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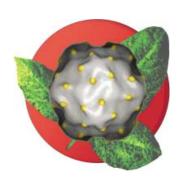
INTERNATION NAL EDITION

2002 41/3

Pages 373-524

COVER PICTURE

The cover picture shows a cowpea plant heavily infected with cowpea mosaic virus (background). A simple isolation procedure provides high yields of pure virus, which can be derivatized selectively by chemical reagents. The particles therefore behave in many respects like prefabricated dendrimers on a nanochemical (30 nm diameter) scale. Their polyvalency is highlighted by the foreground image, showing a cryo-electron microscopy analysis of the virus bearing gold clusters at each of 60 reactive cysteine residues introduced by site-directed mutagenesis. Further details are reported by J. E. Johnson and M. G. Finn and co-workers on p. 459ff.



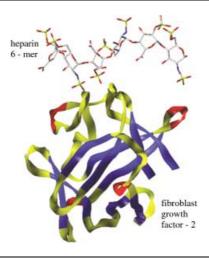
REVIEWS

——Contents

I. Capila, R. J. Linhardt * 390 – 412

Heparin – Protein Interactions

Various important physiological and pathophysiological processes in the human body are thought to be mediated by the interaction of heparin and heparan sulfate with proteins (an example is shown). These interactions have a high degree of specificity in most cases. Thus, understanding their molecular basis is important for the development of highly specific drug candidates.



Angew. Chem. 2002, 114, 426-450

Keywords: carbohydrates • coagulation • heparin • medicinal chemistry • molecular recognition

"Preparing the world for the challenges of the next century" is one of the goals of Agenda 21, the work program adopted for the 21st century in Rio by 179 countries. One of these challenges is that nine billion people will soon live on the earth and—according to the principles of the Rio Declaration—they all are entitled to a healthy and productive life in harmony with nature. If these principles are to be implemented, then the role of chemistry must also be rethought. This review, which coincides with the World Summit on Sustainable Development 2002 in Johannesburg, indicates new ideas on innovations in chemistry with regard to their ecological, economical, and social dimension.

Angew. Chem. 2002, 114, 402-425

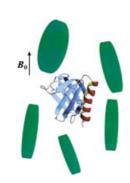
10 Years after Rio—Concepts on the Contribution of Chemistry to a Sustainable Development

Keywords: green chemistry • innovations • oxidations • renewable raw materials • sustainable development

HIGHLIGHT

The three-dimensional structures of biomacromolecules in solution can be determined with NMR spectroscopy. The use of residual dipolar couplings (RDCs) that can be measured in dilute liquid crystalline solution is currently revolutionizing the way structures are determined by NMR spectroscopy. This is highlighted by the recent de novo structure determination of the protein ubiquitin (see picture; liquid crystals are shown in green) using only RDC data.

Angew. Chem. 2002, 114, 453-456



B. Simon, M. Sattler * 437 – 440

De Novo Structure Determination from Residual Dipolar Couplings by NMR Spectroscopy

Keywords: liquid crystals • NMR spectroscopy • protein structures • residual dipolar couplings • structure elucidation

VIPs

The following communications are "Very Important Papers" in the opinion of two referees. They will be published shortly (those 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.com

Nonrelaxable Anisotropic Organization of Organic – Inorganic Hybrid Materials Induced by an Electric Field

G. Cerveau, R. J. P. Corriu,* E. Framery, S. Ghosh, M. Nobili

A Nanoporous Metal-Organic Framework Based on Bulky Phosphane Ligands

X. Xu, M. Nieuwenhuyzen, S. L. James*

Surface Structure and Crystal Growth in Zeolite Beta C

B. Slater,* R. A. Catlow, Z. Liu, T. Ohsuna, O. Terasaki, M. A. Camblor

COMMUNICATIONS



The strict exclusion of tertiary amines during the otherwise standard synthetic approach to the synthesis of the guanidinium-type peptide coupling reagents HBTU (X = CH, see scheme) and HATU (X = N) allows the synthesis of the uronium-type isomers of these guanidinium compounds, whose existence was until now pure speculation. These O isomers (O-HBTU and O-HATU) are more efficient coupling reagents than the N isomers.



Angew. Chem. 2002, 114, 457-461

The Uronium/Guanidinium Peptide Coupling Reagents: Finally the True Uronium Salts

Keywords: acylation • amides • amino acids • peptides • structure elucidation



Covalent modifications of DNA (DNA adducts, see schematic representation) play a key role in chemical carcinogenesis and are regarded as individual, internal dosimeters for exposure to genotoxic compounds. The analysis of DNA adducts has the potential to become an integral component of risk assessment.

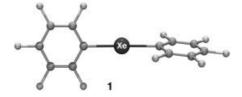
Angew. Chem. 2002, 114, 461-464



Capillary Electrophoresis Analysis of DNA Adducts as Biomarkers for Carcinogenesis

Keywords: DNA adduct · DNA damage · DNA methylation · electrophoresis · laser-induced fluorescence detection

Despite the extreme instability the organoxenon(II) compound $Xe(C_6F_5)_2$ (1; see structure) was determined from X-ray powder diffraction data. Compound 1 crystallizes in the monoclinic space group $P2_1/n$, the C-Xe-C unit is linear, and



H. Bock, D. Hinz-Hübner, U. Ruschewitz,* D. Naumann* 448–450

Structure of Bis(pentafluorophenyl)xenon, $Xe(C_6F_5)_2$

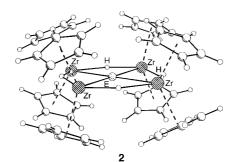
the torsion angle of the C_6F_5 rings is 72.5° . Experimental molecular parameters match well with calculated ones based on ab initio and density functional theory calculations.

Angew. Chem. 2002, 114, 465-467

Keywords: ab initio calculations • density functional calculations • noble gases • powder diffraction • structure elucidation • xenon

Role change: The arsenium salt $As[P(NMe_2)_3]_2^+BPh_4^-$ (1), prepared for the first time, proved to be both an arsenic(i) *and* a phosphorus(i) source. Thus the reaction of 1 with $[Cp_2Zr(H)Cl]$ $(Cp = \eta^5-C_5H_5)$ leads not only to the first arsonium ion with anti-van't Hoff–Le Bel configuration 2a (E = As; see structure), but at the same time to the homologous phosphonium ion 2b (E = P).

Angew. Chem. 2002, 114, 467-470



M. Driess,* H. Ackermann, J. Aust, K. Merz, C. von Wüllen 450–453

As[P(NMe₂)₃]₂⁺ as Simultaneous As¹ and P¹ Source: Synthesis and Density Function Calculations of Planar Tetracoordinate Arsonium and Phosphonium Ions

Keywords: arsenic • density functional calculations • phosphorus • zirconium

Complexes between precious metals and noble gases are more abundant than was initially considered likely. For example, in addition to the already known $[AuXe_4]^{2+}$ species, the cations *cis-* and *trans-* $[AuXe_2]^{2+}$ (whose structure is depicted), $[XeAuFAuXe]^{3+}$, and $[AuXe_2F]^{2+}$ have been prepared and structurally characterized by X-ray crystallography in the form of their $[SbF_6]^-$ or $[Sb_2F_{11}]^-$ salts.

Angew. Chem. 2002, 114, 470-473

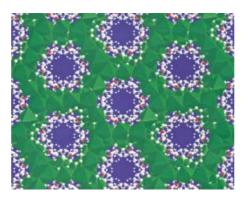
Sb Au F Sb Sb

T. Drews, S. Seidel, K. Seppelt* 454–456 Gold-Xenon Complexes

Keywords: coordination chemistry • gold • noble gases • xenon

Hydrophobic, one-dimensional channels with voids supported by a three-dimensional Ni-O-Ni framework occur in an open-framework modification of nickel succinate that was prepared by biphasic solvothermal synthesis and characterized by single-crystal X-ray diffraction (see picture; green: NiO₆ octahedra, red: oxygen). The unbound and coordinated water molecules are shown to leave the structure above 200°C, and the structure persists to 425°C.

Angew. Chem. 2002, 114, 475-477

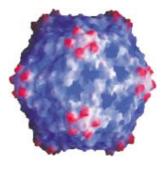


Open-Framework Nickel Succinate, $[Ni_7(C_4H_4O_4)_6(OH)_2(H_2O)_2] \cdot 2H_2O$: A New Hybrid Material with Three-Dimensional Ni-O-Ni Connectivity

Keywords: carboxylate ligands • magnetic properties • microporous materials • nickel • zeolites

Grow your nanochemical dendrimers! Cowpea mosaic virus (see relief image derived from the X-ray structure) can be isolated from its host plant in gram quantities and participates in selective chemical reactions at specific sites of the icosahedrally-arrayed coat protein. Mutant structures can be easily engineered, propagated, and isolated to provide particles with tailored reactivities. Applications for these particles in areas from catalysis to materials science can be conceived.

Angew. Chem. 2002, 114, 477-480

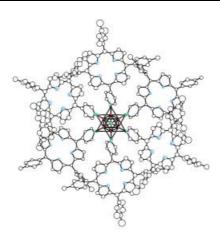


Icosahedral Virus Particles as Addressable Nanoscale Building Blocks

Keywords: electron microscopy • polyvalency • viruses

A porphyrin ball: An octahedral arrangement of six porphyrins is achieved by the coordination of 5-(4-pyridyl)-10,15,20-tritolylporphyrins (H_2PyT_3P) to the octa- $(\mu_3$ - S/μ_3 -Se)hexarhenium(III) core. Six porphyrin ligands are arranged virtually in an S_6 manner as the X-ray structural analysis of [Re_6 - $(\mu_3$ - $S)_8(H_2PyT_3P)_6$](SbF_6)₂ shows (see picture).

Angew. Chem. 2002, 114, 481-484



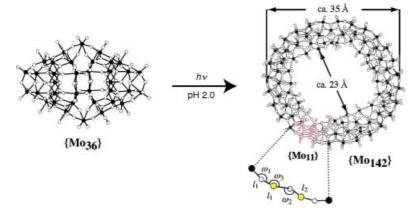
Octahedral Arrangement of Porphyrin Moieties around Hexarhenium(III) Cluster Cores: Structure of (μ_3 -Selenido)hexa-(5-(4-pyridyl)-10,15,20-tritolylporphyrin)hexarhenium(III) (2 +)

Keywords: cluster compounds • porphyrinoids • rhenium • supramolecular chemistry

Big blue-walled tires: A diamagnetic blue 28-electron reduced species $[Mo_{28}^{V}Mo_{114}^{VI}O_{432}H_{28}(H_2\ O)_{58}]^{12-}$ ($\{Mo_{142}\}$) was produced photochemically by the degradative self-assembly of $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ ($\{Mo_{36}\}$). The molybdenum blue photochemistry is not only suitable for the investigation of the mechanism of degradation self-assembly processes but also provides a basis for the molecular design of nanosized ring clusters.

T. Yamase,* P. V. Prokop 466 – 469

Photochemical Formation of Tire-Shaped Molybdenum Blues: Topology of a Defect Anion, [Mo₁₄₂O₄₃₂H₂₈(H₂O)₅₈]¹²⁻



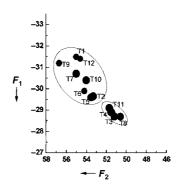
Angew. Chem. 2002, 114, 484-487

Keywords: molybdenum • nanostructures • photochemistry • polyoxometalates • self-assembly



Incorporation of Al atoms in particular sites in the ZSM-5 structure is governed by the Si/Al ratio during synthesis, and their distribution over the twelve types of tetrahedral sites (T1-T12) during crystallization occurs in a nonrandom manner according to the results of ²⁷Al MAS NMR measurements on a series of as-made ZSM-5 zeolites with Si/Al=14-250. Further support for this conclusion was provided by ²⁷Al MQMAS spectra (see picture) simulated with X-ray diffraction data

Angew. Chem. 2002, 114, 487-490



Direct Evidence for the Nonrandom Nature of Al Substitution in Zeolite ZSM-5: An Investigation by ²⁷Al MAS and MQ MAS NMR

Keywords: aluminosilicates • NMR spectroscopy • structure elucidation • zeolites

Simple hydroxyamino acid derivatives act as chiral ligands in osmium-catalyzed dihydroxylation and aminohydroxylation of olefins (see scheme). These are the first examples of asymmetric osmium-catalyzed processes proceeding in the second catalytic cycle with resident ligands on the metal center.

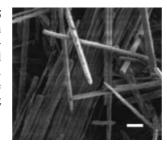
Angew. Chem. 2002, 114, 490-493

A New Approach to Osmium-Catalyzed Asymmetric Dihydroxylation and Aminohydroxylation of Olefins

Keywords: alkenes • aminohydroxylation • dihydroxylation • homogeneous catalysis • osmium

The aluminophosphate molecular sieve AIPO₄-5 was prepared within a reverse microemulsion under hydrothermal conditions. The resulting crystals (see picture; scale 1 μ m) display a novel fiberlike morphology with aspect ratios up to 100. The 100-200 nm thick fibers are aligned with the one-dimensional pores in the direction of the long axis of the fiber.





M. Z. Yates, K. C. Ott, E. R. Birnbaum, T. M. McCleskey* 476–478

Hydrothermal Synthesis of Molecular Sieve Fibers: Using Microemulsions To Control Crystal Morphology

Keywords: crystal growth • micelles • molecular sieves • surfactants • zeolite analogues

Two tandem catalysis approaches: first, a cofactor regeneration procedure with an NAD⁺ model and $[Cp*Rh(bpy)H]^+$, which was formed in situ, provided the 1,4-NADH analogue **1**. Cofactor **1** was then used with horse liver alcohol dehydrogenase (HLADH) for the conversion of prochiral ketones into chiral alcohols (e.g. **2** \rightarrow **3**).

Angew. Chem. 2002, 114, 496-499

H. C. Lo, R. H. Fish* 478-481

Biomimetic NAD⁺ Models for Tandem Cofactor Regeneration, Horse Liver Alcohol Dehydrogenase Recognition of 1,4-NADH Derivatives, and Chiral Synthesis

Keywords: asymmetric synthesis • biomimetic synthesis • cofactors • enzyme catalysis • redox chemistry

Angew. Chem. 2002, 114, 499-502

Transfer of Chiral Information through Achiral Ion Recognition by a Novel Pseudocrown Ether with a Binaphthyl Moiety

Keywords: host – guest systems • molecular devices • molecular recognition • receptors • supramolecular chemistry

An alternative route to benzylamine derivatives is provided by the lithiation of aryltriazenes followed by treatment with an electrophile [Eq. (1)]. The regioselectivity of the reaction can be controlled by means of the substituents X. When the 2- and 6-positions are substituted, tetrahydrobenzotriazines are obtained.

Angew. Chem. 2002, 114, 502-504

K. Nishiwaki,* T. Ogawa, K. Matsuo * 484 – 486

α-Lithiation of 1-Aryl-3,3dialkyltriazenes and Intramolecular Conversion to Benzylamine and Tetrahydrobenzotriazine Derivatives

Keywords: amines • C—C coupling • dearomatization • nitrogen heterocycles • nucleophilic addition



Dramatic quenching of fluorescence is observed both in solution and on a glass surface during hybridization of deazaflavin – oligonucleotide conjugates (see picture, $\boxed{\mathbb{N}}$ = nucleoside) to a complementary strand. This opens up the possibility of a new type of DNA microarray, in which the fluorophore is on the probe and not on the target, with the advantage of possible control over the quality of the array.

Angew. Chem. 2002, 114, 504-507

Fluorescent Deazaflavin – Oligonucleotide Probes for Selective Detection of DNA

Keywords: DNA recognition • flavins • fluorescence • hybridization • oligonucleotides

Bis(imino)pyridineiron complexes are not only highly active for ethylene polymerization, they are shown to catalyze efficient polyethylene chain growth at zinc centers—formally an iron-catalyzed *Aufbaureaktion* on zinc (see scheme). The grown alkyl chains can be displaced from the zinc centers by an olefin exchange reaction catalyzed by, for example, $[Ni(acac)_2]$ (acac = acetylacetonate) to give linear α -olefins with a Poisson distribution.

$$L_n F e$$
 R
 R
 R
 $L_n F e$
 $E t$
 $L_n F e$
 R
 $E t$
 $E t$

Angew. Chem. **2002**, 114, 507 – 509

Iron-Catalyzed Polyethylene Chain Growth on Zinc: Linear α -Olefins with a Poisson Distribution

Keywords: alkenes • iron • polymerization • zinc



Monocyclic and acyclic ketones bearing δ, ε - and ε, ζ -unsaturated side chains such as pulegone derivative **1** undergo *syn*-selective cyclizations with TiCl₄ to form *cis*-1,3-chlorohydrins **2**.

Angew. Chem. 2002, 114, 509-511

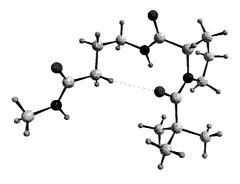
C. E. Davis, R. M. Coates * 491 – 493

Stereoselective Prins Cyclizations of δ , ε -Unsaturated Ketones to cis-3-Chlorocyclohexanols with TiCl₄

Keywords: chlorohydrins • cyclization • diastereoselectivity • electrophilic additions • terpenoids

Similar to the classical β turn: An intramolecular cyclic 10-atom motif is defined in the molecular conformation of Piv-¹Pro- γ -Abu-NHMe (see powder X-ray diffraction structure; Piv: pivaloyl, ¹pro: L-proline, γ -Abu: γ -aminobutyric acid) by a C-H \cdots O interaction. This study emphasizes the considerable potential of powder X-ray diffraction as an alternative to single-crystal X-ray diffraction.

Angew. Chem. 2002, 114, 512-514



C-H \cdots O Hydrogen Bond Mediated Chain Reversal in a Peptide Containing a γ -Amino Acid Residue, Determined Directly from Powder X-ray Diffraction Data

Keywords: hydrogen bonds • peptides • powder diffraction • structure elucidation • X-ray diffraction

Only non-enzymatic transformations were used to synthesize chiral *N*,*N*-ditosylmethylamine (see picture). This facile and convenient synthesis allows access to both enantiomers of the methyl group in an enantiomeric ratio of 83:17.



The Shortest Route to Chiral Ditosylmethylamine

Keywords: deuterium • enantioselectivity • hydrides • isotopic labeling • tritium

Angew. Chem. 2002, 114, 515-516

A linear arrangement of the P-N-B-N-P linkage occurs in the unique extended structure of the cation of the borinium salt 1, which was obtained

tight ion pairing occurs for 1 in nonpolar solvents.

$$[R_3P=N-B^+-N=PR_3]CI^-$$

cation of the borinium salt 1, which was obtained from the reaction of $[tBu_3PN]$ Li with BCl_3 . The related species $(tBu_3PN)_2BH$ was also prepared and shown to react with $[Ph_3C][B(C_6F_5)_4]$ to afford the analogous

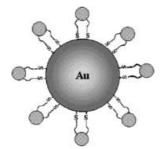
Angew. Chem. 2002, 114, 516-519

The Extended Borinium Cation:[(tBu₃PN)₂B]⁺

Keywords: boranes • boron • cations • N ligands • phosphinimide ligands



Functionalization of *γ*-[SiW₁₀O₃₆]⁸⁻ with the sulfanylalkylsilane HSC₃H₆Si(OMe)₃ affords difunctionalized γ -[SiW₁₀O₃₆(HSC₆H₃Si)₂O]⁴⁻, which on addition to colloidal solutions of gold nanoparticles (4–12 nm) forms a novel hybrid nanosystem (see schematic diagram).



C. R. Mayer, S. Neveu, V. Cabuil* 501 – 503

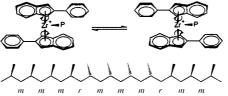
A Nanoscale Hybrid System Based on Gold Nanoparticles and Heteropolyanions

Keywords: colloids • gold • polyoxometalates



Rather than involving the *rac*-like (chiral) and *meso*-like (achiral) conformations, as commonly believed, the "oscillation" of [(2-Ar-indenyl)₂ZrCl₂] propene polymerization catalysts takes place *within* the *rac*-like conformation, between its two

Angew. Chem. 2002, 114, 519-521



enantiomorphous forms with opposite enantioselectivities. The result is the peculiar polypropylene microstructure shown, which degenerates into a (quasi-)-atactic form when the "oscillation" is faster than monomer insertion.

salt [(tBu₃PN)₂B][B(C₆F₅)₄]. NMR data and ab initio computations infer that

Angew. Chem. 2002, 114, 523-526

V. Busico,* R. Cipullo, W. P. Kretschmer, G. Talarico, M. Vacatello,

V. Van Axel Castelli 505 – 508

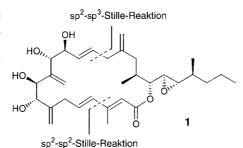
"Oscillating" Metallocene Catalysts: How Do They Oscillate?

Keywords: homogeneous catalysis • metallocenes • oscillating metallocenes • polymerization • polypropylene • reaction mechanisms



Judicious use of both inter- and intramolecular Stille reactions was required in the synthesis of 1, the putative stereostructure of amphidinolide A. Compound 1 was shown to be a diastereomer of the natural product.

Angew. Chem. 2002, 114, 526-529



H. W. Lam, G. Pattenden* 508-511

Total Synthesis of the Presumed Amphidinolide A

Keywords: cross-coupling • macrocycles • macrolides • Stille reaction • total synthesis



Silatropic and ene-like bond reorganizations (see scheme, left) were the key steps in the first total synthesis of the title compounds, which only differ in stereochemistry at the remote C36 stereocenter. Other key steps include a Suzuki biaryl construction, a diastereofacial dihydroxylation reaction, and a macrolactamization.

S. Lin, S. J. Danishefsky* 512 – 515

The Total Synthesis of Proteasome Inhibitors TMC-95A and TMC-95B: Discovery of a New Method To Generate *cis*-Propenyl Amides

Angew. Chem. 2002, 114, 530-533

Keywords: biaryls \cdot inhibitors \cdot macrolactamization \cdot rearrangement \cdot total synthesis

* Author to whom correspondence should be addressed



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





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Issue 2, 2002 was published online on January 18.				

CORRIGENDA

The Communication by **G. M. Whitesides and co-workers** in Issue 12, 2001, pp. 2316–2320 should have referenced a paper that was published at approximately the same time and contained some of the same experimental data: R. E. Holmlin, R. Haag, M. L. Chabinyc, R. F. Ismagilov, A. E. Cohen, A. Terfort, M. A. Rampi, G. M. Whitesides, *J. Am. Chem. Soc.* **2001**, *123*, 5075–5085 ("Electron Transport through Thin Organic Films in Metal-Insulator-Metal Junctions Based on Self-Assembled Monolayers"). This full paper gives the details of the largest part of the experimental work communicated in *Angewandte Chemie*. Omission of this reference gave the impression of "duplicate publication", for which the authors apologize to both journals. The acknowledgement should also have listed the affiliation of Dr. Andreas Terfort as the Institute for Inorganic and Applied Chemistry, University of Hamburg, Germany.

In the Communication by **D. Xiao** and **X. Zhang** in Issue 18, 2001, pp. 3425 – 3428, one of the authors' names was misspelled and should be Dengming Xiao.

The hydantoinase enzyme referred to in Section 3.3 of the Review by **K. Powell et al.** in Issue 21, 2001, pp. 3949 – 3959 was evolved by using error-prone polymerase chain reaction (PCR). The enzyme, which is jointly patented by Caltech and Degussa, is used in the production of L-methionine by Degussa. The authors apologize for the error.