GEWAN

A Journal of the Gesellschaft

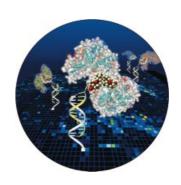
Deutscher Chemiker

ERNATI®NAL EDITION

Pages 3083-3264

COVER PICTURE

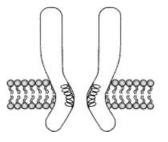
The cover picture shows a new method of arraying small molecules and its application in proteomic profiling. Each small molecule (CPK model) is tethered to a unique peptidonucleic acid (PNA) (yellow ribbon), which encodes its synthetic history. The library is screened against a sample of interest and then hybridized to an oligonucleotide microarray to determine the active compounds and/or the activity of the proteins. More details about this method are provided by Schultz and co-workers on page 3152 ff. Artwork by Nicolas Winssinger, a co-author.



REVIEWS

Key biological information is processed by ligandgated ion channels (see schematic representation). These proteins comprise, among others, important neurotransmitter receptors of the nervous system. Recent crystal structures of channel domains and of related voltage-gated ion channels reveal their functional mechanisms.

Angew. Chem. 2001, 113, 3194-3211



F. Hucho,* C. Weise 3100-3116

Ligand-Gated Ion Channels

Keywords: ion channels • neurotransmitters · proteins · receptors · structure elucidation Is rational design dead? The desire to create highly selective receptor



Differential





Sensing A Paradigm Shift in the Field of Molecular Recognition: From Selective to Differential Receptors

3118 - 3130

J. J. Lavigne, E. V. Anslyn*

Keywords: analytical methods • combinatorial chemistry · molecular recognition • receptors • sensors

molecules is being confronted with the prospect of multicomponent

arrays of differential receptors (see schematic representation). The creation of a series of cross-reactive, nonspecific sensors is the basis behind this approach. The sensing capabilities arise from the study of the pattern created from an array of such receptors.

Angew. Chem. 2001, 113, 3212-3225

HIGHLIGHTS

The single symmetry-breaking transformation of a relatively simple meso compound can provide highly expedient access to a wide variety of usefully functionalized chiral building blocks. Recent advances in asymmetric desymmetrization, through the development of tertiary amines as nonenzymatic catalysts for the ring opening of meso cyclic anhydrides with alcohols [for example, see Eq. (1)], are discussed here.

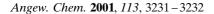
Angew. Chem. 2001, 113, 3227-3230

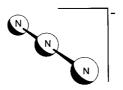
A. C. Spivey,* B. I. Andrews 3131-3134

Catalysis of the Asymmetric Desymmetrization of Cyclic Anhydrides by Nucleophilic Ring-Opening with Alcohols

Keywords: alkaloids • anhydrides • asymmetric catalysis . desymmetrization · ring opening

Azidometalates are not explosive if the solid salts contain sufficiently large cations. Structure determinations on single crystals of such compounds elucidate how the azide ions (see picture) act as covalently bound ligands and have several different bridging modes.





A. Kornath* 3135 – 3136

Homoleptic Azidometalates

Keywords: azides • azidometalates • nitrogen



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

Zero-Strain Intercalation Cathode for Rechargeable Li-Ion Cell

High Turnover Numbers for Catalytic Selective Epoxidation of Alkenes with 1 atm Molecular Oxygen

Experimental Detection of Tetraoxygen

[12.12]Paracyclophanedodecaynes C₃₆H₈ and C₃₆Cl₈: The Smallest Paracyclophynes and Their Transformation into the Carbon Cluster Ion C₃₆

Fluorescence Quenching via Sequential Hydrogen, Electron, and Proton Transfer in the Proximity of a Conical Intersection

J. Cho, Y. J. Kim, T.-J. Kim, B. Park*

Y. Nishiyama, Y. Nakagawa, N. Mizuno*

F. Cacace,* G. de Petris, A. Troiani

Y. Tobe,* R. Furukawa, M. Sonoda, T. Wakabayashi

A. Sinicropi, R. Pogni*, R. Basosi, M. A. Robb, G. Gramlich, W. M. Nau,* M. Olivucci*

COMMUNICATIONS

Solvent-induced self-assembly of oligomer-substituted shape-persistent macrocycles leads to the formation of cylindrical aggregates (see the schematic representation), which have been fully characterized in solution. These aggregates, bound by nonspecific interactions, can be described as supramolecular hollow polymer brushes.



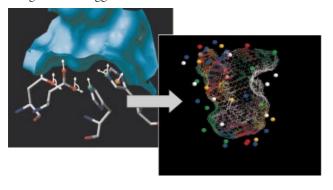
Angew. Chem. 2001, 113, 3234-3237

Coil – Ring – Coil Block Copolymers as Building Blocks for Supramolecular Hollow Cylindrical Brushes

Keywords: aggregation · liquid crystals · macrocycles · solvent effects · supramolecular chemistry

Protein function is almost invariably linked with the specific recognition of substrates or endogenous ligands in particular binding pockets; proteins of related function should, therefore, share comparable recognition pockets. On the basis of this idea a new computer method has been developed to detect functional relationships among proteins, independent of a particular sequence or fold homology, in which the functionality of the residues is translated into simple physicochemical descriptors (see picture). By this method novel ligands in drug design can be suggested.

From Structure to Function: A New Approach to Detect Functional Similarity among Proteins Independent from Sequence and Fold Homology

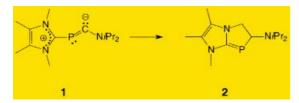


Angew. Chem. 2001, 113, 3237-3241

Keywords: computer chemistry • molecular recognition • protein-ligand interactions • protein structures



Intramolecular C—H insertion into the methyl group of the amino substituent of ${\bf 1}$ is shown by density functional theory calculations to stabilize this intermediate in the formation of the novel 1:1 carbene – phosphaalkyne adduct ${\bf 2}$. Compound ${\bf 2}$ is formed in near quantitative yield by reaction of 1,3,4,5-tetramethylimidazol-2-ylidene with $P\equiv CNiPr_2$.

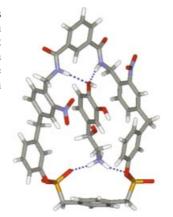


Angew. Chem. 2001, 113, 3241-3244

Unusual Formation of an Azaphospholene from 1,3,4,5-Tetramethylimidazol-2-ylidene and Di(isopropyl)aminophosphaalkyne

Keywords: carbenes • density functional calculations • insertion • phosphaalkynes • phosphorus heterocycles

A new rationally designed receptor molecule binds adrenaline derivatives in water. Its binding pattern (see picture) imitates the interplay of noncovalent interactions operating in the natural receptor. High shape selectivity is achieved for the slim dopamine skeleton, and leads to rejection of substrates with an α -substituent, such as amino acid derivatives.

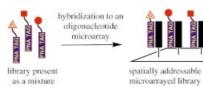


Towards Synthetic Adrenaline Receptors—Shape-Selective Adrenaline Recognition in Water

Keywords: adrenaline · hormones · molecular recognition · receptors · supramolecular chemistry

Angew. Chem. 2001, 113, 3244-3248

Small molecules encoded with peptidonucleic acid (PNA) were used to probe protein function in a microarray format. The PNA tag served to encode the synthetic history of the small molecule and to



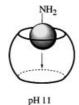
From Split-Pool Libraries to Spatially Addressable Microarrays and Its Application to Functional Proteomic Profiling

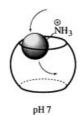
positionally encode the identity of the small molecule by its location upon hybridization to an oligonucleotide microarray (see picture).

Keywords: combinatorial chemistry • cysteine protease • functional genomics • hydrolases • split-pool synthesis

Angew. Chem. 2001, 113, 3254-3258

20 times more rapid is the complexation of the organic ammonium ion receptor cucurbit[6]uril (CB6) with cyclohexylmethylamine than with the cyclohexylmethylammonium species (see scheme). Within the narrow pH region around the pK_a -value of the amine, the com-





C. Marquez, W. M. Nau* 3155 – 3160

Two Mechanisms of Slow Host – Guest Complexation between Cucurbit[6]uril and Cyclohexylmethylamine: pH-Responsive Supramolecular Kinetics

plexation kinetics are accelerated but the binding constant remains essentially unaffected. In this region, the ammonium complex is formed through binding of the amine form followed by fast protonation and not through direct complexation of the ammonium form. Molecular dynamics calculations suggest that the amine form undergoes a direct inclusion into CB6 while the ingression of the ammonium form is retarded by the formation of an association complex, which reacts through a different, higher lying transition state to the inclusion complex.

Angew. Chem. 2001, 113, 3248-3254

Keywords: cucurbituril • host – guest systems • kinetics • protonation equilibria • supramolecular chemistry

Doped with up to 70 different metal salts, three semiconductor oxides (TiO_2 , SnO_2 , and WO_3) formed the basis of three libraries of mixed oxides. From a high-throughput method, over 30 oxides were found to have activities similar to the well-studied Pt-doped TiO_2 towards the catalyzed decomposition of a model pollutant 4-chlorophenol in water on irradiation with visible light. Two of the new materials (Ir-doped WO_3 and Ce-doped SnO_2) have been reproduced by conventional synthesis, and their catalytic activity was confirmed.

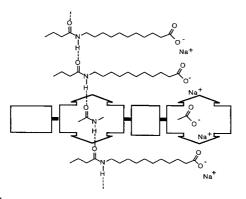
Angew. Chem. 2001, 113, 3258-3262

Combinatorial Discovery of New Photocatalysts for Water Purification with Visible Light

Keywords: combinatorial chemistry • photocatalysts • tin • titanium • tungsten • water purification

N-Acyl amino acids RCONH- $(CH_2)_n$ COOR¹ represent a new family of organogelators that can be obtained in a combinatorial approach from libraries of activated acids and amino acids. The amounts required for gel formation (see picture) in solvents such as DMF are less than 1 mg mL⁻¹ and the gels formed are very stable. n = 5, 7, 10, 12; R = aromatic or aliphatic group; R¹ = H or alkali metal (Na).

Angew. Chem. 2001, 113, 3266-3267



Rational Design of Low Molecular Mass Organogelators: Toward a Library of Functional *N*-Acyl-1,ω-Amino Acid Derivatives

Keywords: amino acids • fatty acids • gels • self assembly • supramolecular chemistry

By using chemical vapor deposition (CVD) a range of substrates can be coated with a highly reactive polymer containing pentafluorophenol ester groups (see scheme). A biotin-modified pattern is generated on the substrate by microcontact printing; such a pattern interacts specifically with fluorescein-conjugated streptavidin and thereby the pattern becomes observable with fluorescence microscopy.

A New Method toward Microengineered Surfaces Based on Reactive Coating

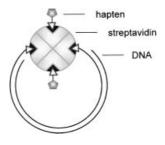
$$F_5$$
 CVD
 m
 m

Angew. Chem. 2001, 113, 3273-3276

Keywords: CVD · cyclophanes · immobilization · microcontact printing · reactive coating

Analysis with nanorings: The endogeneous proteins of supramolecular DNA nanocircles, obtained in high yields from oligomeric precursors containing bisbiotinylated DNA and streptavidin, are conveniently functionalized with biotinylated hapten moieties (see schematic representation). These modular conjugates can be used as reagents in a novel competitive immunoassay for the high-sensitivity detection of low molecular weight analytes.

Angew. Chem. 2001, 113, 3262-3265



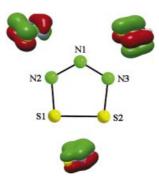
Hapten-Functionalized DNA-Streptavidin Nanocircles as Supramolecular Reagents in a Competitive Immuno-PCR Assay

Keywords: analytical methods • DNA conjugates • nanostructures • streptavidin • supramolecular chemistry



Surprisingly stable is the first example of a binary $\sin \pi$ electron aromatic SN cation with an N_3 unit, $S_2N_3^+$ (see picture). It can be isolated on a macroscopic scale when a large counter anion is present. The structure determined by X-ray investigations is in good agreement with theoretical data. The unequivocal identification was supported by Raman and infrared studies. The structure and bonding are discussed on the basis of MO (molecular orbital) and AIM (atoms-in-molecules) analysis.

Angew. Chem. 2001, 113, 3270-3273



S. Herler, P. Mayer, H. Nöth, A. Schulz,* M. Suter, M. Vogt 3173–3175

S₂N₃⁺: An Aromatic SN Cation with an N₃ Unit

Keywords: ab initio calculations \cdot bond theory \cdot cations \cdot nitrogen \cdot sulfur

Two new starting materials for a new chemistry of low-valent lanthanide compounds are the first crystallographically characterized molecular complexes of the rare Nd^{2+} ion, $[NdI_2(thf)_5]$ (1), and $[TmI_2(thf)-(dme)_2]$ (2; dme=1,2-dimethoxyethane). These have a pentagonal-bipyramidal structure in which the two iodine atoms are in axial positions.

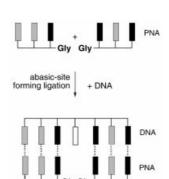
Angew. Chem. 2001, 113, 3268-3270

[NdI₂(thf)₅], the First Crystallographically Authenticated Neodymium(II) Complex

Keywords: lanthanides • neodymium • structure elucidation • subvalent compounds • thulium

An abasic-site-forming ligation reaction might allow multiplex analysis of single-base mutations to be performed in homogeneous solution. The ligation strategy capitalizes upon the use of the non-ionic DNA-analogue peptide nucleic acids (PNAs) and combines the highly sequence-selective base pairing of short-length PNA (see scheme) with its ease and accuracy of detection by MALDITOF mass spectrometry.

Angew. Chem. 2001, 113, 3277-3280



A. Mattes, O. Seitz* 3178-3181

Mass-Spectrometric Monitoring of a PNA-Based Ligation Reaction for the Multiplex Detection of DNA Single-Nucleotide Polymorphisms

Keywords: DNA recognition • mass spectrometry • multiplex detection • nucleic acids • peptide nucleic acids

An extremely high thermal and chemical stability as well as a unique "out-of-plane" position of the metal atom is shown by the first stable transition metal complexes formed with the proton sponge 1 as the ligand. The properties of these complexes await wide application in catalysis and medicine.

Transition Metal Complexes with the Proton Sponge 4,9-Dichloroquino-[7,8-h]quinoline: Highly Twisted Aromatic Systems and an Extreme "Out-of-Plane" Position of the Coordinated Transition Metal Atom

Keywords: N ligands \cdot platinum \cdot proton sponge \cdot rhenium

Angew. Chem. 2001, 113, 3280-3282



No problems have been encountered while using bithiazoles in Pd-catalyzed cross-coupling reactions. It was thus possible to achieve the first synthesis of cystothiazole E (1) with a Suzuki coupling of the building blocks **2** and **3** as the pivotal C–C bond-formation step (94% yield, TBDMS=*t*BuMe₂Si). The bithiazole **3** could be prepared very conveniently from 2,4-dibromothiazole by regioselective cross-coupling reactions.

Angew. Chem. 2001, 113, 3283-3284

T. Bach,* S. Heuser 3184-3185

Regioselective Cross-Coupling Reactions as an Entry into Biologically Relevant Bithiazoles: First Total Synthesis of Cystothiazole E

Keywords: aldol reaction • asymmetric synthesis • cross-coupling • heterocycles • total synthesis

The left-hand fragment 2 of the novel antibiotic kendomycin (1) has been synthesized by an aldol addition and a Michael-type 1,4-addition of a C5 alcohol with a C9-C11 enone. Compound 2 shows an interesting atropisomerism around the C4a-C5-sp²-sp³ bond. The atropisomers can be separated

in pure forms by low-temperature high-pressure liquid chromatography.

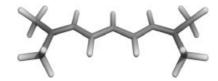
Angew. Chem. 2001, 113, 3287-3289

H. J. Martin, M. Drescher, H. Kählig, S. Schneider, J. Mulzer* 3186–3188

Synthesis of the C1-C13 Fragment of Kendomycin: Atropisomerism around a C-Aryl Glycosidic Bond

Keywords: aldol reaction • antibiotics • atropisomerism • glycosides • Michael addition

Sometimes the simplest systems need the most sophisticated treatment! Only with multiconfigurational SCF methodology including second-order correction (CASPT2) is it possible to quantitatively repro-



duce the position of the high-intensity methine band of streptocyanine dyes such as the one shown.

Angew. Chem. 2001, 113, 3284-3286

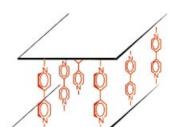
Nonempirical Calculation of Polymethine Excited States

Keywords: ab initio calculations • chromophores • computer chemistry • cyanines • polymethines

Coordination of Mn(CO)₃⁺ **to the** π system in hydroquinone facilitates proton loss to afford benzoquinone complexes (see figure). Subsequent σ coordination of the benzoquinone oxygen atoms to added metal ions results in neutral one-, two-, or three-dimensional quinoid polymers. The geometrical requirements of the metal ion and the presence of added "spacer" ligands dictate the type of polymer formed.

Mn(CO)₂

Mn(CO)



M. Oh, G. B. Carpenter, D. A. Sweigart* 3191 – 3194

Metal-Mediated Self-Assembly of π -Bonded Benzoquinone Complexes into Polymers with Tunable Geometries

Mn(CO)₃ Mn(CO)₃

Angew. Chem. **2001**, 113, 3291 – 3294

Keywords: host – guest systems • manganese • polymers • quinone complexes • self assembly



π-Electronic conjugation is not necessary to facilitate long-range energy migration and transfer: A rapid ($k_{\rm ENT} = 1.04 \times 10^9~{\rm s}^{-1}$) and efficient ($\Phi_{\rm EXT} = 71~\%$) energy transfer from the 28 photoexcited zinc porphyrin units to the focal free-base porphyrin unit occurs in a large, star-shaped dendritic multiporphyrin array in which the chromophore units are linked through flexible ether groups (see picture).

Mn(CO)



Angew. Chem. 2001, 113, 3294-3298

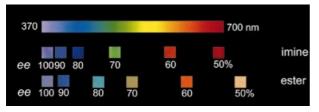
A Large Dendritic Multiporphyrin Array as a Mimic of the Bacterial Light-Harvesting Antenna Complex: Molecular Design of an Efficient Energy Funnel for Visible Photons

Keywords: dendrimers • energy transfer • fluorescence spectroscopy • photosynthesis • porphyrinoids

A simple color test for enantiomeric excess requires no chiral auxiliaries and only microgram quantities of chiral products. The method is based on a chirality-dependent color generation in doped LC films on formation of an imine or ester (see picture) from an amine and carbaldehyde or alcohol and acid chloride, respectively, and will enable the rapid screening of libraries of nonracemic compounds.



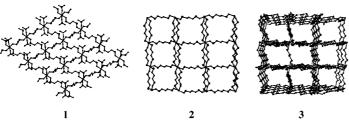
Color Indicators of Molecular Chirality Based on Doped Liquid Crystals



Angew. Chem. 2001, 113, 3298-3300

Keywords: asymmetric catalysis • chirality • combinatorial chemistry • enantioselectivity • liquid crystals

Fillings and cavities: Three novel pseudo-octahedral metal – organic frameworks, 1-3, consisting of macrometallacyclic noninterpenetrating *meso* networks and exhibiting weak antiferromagnetic interactions, have been constructed from Cu^{II} centers and structurally flexible R,S-bis(sulfinyl) ligands. Varying the chain length of ligands is found to control the cavity sizes of the networks.



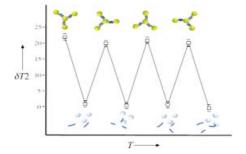
Angew. Chem. 2001, 113, 3301-3303

Flexible *meso*-Bis(sulfinyl) Ligands as Building Blocks for Copper(II) Coordination Polymers: Cavity Control by Varying the Chain Length of Ligands

Keywords: coordination polymers • copper • crystal engineering • magnetic properties • S ligands

Superparamagnetic nanoparticles conjugated to oligonucleotides exert sensitive and reversible effects on the spin-spin relaxation rates of adjacent water protons when the conjugates hybridize to target oligonucleotides (see temperature cycle in the picture). The fluid-phase magnetic sensors provide the basis for detecting specific nucleic acid sequences in turbid media and potentially in tissues in vivo.





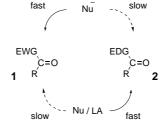
L. Josephson, J. M. Perez, R. Weissleder* 3204–3206

Magnetic Nanosensors for the Detection of Oligonucleotide Sequences

Keywords: DNA recognition • magnetic properties • nanostructures • oligonucleotides



A crucial role in the chemoselective synthesis of primary, secondary, and homoallylic alcohols and of Diels-Alder adducts is played by Lewis acids (LA) in the addition of nucleophiles (Nu) to carbonyl compounds (see scheme; EWG = electron-withdrawing group, EDG = electron-donating group).



Do More Electrophilic Aldehydes/ Ketones Exhibit Higher Reactivity toward Nucleophiles in the Presence of Lewis Acids?

Keywords: chemoselectivity • electrophiles • Lewis acids • nucleophilic addition

Angew. Chem. 2001, 113, 3306-3308



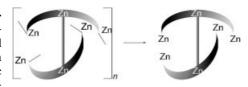
The mere presence or absence of PPh₃ suffices to control the reactivity of bis(η^3 -allyl)palladium complexes. In the absence of PPh₃ they undergo chemoselective allylic addition to aldehydes or imines, even in the presence of allylic chlorides, whereas in the presence of PPh₃ the Stille coupling reaction takes place chemoselectively, even when aldehydes or imines are also present (see scheme).

Angew. Chem. 2001, 113, 3308-3310

The Fate of Bis(η^3 -allyl)palladium Complexes in the Presence of Aldehydes (or Imines) and Allylic Chlorides: Stille Coupling versus Allylation of Aldehydes (or Imines)

Keywords: allylation • allyl ligands • C—C coupling • palladium • Stille coupling

The controlled cleavage of coordination polymers consisting of well-defined large units can be employed for the rational synthesis of high nuclearity clusters. This synthetic concept is demonstrated by the



conversion (schematically shown) of a three-dimensional Zn^{II} coordination polymer containing repeating hexameric units with a "twin-anchor" arrangement of the metal ions into the corresponding hexanuclear cluster by reaction with a donor solvent.

High Nuclearity Zn^{II}/MeCO₂^{-/} (C₅NH₄)₂CO₂²⁻ Clusters by "Depolymerization": Conversion of a Three-Dimensional Coordination Polymer Containing Hexameric Units into Its Constituent Hexanuclear Complex

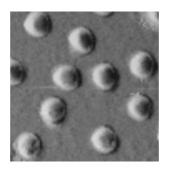
Keywords: cluster compounds · coordination polymers · N ligands · synthetic methods · zinc

Angew. Chem. 2001, 113, 3311-3314

A reactor for the synthesis of gold nanoparticles

(see atomic force microscopy image) is one of the uses of a poly(styrene)-block-poly(2-vinylpyridine)-block-poly(ethylene oxide) triblock copolymer (PS-b-P2VP-b-PEO) which forms coreshell—corona micelles in water. Very low polydispersity spherical micelles are observed that consist of a PS core surrounded by a pH-sensitive P2VP shell and a corona of PEO chains end-capped by a hydroxyl group. The corona can act as a site for attaching responsive or sensing molecules.



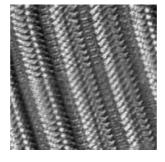


J.-F. Gohy, N. Willet, S. Varshney, J.-X. Zhang, R. Jérôme* 3214–3216

Core – Shell – Corona Micelles with a Responsive Shell

Keywords: gold • micelles • nanostructures • polymers • self assembly

Enantiomorphous monolayers of enantiopure formamides form on a graphite surface, while the racemic compound does not undergo a spontaneous resolution under similar conditions. This difference in the two-dimensional behavior has been studied by scanning tunneling microscopy (see image of the racemate adsorbed on graphite). A study of the three-dimensional crystallization of the racemic formamide by X-ray crystallographic analysis also shows that it forms racemic tapes.



Homo- and Heterochiral Supramolecular Tapes from Achiral, Enantiopure, and Racemic Promesogenic Formamides: Expression of Molecular Chirality in Two and Three Dimensions

Keywords: chirality • scanning tunneling microscopy • self assembly • surface chemistry • X-ray diffraction

Angew. Chem. 2001, 113, 3317-3320

Only the 1,2-diphosphacyclobutadiene and none of its 1,3 isomer was obtained in the reaction of 1 with $tBuC \equiv P$ to give 2. In complex 1, which was prepared from $[TaCl_2(\eta^5-C_5Me_5)(CO)_2(thf)]$ and $tBuC \equiv P$, the phosphaalkyne adopts an $\eta^2(4e)$ bonding mode according to NMR data, crystal structure analysis, and theoretical calculations.

$$[TaCl_{2}(\eta^{5}-C_{5}Me_{5})(CO)_{2}(thf)] \xrightarrow{tBuC = P} Cl \xrightarrow{Ta} tBu \xrightarrow{tBu} tBu$$

$$1 \qquad 2$$

Angew. Chem. 2001, 113, 3321-3324

Mononuclear $\eta^2(4e)$ -Bonded Phosphaalkyne Complexes; Selective Formation of a 1,2-Diphosphacyclobutadiene Tantalum Complex

Keywords: density functional calculations • phosphaalkynes • phosphorus heterocycles • tantalum

An oxo-hexaene macrolide antibiotic, dermostatin A (see picture) has been synthesized. Key features of the synthesis include the application of cyanohydrin acetonide couplings for the synthesis of the polyol portion, and the convergent introduction of the polyene segment by means of a Stille coupling.

Angew. Chem. 2001, 113, 3324-3327

C. J. Sinz,

Total Synthesis of Dermostatin A

Keywords: alkylation • asymmetric synthesis • cross-coupling • polyenes • total synthesis

One of the most facile routes to prepare carboxylate-substituted imidazolines is by the palladium-catalyzed coupling of an imine, carbon monoxide, and an acid chloride. In this reaction, a peptide unit is constructed and directly incorporated into the heterocyclic core (see scheme).

$$\begin{array}{c} R^2 \\ \stackrel{\longrightarrow}{\underset{\longrightarrow}{\longrightarrow}} R^1 \\ \stackrel{\longrightarrow}{\underset{\longrightarrow}{\longrightarrow}} CO \\ \stackrel{\longrightarrow}{\underset{\longrightarrow}{\longrightarrow}} CO \end{array} \xrightarrow{\begin{array}{c} Pd \\ \text{catalysis} \\ \text{catalysis}$$

Angew. Chem. 2001, 113, 3328-3330

R. D. Dghaym, R. Dhawan, B. A. Arndtsen* 3228–3230

The Use of Carbon Monoxide and Imines as Peptide Derivative Synthons: A Facile Palladium-Catalyzed Synthesis of α -Amino Acid Derived Imidazolines

Keywords: homogeneous catalysis • multicomponent reactions • nitrogen heterocycles • palladium • peptides

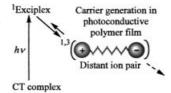
44 members are in the trisaccharide library synthesized by the method described here. Six differently protected glucoside building blocks were sulfonylated with $\bf 1$, coupled to the solid support $\bf 2$ (a crown compound) by Pd^0 -catalyzed carbonylative amidation, glycosylated twice, and cleaved from the sulfonate linker with four nucleophiles.

Angew. Chem. 2001, 113, 3330-3333

Synthesis of a Trisaccharide Library by Using a Phenylsulfonate Traceless Linker on Synphase Crowns

Keywords: carbohydrates • combinatorial chemistry • solid-phase synthesis • trisaccharides

Photoconduction in charge transfer materials apparently occurs through a distant geminate ion pair with an interionic separation of about 8 Å, as demonstrated by time-resolved EPR spectroscopy of a doped poly(*N*-vinylcarbazole) film (see scheme).



Angew. Chem. 2001, 113, 3334-3336

T. Ikoma,* M. Nakai, K. Akiyama, S. Tero-Kubota,* T. Ishii 3234–3236

Direct Observation of a Distant Ion Pair Generated in a Photoconductive Poly-(*N*-vinylcarbazole) Film with Dopant

Keywords: electron transfer • EPR spectroscopy • ion pairs • photoconductive polymers • thin films

Thermolysis of the dithiocarbamate complex 1 led to the formation of the thiocarbenoid complex **2** and two double cubanes: **3**, which has an intercubane Cr–Cr bond and a dithiooxamide ligand in the μ - η^2 , η^4 bonding mode, and **4**, which contains two dithiocarbamate ligands in the μ - η^1 , η^2 bonding mode.

Angew. Chem. 2001, 113, 3336-3339

C–S Bond Cleavage and C–C Coupling in Cyclopentadienylchromium Complexes To Give the First Dithiooxamide-Bridged and Doubly Dithiocarbamate-Bridged Double Cubanes: [Cp₆Cr₈S₈{(C(S)NEt₂)₂]] and [Cp₆Cr₈S₈(S₂CNEt₂)₂]

Keywords: chromium • cluster compounds • cubanes • S ligands

Getting the right balance between intermolecular interactions is crucial for the synthesis of supermolecules in a preconceived manner. The three-component supermolecule (see picture) in the ternary cocrystal

of 3,5-dinitrobenzoic acid, isonicotinamide, and 4-(dimethylamino)benzoic acid (1:1:1) assembles through a "primary" (between the stronger acid and pyridine) and a "secondary" hydrogen-bonding interaction (between the weaker acid and amide).

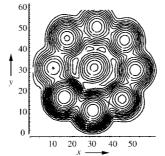
Angew. Chem. 2001, 113, 3340-3342

"Total Synthesis" Supramolecular Style: Design and Hydrogen-Bond-Directed Assembly of Ternary Supermolecules

Keywords: cocrystals • crystal engineering • hydrogen bonds • molecular recognition • supramolecular chemistry

A reduction of a factor of 10 in the time needed to measure highly resolved NMR spectra of multiple samples can be achieved with any NMR spectrometer by using a combination of chemical shift imaging and a compartmented detection volume consisting of a bundle of capillaries. The picture shows the cross-sectional image of a bundle of nine 1-mm capillaries after Fourier transformation along the spatial dimensions only.

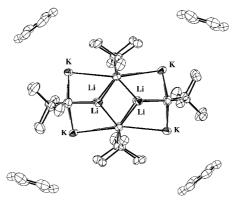
Angew. Chem. 2001, 113, 3343-3345



Application of Chemical Shift Imaging for Simultaneous and Fast Acquisition of NMR Spectra on Multiple Samples

Keywords: analytical methods • chemical shift imaging • high-throughput screening • NMR spectroscopy

At long last an experimentally utilized superbase has been crystallographically characterized. Isolated from a lithium amide-potassium alkoxide-arene mixture, this landmark compound adopts a novel sixteen-vertex "carousel" arrangement stabilized by two distinct types of benzene ligation (see structure).

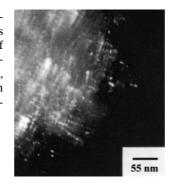


Landmark Crystal Structure of an Experimentally Utilized Tetralithium – Tetrapotassium Amide – Alkoxide Superbase

Keywords: alkali metals • alkoxides • amides • structure elucidation • superbases

Angew. Chem. 2001, 113, 3345-3347

Crystallizing walls: Following the templated solidstate secondary crystallization of an amorphous mesoporous material the amorphous pore walls of the mesoporous precursor are partially reorganized into a crystalline material, the zeolite ZSM-5, as indicated by the dark-field transmission electron micrograph image shown. The bright spots correspond to the ZSM-5 nanocrystals.



D. Trong On, S. Kaliaguine * 3248 – 3251

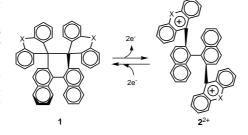
Large-Pore Mesoporous Materials with Semi-Crystalline Zeolitic Frameworks

Angew. Chem. 2001, 113, 3348-3351



Helicity and axial chirality are reversibly interconverted in the novel redox pair 1 and 2^{2+} ; the compounds exhibit drastic UV/Vis and circular dichroism spectral changes as well as dynamic structural changes upon electron transfer, thus furnishing an unprecedented multi-output response system with high bistability. X = S or O.

Angew. Chem. 2001, 113, 3351-3354



template synthesis · zeolites

Keywords: crystal growth • mesoporous materials • microporous materials •

A Redox Switch Based on Dihydro[5]helicene: Drastic Chiroptical Response Induced by Reversible C–C Bond Making/Breaking upon Electron Transfer

Keywords: chirality • circular dichroism • electrochemistry • helical structures • redox chemistry

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

 st Author to whom correspondence should be addressed



BOOKS

Comprehensive Asymmetric Catalysis	Eric N. Jacobsen, Andreas Pfaltz, H. Yamamoto	O. Reiser 3255
Catalytic Asymmetric Synthesis	Iwao Ojima	O. Reiser 3255
Transition Metal Carbonyl Cluster Chemistry	Paul J. Dyson, J. Scott McIndoe	L. H. Gade 3257
The New Chemistry	Nina Hall	R. Faust
Enzymes: Biochemistry, Biotechnology, Clinical Chemistry	Trevor Palmer	U. Bornscheuer 3258
Essentials of Biological Chemistry	Lorraine Buckberry, Paul Teesdale	<i>R. Breinbauer</i> 3259

Chemical Societies on the Web

M. Müller 3261

SERVICE-

Sources

3086 Classified A104

3099 • Contents of Chemistry— Authors 3263 A European Journal

 Keywords 3262 Preview 3264

Issue 16, 2001 was published online on August 15, 2001.

A103

Don't forget all the Tables of Contents from 1998 onwards may be still found on the WWW under: http://www.angewandte.com

Become an expert in the field of carbohydrate chemistry

University of Hamburg, Germany

Essentials of Carbohydrate Chemistry and Biochemistry

2000. XIV, 218 pages with 244 figures and 11 tables. Softcover. DM 98.-/ £ 32.50 ISBN 3-527-29543-7

Carbohydrates are probably nature's most common product. Plants and algae biosynthesize millions of tons of them every year. Carbohydrates are stores of energy and structural building blocks; they are versatile enough to serve as encoders of biological information and, last but not least, they are involved in recognition processes at a molecular level. Research into carbohydrate and glycoconjugate functions in cell-to-cell communication processes has even created a new and rapidly developing field of study: glycobiology.

Thisbe K. Lindhorst is one of the leading "next generation" scientists in the area of carbohydrate research. Within her current book she presents a comprehensive introduction to the fascinating world of carbohydrates. In a lucid, explicit language she explains carbohydrate structures and the basic concepts of saccharide chemistry and saccharide biochemistry. With the same clarity she spans the gap to the glycobiological aspects of modern "glycoscience". Sample descriptions of research methods supplement the vital teaching text and open an experienced scientist's bag of tricks required to synthesize and analyze sugar derivatives easily and successfully.

This book offers valuable guidance for students as well as for researchers Become an expert in the field of Carbonydrate chemistry working in chemistry, biochemistry and



Thisbe K. Lindhors

Essentials of Carbohydrate Chemistry and Biochemistry



From the Contents:

- Introduction
- Structure of saccharides
- · Protecting groups for carbohydrates
- Glycoside synthesis
- · Important modifications and functionalizations of the sugar ring
- · Structure and biosynthesis of glycoconjugates
- Glycobiology
- · Analysis of carbohydrates
- . The literature of carbohydrate chemistry



John Wiley & Sons, Ltd., Baffins Lane Chichester, West Sussex, P0 19 1UD, UK

WILEY-VCH, P.O., Box 10 11 61

