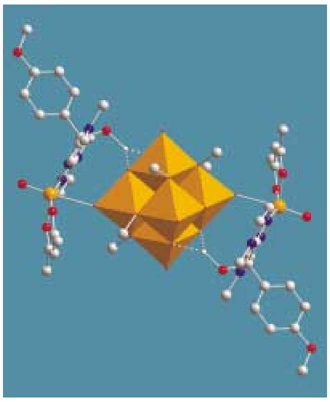
Cluster catalysts for directed oxygen transfer? In attempts towards the creation of novel catalytic systems for directed oxygen-transfer processes a novel type of polyoxometalate cluster containing vanadium was synthesized. The first example of a polyoxovanadate composed of a hexavanadate molecular center and two reactive, exchangeable, vanadium-centered complexes which are tilted towards the polyoxometalate center is presented (see picture).

Angew. Chem. **2002**, *114*, 2633–2635



M. Piepenbrink, M. U. Triller,
N. H. J. Gorman, B. Krebs* . 2523–2525

Bridging the Gap between Polyoxometalates and Classic Coordination Compounds: A Novel Type of Hexavanadate Complex

Keywords: coordination chemistry · N ligands · polyoxometalates · structure elucidation · vanadium

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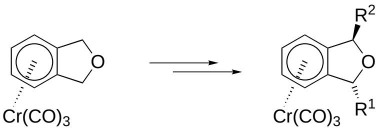
A completely stereoselective synthesis of pharmacologically relevant *trans*-1,3-disubstituted dihydroisobenzofurans utilizes the surprising selectivity during the benzylic deprotonation of a silylated [phthalan–$Cr(CO)_3$] complex (see scheme).

Angew. Chem. **2002**, *114*, 2635–2638



S. Zemolka, J. Lex,
H.-G. Schmalz* 2525–2528

Benzylic *endo*-Alkylation of Phthalan–$Cr(CO)_3$ Complexes via Temporary Silylation: An Entry to *trans*-1,3-Disubstituted Dihydroisobenzofurans

Keywords: alkylation · arenes · chromium · deprotonation · enantioselectivity

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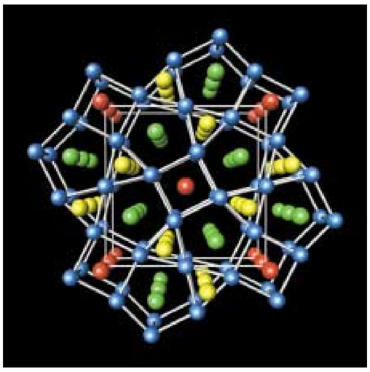
Quaternary rhodium borides of general formula $A_2MRh_5B_2$ (see picture: Mg green, Mn red, Rh blue, B yellow) offer a nice playground for combined synthetic–theoretical investigations. The relative robustness of the underlying structure type allows various adjustments of the valence-electron concentration to be explored. In synthesizing new magnetic materials by following a chemical theory of cooperative magnetic phenomena, it is demonstrated how physical properties, such as antiferromagnetic or ferromagnetic behavior can be understood, predicted, and, eventually, realized.

Angew. Chem. **2002**, *114*, 2638–2642



R. Dronskowski,* K. Korczak,
H. Lueken, W. Jung 2528–2532

Chemically Tuning between Ferromagnetism and Antiferromagnetism by Combining Theory and Synthesis in Iron/Manganese Rhodium Borides

Keywords: borides · density functional calculations · intermetallic phases · magnetism · solid-state structures

1433-7851/02/4114-2429 $ 20.00+.50/0

Catalytically active nanoparticle sites: Different catalytic activity of different active sites coexisting on a supported nanoparticle has been directly observed using molecular-beam techniques and in situ surface vibrational spectroscopy. For methanol decomposition on a supported Pd model catalyst (see picture), it is shown that carbon–oxygen-bond breakage and dehydrogenation occur as competing reaction pathways at particle defects and on regular facets, respectively.

Angew. Chem. **2002**, *114*, 2643–2646

S. Schauermann, J. Hoffmann,
V. Johánek, J. Hartmann, J. Libuda,*
H.-J. Freund 2532–2535

Catalytic Activity and Poisoning of Specific Sites on Supported Metal Nanoparticles

Keywords: heterogeneous catalysis · kinetics · molecular beams · supported catalysts · surface chemistry

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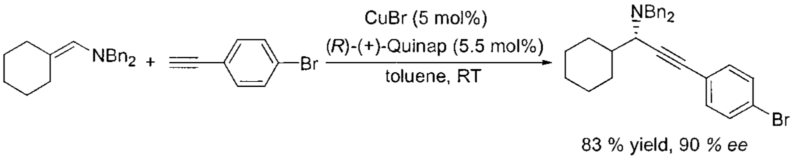
Enantiomerically enriched, functionalized, and protected propargylamines are obtained under mild conditions in a new copper(I)/Quinap-catalyzed addition reaction of alkynes to enamines (see scheme).



Angew. Chem. **2002**, *114*, 2651–2654

C. Koradin, K. Polborn,
P. Knochel* 2535–2538

Enantioselective Synthesis of Propargylamines by Copper-Catalyzed Addition of Alkynes to Enamines

Keywords: alkynes · asymmetric synthesis · C–H activation · heterogeneous catalysis · propargylamines

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Despite being unreactive towards many neutral compounds even in the sense of association, Cr$^+$ undergoes gas-phase adduct formation with hexafluoroacetone. In the presence of water, the monoadduct undergoes three consecutive C–F bond hydrolysis reactions, which may be followed, after complexation of water, by even a fourth C–F bond cleavage (see scheme).

$$\mathrm{Cr^+} \xrightarrow{+\,C_3F_6O} \mathrm{CrC_3F_6O^+} \xrightarrow[-\,HF]{+\,H_2O} \dots \xrightarrow[-\,HF]{+\,H_2O} \mathrm{CrC_3F_3O_3H^+}$$

Angew. Chem. **2002**, *114*, 2648–2651

U. Mazurek, D. Schröder,
H. Schwarz 2538–2541

Hydrolytic Activation of C–F Bonds in the Gas Phase by Intrinsically Unreactive Chromium Cations

Keywords: C–F activation · chromium · gas-phase reactions · hydrolysis · mass spectrometry

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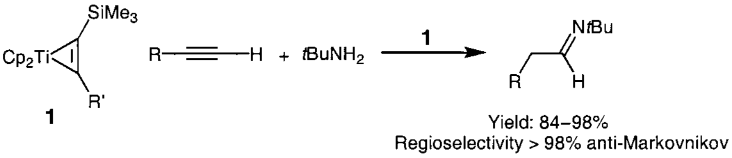
Titanocene-η-alkyne complexes such as **1** are efficient catalysts for the hydroamination of terminal alkynes to imines (see scheme; R = alkyl, R′ = SiMe$_3$ or Ph). Excellent yields of imines and good to excellent regioselectivities for the anti-Markovnikov products were obtained.



Angew. Chem. **2002**, *114*, 2646–2648

A. Tillack, I. Garcia Castro,
C. G. Hartung, M. Beller* .. 2541–2543

Anti-Markovnikov Hydroamination of Terminal Alkynes

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

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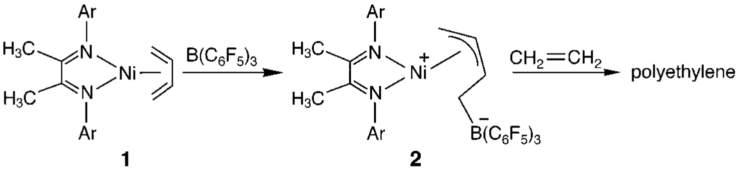
Addition of B(C$_6$F$_5$)$_3$ to the butadiene ligand in **1** leads to the zwitterionic complex **2** (characterized by single-crystal X-ray diffraction; Ar = 2,6-diisopropylphenyl), which is an active catalyst for the polymerization of ethylene. The formation of **2** could have model character for an activation pathway for homogeneous Ziegler–Natta catalysts of late transition metals without σ-alkyl ligands.



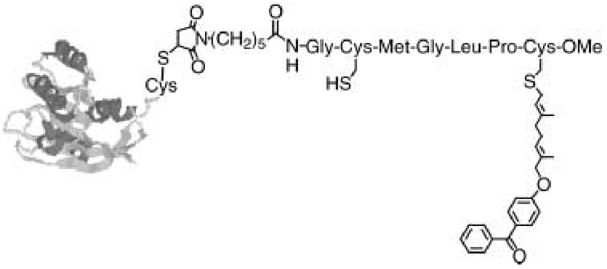
Angew. Chem. **2002**, *114*, 2662–2664

J. W. Strauch, G. Erker,* G. Kehr,
R. Fröhlich 2543–2546

Formation of a Butadienenickel-Based Zwitterionic Single-Component Catalyst for Ethylene Polymerization: An Alternative Activation Pathway for Homogeneous Ziegler–Natta Catalysts of Late Transition Metals

Keywords: diene ligands · homogeneous catalysis · nickel · polymerization · Ziegler–Natta catalysis

The combination of organic synthesis with cell biology provides access to a chimera of the signal-transducing Ras protein, which contains a photoactivatable benzophenone group in its isoprenoid membrane anchor, yet retains biological activity. The semisynthetic protein is a new tool to address open questions concerning the mechanism of selective plasma membrane localization of Ras and to identify putative binding partners of Ras.



Angew. Chem. **2002**, *114*, 2655 – 2658

J. Kuhlmann,* A. Tebbe, M. Völkert,
M. Wagner, K. Uwai,
H. Waldmann* .... 2546 – 2550

Photoactivatable Synthetic Ras Proteins: “Baits” for the Identification of Plasma-Membrane-Bound Binding Partners of Ras

Keywords: lipoproteins • photoactivation • protein engineering • signal transduction

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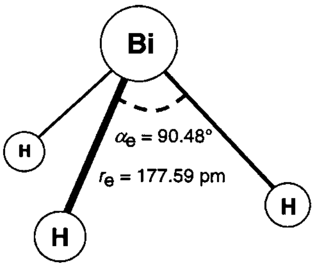
Fact! That is the answer to the question posed in the title. Over 40 years passed before the synthesis of bismuthine (BiH_3; see picture) by Amberger was confirmed successfully. High-resolution IR and millimeter-wave spectroscopy as well as ab initio calculations now provide a detailed picture of the molecular structure of this compound.



Angew. Chem. **2002**, *114*, 2659 – 2661

W. Jerzembeck, H. Bürger,*
L. Constantin, L. Margulès, J. Demaison,
J. Breidung, W. Thiel .... 2550 – 2552

Bismuthine BiH_3: Fact or Fiction? High-Resolution Infrared, Millimeter-Wave, and Ab Initio Studies

Keywords: ab initio calculations • bismuth • hydrides • IR spectroscopy • rotational spectroscopy

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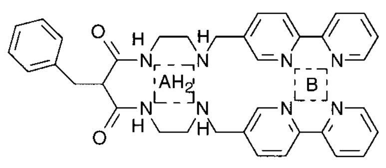

Shedding light on the environment: An auxillary light-emitting fragment (coumarin-343) binds to a Cu^{II} ion in the right-hand compartment (B) of the ligand shown and its fluorescence is “switched off”. If the pH value is raised from 7 to $\geq$11 the metal moves to the left compartment (A), which imposes a square stereochemistry and forces dissociation of the indicator, thus “switching on” the fluorescence. The pH-driven metal translocation is reversible and can be carried out for many cycles.

Angew. Chem. **2002**, *114*, 2665 – 2668

V. Amendola, L. Fabbrizzi,* C. Mangano,
H. Miller, P. Pallavicini, A. Perotti,
A. Taglietti .... 2553 – 2556

Signal Amplification by a Fluorescent Indicator of a pH-Driven Intramolecular Translocation of a Copper(II) Ion

Keywords: copper • fluorescent probes • molecular devices • N ligands • transition metals

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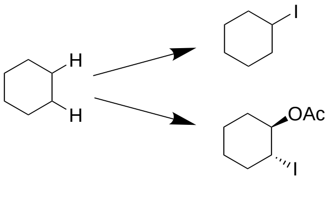
You can also choose from alkanes! Either mono- or bifunctional iodo derivatives can be prepared from alkanes (see scheme) in an efficient and selective manner by using $PhI(OAc)_2$, I_2, and an alcohol.



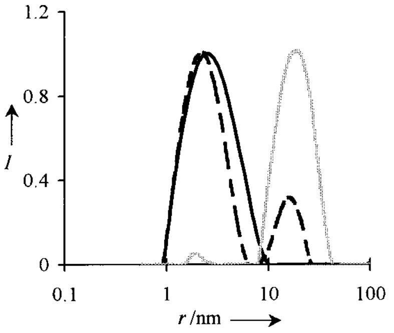
Angew. Chem. **2002**, *114*, 2668 – 2670

J. Barluenga,* F. González-Bobes,
J. M. González .... 2556 – 2558

Activation of Alkanes upon Reaction with $PhI(OAc)_2-I_2$

Keywords: alkanes • C–H activation • iodination • iodine • photochemistry

In situ dynamic light scattering (DLS) and high-resolution transmission electron microscopy (HRTEM) can be used, in conjunction with other techniques, to improve our understanding of the mechanism of zeolite formation. The effects of aging and hydrothermal pre-treatment of precursors cause variations in the size distribution (see diagram; r = particle size, I = intensity) and relative crystallinity of the as-prepared zeolitic materials.



Angew. Chem. **2002**, *114*, 2670–2673

S. Mintova,* N. H. Olson, J. Senker, T. Bein* 2558–2561

Mechanism of the Transformation of Silica Precursor Solutions into Si-MFI Zeolite

Keywords: dynamic light scattering · electron microscopy · silicon · zeolites

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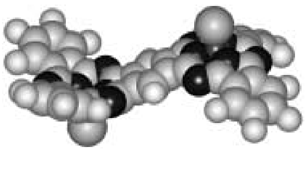
The *syn* and *anti* topoisomers of fused subphthalocyanine dimers were synthesized and characterized. The space-filling model of the *anti* topoisomer is depicted. These compounds are the first step towards the synthesis of larger curved π surfaces.



Angew. Chem. **2002**, *114*, 2673–2677

C. G. Claessens, T. Torres* .. 2561–2565

Synthesis, Separation, and Characterization of the Topoisomers of Fused Bicyclic Subphthalocyanine Dimers

Keywords: boron · electronic spectroscopy · macrocycles · phthalocyanines

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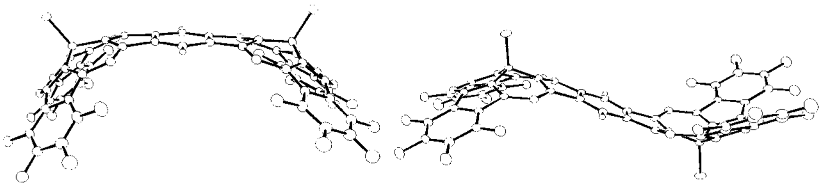
The structures of *cis* and *trans* forms of a binuclear subphthalocyanine (SubPc) have been determined by X-ray crystallography (see pictures). Electronic absorption and magnetic circular dichrosim spectra of these dimers are similar in shape, but the Q band of the *trans* isomer appears at longer wavelength than that of the *cis* isomer by about 3–4 nm.



Angew. Chem. **2002**, *114*, 2677–2680

T. Fukuda, J. R. Stork, R. J. Potucek, M. M. Olmstead, B. C. Noll, N. Kobayashi,* W. S. Durfee* 2565–2568

cis and *trans* Forms of a Binuclear Subphthalocyanine

Keywords: boron · electronic spectroscopy · macrocycles · phthalocyanines · structure elucidation

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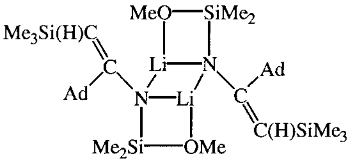
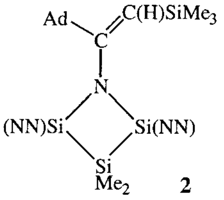
A novel reaction of a thermally stable silylene with **1**, obtained by regio- and stereospecific insertion of the α-halogen-free adamantyl cyanide into the Li–C bond of the bis(silyl)methyl compound $Li[CH(SiMe_2OMe)(SiMe_3)]$, yielded the new azatrisilacyclobutane **2**. NN = $1,2\text{-}[(t\text{BuCH}_2)\text{N}]_2\text{C}_6\text{H}_4$.



1



2

Angew. Chem. **2002**, *114*, 2680–2683

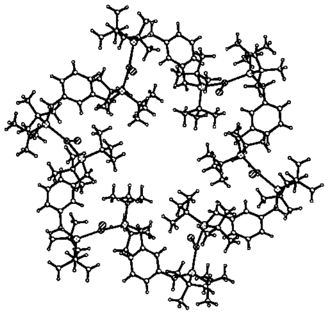
F. Antolini, B. Gehrhus,* P. B. Hitchcock, M. F. Lappert* 2568–2571

Synthesis and Structure of an Azatrisilacyclobutane and Its Precursor, a Novel Lithium Enamide Having a Tricyclic $(LiNSiO)_2$ Skeleton

Keywords: allylic compounds · heterocycles · insertion · silicon · silylenes

With an outside diameter of approximately 2 nm, the title complex comprises six copper chloride moities bridged by six 1,3-$(CH_2PtBu_2)_2C_6H_4$ ligands (see X-ray crystal structure). The solution properties of the resulting 48-atom macrocycle have been studied by variable-temperature NMR and UV/Vis spectroscopy, as well as by electrochemical studies.

Angew. Chem. **2002**, *114*, 2683 – 2685



E. D. Blue, T. B. Gunnoe,*
N. R. Brooks .... 2571 – 2573

Synthesis, Spectroscopy, and Solid-State Structural Characterization of the Hexanuclear Copper Macrocycle $[Cu_6Cl_6(\mu\text{-PCHP})_6]$

Keywords: copper • electrochemistry • fluorescence • macrocycles • phosphane ligands

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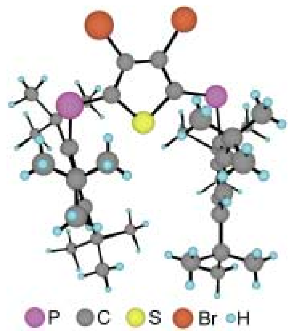
The first diphosphaheteroquinoid compound, which contains two low-coordinate phosphorus atoms and a thienoquinoid skeleton (see picture), was isolated as air-stable orange crystals. Its quinoid nature was confirmed by X-ray crystallography and cyclic voltammetry, which revealed the expected redox behavior.

Angew. Chem. **2002**, *114*, 2686 – 2688



F. Murakami, S. Sasaki,
M. Yoshifuji* .... 2574 – 2576

Synthesis, Structure, and Redox Properties of Diphosphathienoquinones

Keywords: phosphaalkenes • quinones • radical ions • redox chemistry • sulfur heterocycles

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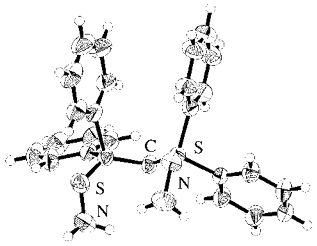
Double ylidic character in the S-C-S bonds is apparent from the single-crystal X-ray analysis of the title compound (see structure). This electronic configuration was supported by ab initio calculations on a model compound in which the phenyl groups were replaced by methyl groups.

Angew. Chem. **2002**, *114*, 2688 – 2690



T. Fujii, T. Ikeda, T. Mikami, T. Suzuki,
T. Yoshimura* .... 2576 – 2578

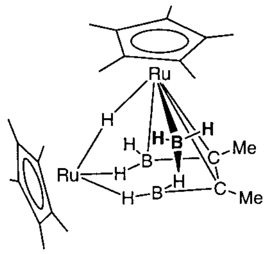
Synthesis and Structure of $(MeN)Ph_2S{=}C{=}SPh_2(NMe)$

Keywords: bond theory • carbanions • multiple bonds • sulfur • ylides

---

Make the weak bonds first: Addition of carbon to a metallaborane rather than a metal to a carborane permits the isolation of metallacarboranes with a) identical compositions and different shapes, b) an exocluster bridging boryl group (see picture), and c) isomers with two CMe or CH and CEt fragments.

Angew. Chem. **2002**, *114*, 2690 – 2693



H. Yan, A. M. Beatty,
T. P. Fehlner* .... 2578 – 2581

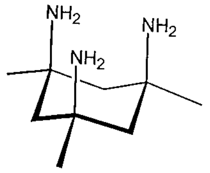
Reaction of 2-Butyne with *nido*-$[1,2\text{-}(Cp^*RuH)_2B_3H_7]$: Improved Kinetic Control Leads to Metallacarboranes of Novel Composition and Structure

Keywords: alkynes • boranes • cluster compounds • metallacarboranes • ruthenium

---

A "two-protons-plus-one-lone-pair" bifurcated relationship is adopted by the amine groups in the amino equivalent of Kemp's triacid (see structure). Intramolecular proton transfer occurs in the aminolysis of three esters with this triamine, whereas two diamines, studied for comparison, switch abruptly from intramolecular to intermolecular proton transfer, depending upon the ester reactivity. The triamine offers attractive possibilities as a framework for bioorganic modeling.

Angew. Chem. **2002**, *114*, 2693 – 2696

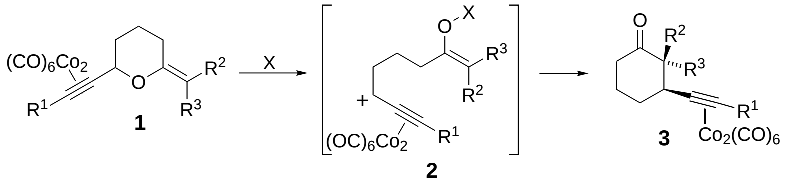


F. M. Menger,* J. Bian,
V. A. Azov .... 2581 – 2584

A 1,3,5-Triaxial Triaminocyclohexane: The Triamine Corresponding to Kemp's Triacid

Keywords: amines • enzyme models • hydrogen bonds • reaction mechanisms

Simultaneous generation of an enolate and Nicholas carbocation unit (**2**) occurs on treatment of enol ether–cobalt complexes **1** with Lewis acids (X). Subsequent cyclization provides α-functionalized β-alkynyl cycloalkanones **3** in a regiospecific fashion. The scope of this rearrangement process is discussed, as is the stereoselectivity of α-alkyl incorporation.



Angew. Chem. **2002**, *114*, 2696–2699

D. R. Carbery, S. Reignier, J. W. Myatt, N. D. Miller, J. P. A. Harrity* 2584–2587

Development of a Co-Mediated Rearrangement Reaction

Keywords: alkyne ligands · carbocations · cobalt · cyclization · enol ethers

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The nature of oxide-supported metal catalysts may change in oxidizing conditions: Studies on the correlation between the Rh phase in the structure of the Rh/Al_2O_3 catalyst and the catalytic performance for the reduction of NO by H_2 to N_2 (on reduced, metallic sites) and N_2O (on oxidized sites) reveal that the phases of the supported metal species can be interconverted on time scales that can be deterministic in terms of the activity and selectivity of the catalysts.

Angew. Chem. **2002**, *114*, 2699–2701

M. A. Newton, A. J. Dent, S. Diaz-Moreno, S. G. Fiddy, J. Evans* 2587–2589

Rapid Phase Fluxionality as the Determining Factor in Activity and Selectivity of Highly Dispersed, Rh/Al_2O_3 in $deNO_x$ Catalysis

Keywords: heterogeneous catalysis · nanostructures · rhodium · structure–activity relationships · X-ray absorption spectroscopy

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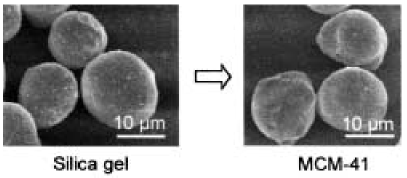
Pores for order: Particles of silica gel can be transformed into MCM-41 without losing their size and shape by a low-temperature hydrothermal treatment (see electron micrographs). This method allows easy preparation of custom-tailored materials for chromatography and separation.



Angew. Chem. **2002**, *114*, 2702–2704

T. Martin, A. Galarneau, F. Di Renzo,* F. Fajula, D. Plee 2590–2592

Morphological Control of MCM-41 by Pseudomorphic Synthesis

Keywords: microporous materials · particles · pseudomorphism · silicates · zeolites

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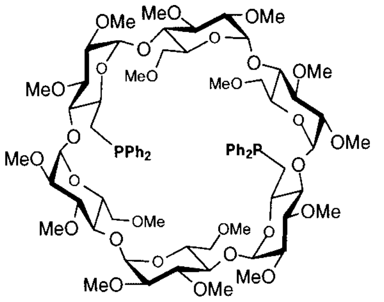
Are α-cyclodextrin cavities chlorophillic? The α-CD-derived diphosphane **1**, a ligand which shows a marked tendency to act as a *trans*-spanning chelator, provides an answer to this question. Reaction of **1** with a variety of transition metal chlorides systematically afforded complexes in which the M–Cl bond(s) is(are) captured by the cavity and results in weak interactions between the sequestered Cl atoms and inwardly oriented C–H bonds. The shortest H-5 ⋯ Cl distance in the Pd complex is 2.64(2) Å.



1

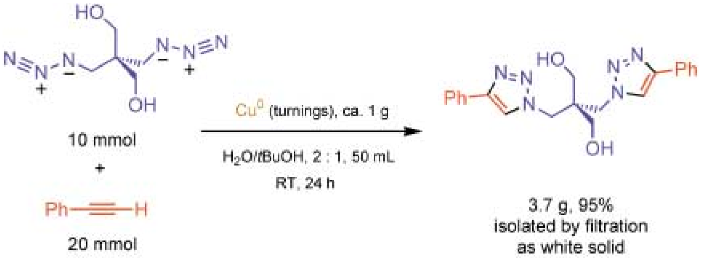
Angew. Chem. **2002**, *114*, 2705–2708

E. Engeldinger, D. Armspach,* D. Matt,* P. G. Jones, R. Welter 2593–2596

A Cyclodextrin Diphosphane as a First and Second Coordination Sphere Cavitand: Evidence for Weak C–H ⋯ Cl–M Hydrogen Bonds within Metal-Capped Cavities

Keywords: chelates · cyclodextrins · metallocavitands · noncovalent interactions · phosphanes

By simply stirring in water, organic azides and terminal alkynes are readily and cleanly converted into 1,4-disubstituted 1,2,3-triazoles through a highly efficient and regioselective copper(I)-catalyzed process (see scheme for an example).



Angew. Chem. **2002**, *114*, 2708–2711

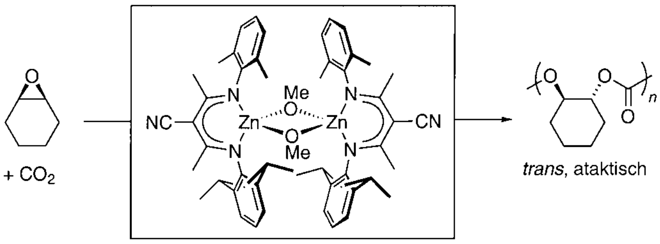
V. V. Rostovtsev, L. G. Green,
V. V. Fokin,*
K. B. Sharpless* 2596–2599

A Stepwise Huisgen Cycloaddition Process: Copper(I)-Catalyzed Regioselective "Ligation" of Azides and Terminal Alkynes

Keywords: azides • copper • cycloaddition • homogeneous catalysis • nitrogen heterocycles

---

CO_2 is perhaps the most attractive carbon-based feedstock owing to its abundance and low toxicity. Utilization of this contributor to global warming is a long-standing goal. Reported here are new single-site β-diiminate zinc catalysts that exhibit unprecedented activities for CO_2/epoxide polymerization (see scheme).



Angew. Chem. **2002**, *114*, 2711–2714

D. R. Moore, M. Cheng, E. B. Lobkovsky,
G. W. Coates* 2599–2602

Electronic and Steric Effects on Catalysts for CO_2/Epoxide Polymerization: Subtle Modifications Resulting in Superior Activities

Keywords: carbon dioxide fixation • green chemistry • homogeneous catalysis • ligand effects • ring-opening polymerization

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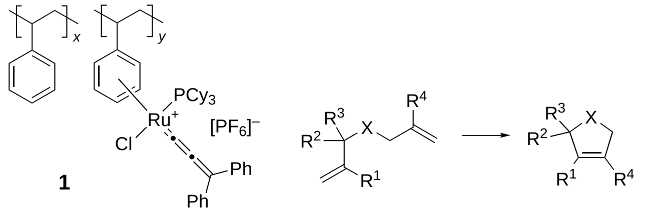
Styrene as ligand and support: An excellent polymer-supported ruthenium catalyst **1** has been developed in which the benzene rings of polystyrene are utilized as ligands to immobilize the ruthenium onto the polymer. In the presence of **1**, ring-closing olefin metathesis proceeded smoothly to afford adducts in high yields. Furthermore, the catalyst was recovered quantitatively by filtration, and could be reused without loss of activity.



Angew. Chem. **2002**, *114*, 2714–2716

R. Akiyama, S. Kobayashi* . 2602–2604

A Novel Polymer-Supported Arene–Ruthenium Complex for Ring-Closing Olefin Metathesis

Keywords: alkenes • metathesis • microencapsulation • ruthenium • supported catalysts

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 book review on *Voodoo Science: the road from foolishness to fraud* by N. J. Turro (*Angew. Chem.* **2002**, *41*, 1069), the references were inadvertantly omitted. The editorial office apologies for this, and the references are now given.

[1] T. S. Kuhn, *The Nature of Scientific Revelutions, 2nd ed.*, University of Chicago Press, Chicago, IL, **1970**.
[2] a) N. J. Turro, *Angew. Chem.* **2000**, *112*, 2343; *Angew. Chem. Int. Ed.* **2000**, *39*, 2255; b) N. J. Turro, *Angew. Chem.* **2000**, *98*, 872; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 882.
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[4] M. Shermer, *Why People Believe Weird Things*, Freeman, NY, **1997**.
[5] W. Gratzer, *The Undergrowth of Science*, Oxford University Press, Oxford, **2000**.
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