ANGEWANDTE CHEMIE

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Deutscher Chemiker

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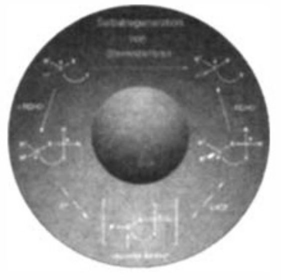
COVER PICTURE

The cover picture shows the principle of the "Self-Regeneration of Stereocenters (SRS), a synthetic method in which a stereogenic center is temporarily destroyed with formation of an intermediate having a trigonal center. A subsequent diastereoselective reaction results in the formation of the stereogenic center once more. The additional center of chirality essential for the diastereoselective reaction is generated by acetalization (with an aldehyde) of the functional groups X and Y in the chiral starting material. The reaction sequence leads to a dissociative, enantioselecitve substitution at a single stereogenic center in a chiral compound without the use of a chiral auxiliary—hence the name "self-regeneration".
The general formula of typical glycine derivatives is shown in yellow in the center of the scheme. These are easily prepared in enantiomerically pure form by resolution of the appropriate racemate and have been shown to be particularly useful for the synthesis of α,α-disubstituted amino acids. As these compounds are prepared from chiral starting materials, they also represent the abandonment of the synthetic principle. D. Seebach et al. report more on SRS on p. 2708 ff.



REVIEWS

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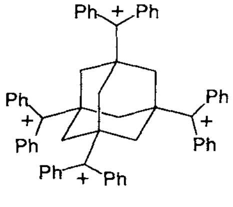
HIGHLIGHTS

In the first carbotetracation, 1, the charged groups are tetrahedrally arranged on an adamantane cage. Carbocations are no longer a domain of physical organic chemistry. They also play a role in organometallic chemistry and biochemistry, as a new samarocene complex containing a norbornadienyl cation fragment and the newly coined term "Olah enzyme" testify.



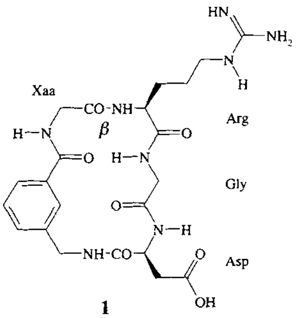
1

T. Laube* 2765–2766

New Carbocations—From Physical Organic Chemistry to Biochemistry

---

In the design of peptide-based drugs the β turn has been promoted to a design principle in recent years. In research on antiadhesive RGD mimetics, receptor selectivity has been shown to be encoded in the β-turn type within cyclic peptides of type **1** having an identical lead sequence. Switching the turn type from βII′ to βI inverts the selectivity profile so that a compound originally with antithrombotic activity becomes an antimetastatic agent.



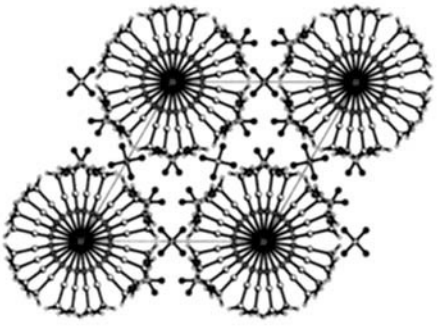
1

G. Müller* 2767–2769

The β Turn as a Selectivity Switch: βI or βII′? That Is the Question

COMMUNICATIONS

One-electron reduction of the rhodium complex **1** has resulted in the first successful conversion of a discrete metal–metal bonded "dimer" into a one-dimensional polymer (**2**). The doped material **2** (depicted on the right) differs significantly from the well-known tetracyanoplatinates in that the metal backbone is cationic. In addition, there is the possibility of fine-tuning the material properties by varying the organic group.



$[Rh_2(MeCN)_{10}](BF_4)_4$ **1**

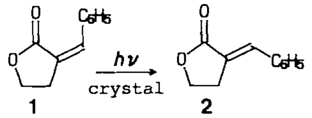
$\{[Rh(MeCN)_4](BF_4)_{1.5}\}_\infty$ **2**

G. M. Finniss, E. Canadell, C. Campana, K. R. Dunbar* 2772–2774

Unprecedented Conversion of a Compound with Metal–Metal Bonding into a Solvated Molecular Wire

---

Three solid-state techniques—atomic force microscopy, X-ray structure analysis, and diffuse reflectance spectroscopy—were combined to discover why E/Z isomerizations in the crystal, for example **1** → **2**, are possible despite their large spatial demands. These studies revealed, for instance, that on irradiation with wavelengths corresponding to the absorption tail of the crystals, anisotropic surface features appear.

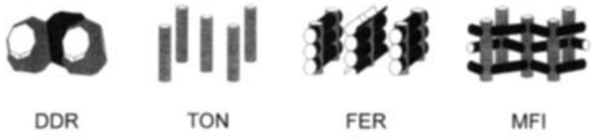


G. Kaupp,* M. Haak 2774–2777

E/Z Isomerization in Crystals—Phase Rebuilding on Photolysis with Long-Wavelength Radiation

---

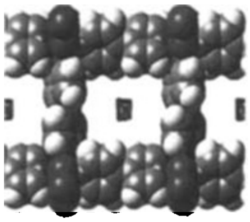
Templates for the arrangement of guest molecules—that is the role played by microporous crystalline SiO_2 modifications in the insertion compounds presented. The electronic interactions between the guest species can be controlled by the dimensionalities of the void systems. When iodine is the guest component, this is directly apparent from the colors of the insertion compounds, which for the host structures shown below range from violet to red-brown.



G. Wirnsberger, H. P. Fritzer, A. Popitsch, G. van de Goor, P. Behrens* 2777–2779

Designed Restructuring of Iodine with Microporous SiO_2

Not interpenetrated, but filled with solvent molecules, the large cavities of the polymer $[Co(NO_3)_2(4,4'\text{-bpy})_{1.5}]_n$ form different structures depending on the solvent system from which it crystallizes. One of the two possible structures (section of structure shown on the right) exhibits hydrophobic cavities about 11 × 11 Å in size. The solvent molecules can be readily removed, but the process has not yet been proven reversible.

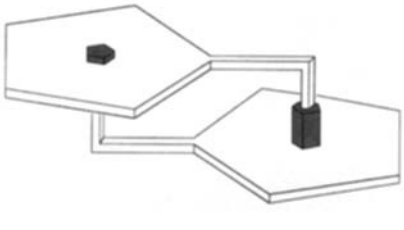


P. Losier, M. J. Zaworotko* ... 2779–2782

A Noninterpenetrated Molecular Ladder with Hydrophobic Cavities

---

Anion complexation drives the self-assembly of appropriately designed macrocycles (sapphyrin and/or calix[4]pyrrole) containing pendant carboxylic arms (black in the schematic representation on the right). The self-assembly process can be disrupted by addition of F^- ions (sapphyrin) or in the case of calix[4]pyrrole, polar solvents.



J. L. Sessler,* A. Andrievsky,
P. A. Gale, V. Lynch 2782–2785

Anion Binding: Self-Assembly of Polypyrrolic Macrocycles

The total concentrations of reactants and products within a flow-through reactor can be monitored as a function of both position and time by detecting gamma photons arising from the radioactive positron decay of injected ^{11}C nuclei. The method was demonstrated by directly observing catalyst preconditioning and deactivation of a Pt/H-mordenite catalyst bed during the industrially important hexane hydroisomerization reaction.

R. A. van Santen,* B. G. Anderson,
R. H. Cunningham, A. V. G. Mangnus,
Dr. L. J. van IJzendoorn,
M. J. A. de Voigt 2785–2787

In Situ Observation of Transient Reaction Phenomena Occurring on Zeolite Catalysts with the Aid of Positron Emission Profiling

---

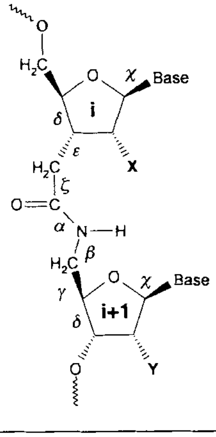
A high catalytic activity towards alkene epoxidation is shown by titanium-modified MCM41 mesoporous silicas if 2-methyl-1-phenyl-2-propyl hydroperoxide (MPPH) is used as oxidant. This first example in which MPPH has been used as an efficient two-electron oxidizing agent demonstrates that it is a competent replacement for *tert*-butyl hydroperoxide (TBHP) in metal-catalyzed, nonradical hydrocarbon oxidations and that the Ti-MCM41 catalyzed epoxidation of alkenes proceeds by a nonradical mechanism.

R. D. Oldroyd, J. M. Thomas,*
T. Maschmeyer, P. A. MacFaul,
D. W. Snelgrove, K. U. Ingold,*
D. D. M. Wayner 2787–2790

The Titanium(IV)-Catalyzed Epoxidation of Alkenes by *tert*-Alkyl Hydroperoxides

---

An increased stability of duplexes between amide-modified oligonucleotides (depicted on the right) and RNA was achieved by the introduction of 2'-OMe groups. Since the modified oligonucleotides display a very high affinity for their RNA complement and are more stable towards nucleases, they can be considered as promising antisense agents. X = H, OH, OMe; Y = H, OMe.

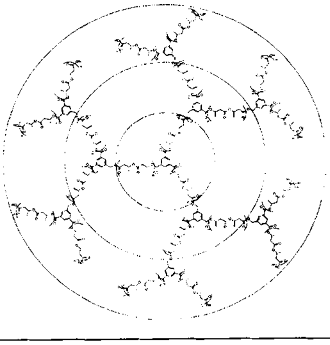


A. De Mesmaeker,* C. Lesueur,
M.-O. Bévièrre, A. Waldner,
V. Fritsch, R. M. Wolf 2790–2794

Amide Backbones with Conformationally Restricted Furanose Rings: Highly Improved Affinity of the Modified Oligonucleotides for Their RNA Complements

---

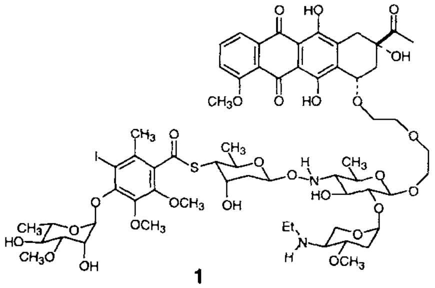
Monodisperse, chiral dendrimers from trimesic acid and (*R*)-3-hydroxybutanoic acid were synthesized and characterized. Preliminary investigations have shown that these biodegradable dendrimers (depicted on the right) are substrates for hydrolases.



D. Seebach,* G. F. Herrmann,
U. D. Lengweiler, B. M. Bachmann,
W. Amrein 2795–2797

Synthesis and Enzymatic Degradation of Dendrimers from (*R*)-3-Hydroxybutanoic Acid and Trimesic Acid

In calichearubicin B (1) the aglycon of daunorubicin and the carbohydrate domain of calicheamicin γ_1^1 are linked by a spacer (calichearubicin A lacks this spacer). The aglycone serves as an anthracycline-like intercalator, while the carbohydrate portion binds to the minor groove of DNA. Thus calichearubicin B exhibits properties of both parent compounds.

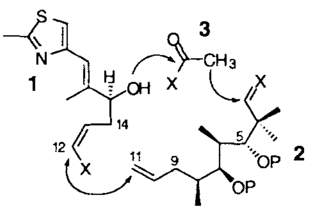


1

K. M. Depew, S. M. Zeman,
S. H. Boyer, D. J. Denhart,
N. Ikemoto, S. J. Danishefsky,*
D. M. Crothers 2797–2801

Synthesis and a Preliminary DNA Binding Study of Hybrids of the Carbohydrate Domain of Calicheamicin γ_1^1 and the Aglycone of Daunorubicin: Calichearubicins A and B

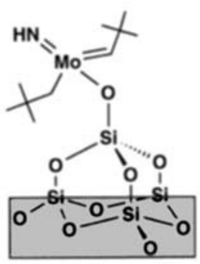
An audacious macroaldolization is the key step in the first total synthesis of the cytotoxic epothilone A, which starts with the units **1**, **2**, and **3**. This condensation closes the ring to form the macrolide, whose structure was determined and published (also in *Angewandte Chemie*) as recently as July 1996.



A. Balog, D. Meng, T. Kamenecka,
P. Bertinato, D.-S. Su, E. J. Sorensen,
S. J. Danishefsky* 2801–2803

Total Synthesis of (−)-Epothilone A

1,2-Addition of the surface silanol groups on SiO_2 to the nitridomolybdenum fragment of the title compound and subsequent α-elimination of neopentane forms the catalytically active surface species **I**. This is the first case in which an alkylated complex is converted into a heterogeneous catalyst in a well-defined way. The immobilized compound is significantly more active in ring-opening metathesis polymerization than the molecular precursor.

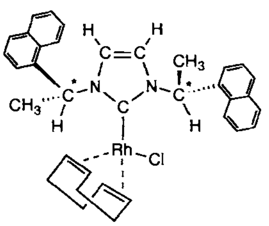


I

W. A. Herrmann,* A. W. Stumpf,
T. Priermeier, S. Bogdanović,
V. Dufaud, J.-M. Basset 2803–2805

A Molecularly Defined, Grafted Olefin Metathesis Catalyst from Tris(neopentyl)nitridomolybdenum(VI)

The *ee* values of the hydrosilylation of acetophenone with the rhodium catalyst **1** are only small; nevertheless, the robustness of the catalyst is impressive: The chiral carbene ligand, which is readily available and can be easily varied, remains bound to the metal in solution to over 100 °C. Thus, no excess of ligand is necessary in the catalytic reactions.



1

W. A. Herrmann,* L. J. Goossen,
C. Köcher, G. R. J. Artus 2805–2807

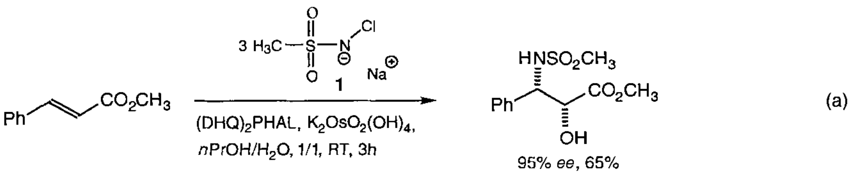
Chiral Heterocylic Carbenes in Asymmetric Homogeneous Catalysis

In a one-pot reaction from 15 components, a tetrahedral host-guest compound forms by self-assembly. Its tripod–iron(II) groups are the corners of a tetrahedron (depicted on the right). The edges of the tetrahedron are bridged by 1,2-dinitrile ligands, and a BF_4^- ion is encapsulated in the tetrahedral cavity.

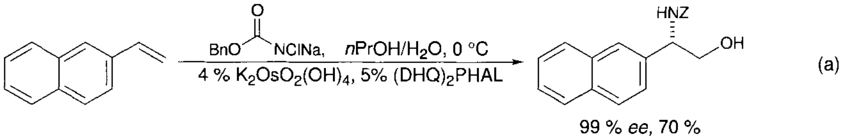
S. Mann, G. Huttner,* L. Zsolnai,
K. Heinze 2808–2809

Supramolecular Host–Guest Compounds with Tripod–Metal Templates as Building Blocks at the Corners

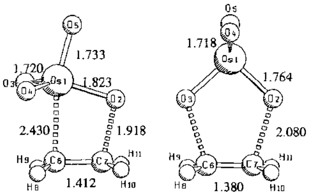
All of the selectivity criteria for catalytic asymmetric aminohydroxylation with sulfonamides [Eq. (a)] are improved when the original nitrogen source, Chloramine-T, is replaced by its methyl analogue, Chloramine-M (**1**). This newly introduced reagent exhibits substantially higher ligand dependence, and for most substrates the desirable phenomenon of ligand-accelerated catalysis was observed. DHQ-H = dihydroquinine, PHAL = 1,3-phthalazinediyl.



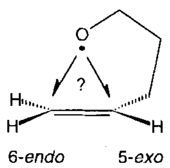
Better enantioselectivities and convenient deprotection make the sodium salts of *N*-chlorocarbamates the oxidant/nitrogen source of choice for the osmium/cinchona alkaloid catalyzed asymmetric aminohydroxylation (AA) of olefins [e.g. Eq. (a)]. This methodology simplifies the synthesis of a vast array of compounds such as unnatural amino acids and other pharmacologically important compounds. DHQ-H = dihydroquinine, PHAL = 1,3-phthalazinediyl, Z = benzyloxycarbonyl.



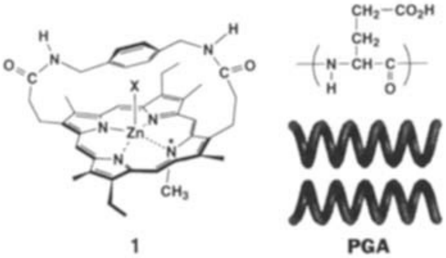
A difference of at least 35 kcal mol^{-1} between the activation barriers results from ab initio calculations for the competing [2+2] and [3+2] additions of OsO_4 to ethylene, clearly favoring the latter pathway (the two transition state structures are pictured on the right). The relative barrier heights for the proposed reaction paths hardly change in the presence of NH_3, used to model the base-catalyzed reaction. These theoretical findings on asymmetric dihydroxylation contradict the conclusions drawn from kinetic studies by Sharpless et al., but support the recent kinetic investigations by Corey et al.



An *exo*:*endo* ratio of 98:2! Thermochemistry would have predicted the opposite, but in the rearrangements of 5-hexenyl radicals the *exo* pathway is preferred due to kinetic reaction control. Selected ab initio methods are able to properly describe cyclizations of the 4-penten-1-oxyl radical (see sketch).

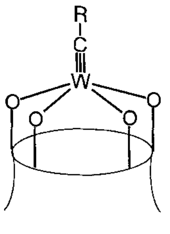


The secondary structure is of primary importance! The D and L forms of α-helical poly(glutamic acid) (PGA) are complexed selectively by the (*R*) and (*S*) isomers, respectively, of the porphyrin-based, chiral receptor **1**, which has a xylylenediamide strap. Helical polypeptides can thus be separated by complexation with enantiomerically pure **1**.

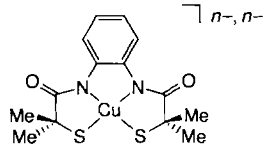


1

Anchoring gives stability. The recently synthesized anionic tungsten alkylidynes fixed over a planar tetraoxo surface of calix[4]arene (see picture) can undergo reversible protonation and metalation by carbophilic metals without disturbing the calixarene ligand. R = Ph, *n*Pr, $SiMe_3$.



Although it was once deemed a nearly impossible task (since Cu^{II} centers are generally readily reduced by thiolates), authentic Cu^{II} and Cu^{III} complexes with aliphatic thiolates in the metal coordination sphere have been synthesized. The unusual pair of square-planar complexes $(NEt_4)_2[Cu(phmi)] \cdot H_2O$ and $(PPh_4)[Cu(phmi)]$ (the anion is depicted on the right) displays the lowest known redox potential ever recorded for a Cu^{III}/Cu^{II} redox couple and has been completely characterized. H_4phmi = *N,N'*-1,2-phenylenebis(2-mercapto-2-methylpropionamide).



$[Cu(phmi)]^{2-,1-}$

J. Hanss, H.-J. Krüger* 2827–2830

The First Stable Copper(III) Complex Containing Aliphatic Thiolates as Ligands: Structural and Spectroscopic Evidence for Cu^{II} and Cu^{III} Ions in Complexes with Square-Planar CuN_2S_2 Coordination Environments

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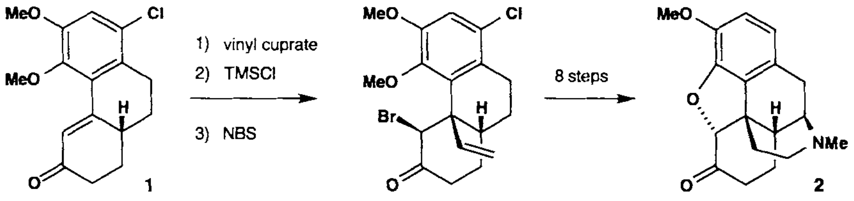
Conjugate addition of a vinyl cuprate to the sterically and electronically very demanding enone **1** is the key step of a short asymmetric total synthesis of (−)-dihydrocodeinone (**2**), an immediate precursor of (−)-morphine.

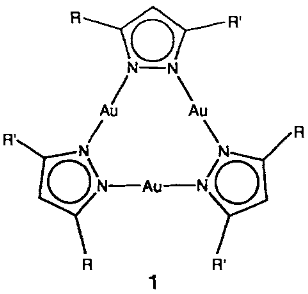


J. Mulzer,* D. Trauner, G. Dürner 2830–2832

Formal Total Synthesis of (−)-Morphine by Cuprate Conjugate Addition

---

Trinuclear gold(I) pyrazolate complexes of type **1** show liquid crystalline phases at room temperature. The molecules are arranged in a hexagonal columnar structure. The mesogenic behavior of these compounds is strongly related to the molecular symmetry, which is determined by the substituents R and R'. R = 3,4-$(H_{21}C_{10}O)_2C_6H_3$, R' = R, 3,4,5-$(H_{21}C_{10}O)_3C_6H_2$.



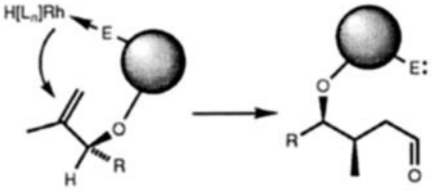
1

J. Barberá, A. Elduque, R. Giménez, L. A. Oro,* J. L. Serrano* 2832–2835

Pyrazolate "Golden" Rings: Trinuclear Complexes That Form Columnar Mesophases at Room Temperature

---

A reversibly coordinating auxiliary is the key to the first highly diastereoselective hydroformylation of acyclic methallylic alcohols (*syn*:*anti* up to 96:4; in the representation on the right the auxiliary is shown as a sphere). The reaction can be used for the efficient construction of stereotriades, the central structural units of polyketide natural products. R is, for example, Ph, CO_2Me, Me, CH_2Ph.



B. Breit* 2835–2837

Substrate-Directed Diastereoselective Hydroformylation of Methallylic Alcohols

---

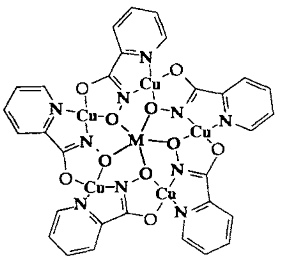
In vitro selection experiments yield unexpected results. An RNA-cleaving DNA enzyme that was selected in the presence of Mg^{2+} ions is much more efficient with Ca^{2+} as the cofactor. The result is even more surprising because of the lower hydrolytic efficiency of Ca^{2+} itself.

D. Faulhammer, M. Famulok* 2837–2841

The Ca^{2+} Ion as a Cofactor for a Novel RNA-Cleaving Deoxyribozyme

---

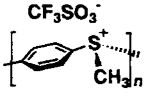
A novel "copper crown" complexes UO_2^{2+} preferentially (see picture), as competition experiments with Ca^{2+} and Cu^{2+} showed. This ligand thus provides an alternative to expanded porphyrins for the complexation of actinides and lanthanides by high denticity, planar ligands.



A. J. Stemmler, J. W. Kampf, V. L. Pecoraro* 2841–2843

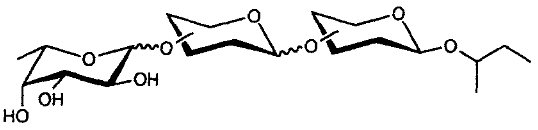
A Planar [15]Metallacrown-5 That Selectively Binds the Uranyl Cation

Alternating phenylene units and methylsulfonium groups make up polymer **1**, which is formed by polymerizing benzene with sodium methanesulfinate. This reaction is conducted in trifluoromethanesulfonate, and xylene and diphenyl ether are also suitable monomers.

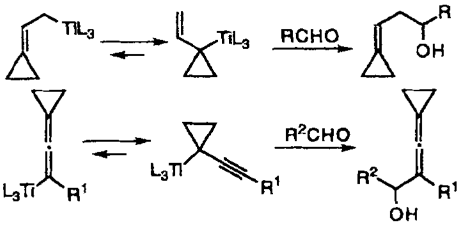


1

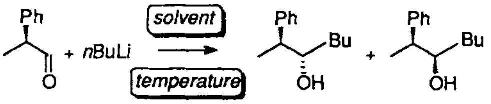
Many different trisaccharides (theoretically 256) can in principle be constructed from only four protected building blocks by following the strategy described for the synthesis of trisaccharide libraries. The method relies on latent-active glycosylation. The formula below gives an idea of the compounds in these libraries.



Steric strain shifts the equilibrium between the two isomeric allyltitanium compounds and isomeric allenyl- and propargyltitanium compounds containing cyclopropane units. This leads to unusual regioselectivity in their additions to electrophilic carbonyl compounds (shown on the right) and thus provides easy access to alkylidenecyclopropane derivatives.

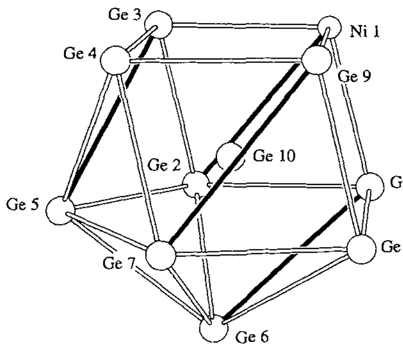


The length of the linear hydrocarbon chain in the solvent is a key factor in the facial diastereoselectivity of the nucleophilic addition of *n*-butyllithium to 2-phenylpropanal [Eq. (a)]. The reaction in these solvents shows inversion temperatures that correlate with the melting point of the solvent.



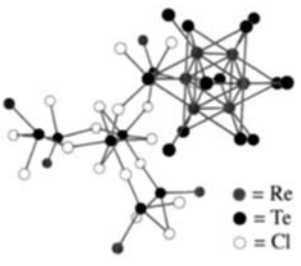
(a)

The first metalated germanide ion and only the second example of a cluster of the rare *nido*-10 (iv + iv) structural type, the anion **1**, was isolated from the reaction of $[Ni(CO)_2(PPh_3)_2]$, K_4Ge_9, and [2.2.2]cryptand in ethylenediamine (en). However, the structure of the $Ge_{10}Ni$ cluster (see picture) is distinctly distorted relative to the ideal *nido*-10 (iv + iv) geometry.

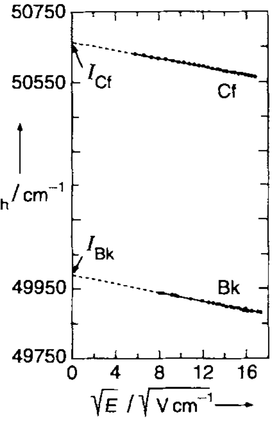


$[K([2.2.2]cryptand)]_2[Ge_9(\mu_{10}\text{-}Ge)Ni(PPh_3)]\cdot en$ **1**

Re_6 octahedra inside Te_8 cubes is a common feature of both title compounds. The picture on the right shows a section of the structure of $Re_6Te_{16}Cl_{18}$, in which the Re_6 octahedron and the binding of the cluster to the $[Te_8Cl_{18}]^{2-}$ ligand are apparent. Different binding to ligands results in a three-dimensional structure for $Re_6Te_{16}Cl_{18}$, and a two-dimensional structure for $Re_6Te_{16}Cl_6$.



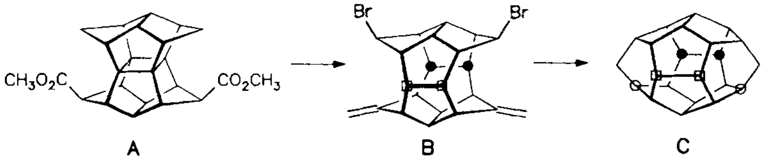
Only 10^{12} atoms of an element are required for the determination of its first ionization potential by resonance ionization with laser light in the presence of an electric field and subsequent mass spectrometry. The figure on the right shows the ionization thresholds W_{th} of berkelium and californium and the extrapolation to the external field strength $E = 0$, which yields the ionization potentials I (49989(2) and 50665(2) cm^{-1}, respectively).



S. Köhler, N. Erdmann,
M. Nunnemann, G. Herrmann,
G. Huber, J. V. Kratz, G. Passler,
N. Trautmann* 2856–2858

First Experimental Determination of the Ionization Potentials of Berkelium and Californium

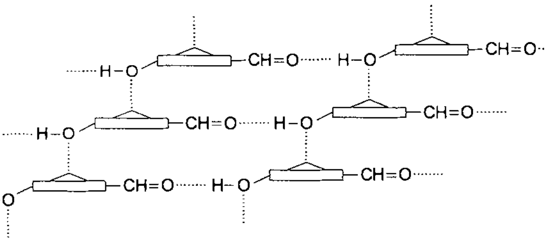
Twofold, transannular cyclization of the bis(methylene)bisseco intermediates **B**, obtained from the pagodane diester **A**, provides access to the parent nonpentagonal bis(homo)dodecahedrane **C** and pairwise symmetrically functionalized derivatives. Some of these products are important model compounds for quantifying the factors that determine the transannular electronic interactions in cage compounds of this type.



V. Sharma, M. Keller,
A. Weiler, D. Hunkler,
H. Prinzbach* 2858–2861

From Pagodanes to Nonpentagonal (Homo)Dodecahedranes—The Undecacyclo[$10.10.0.0^{2,20}.0^{3,10}.0^{4,19}.0^{5,9}.0^{6,18}.0^{7,15}.0^{8,13}.0^{19,22}.0^{16,21}$]docosane Cage

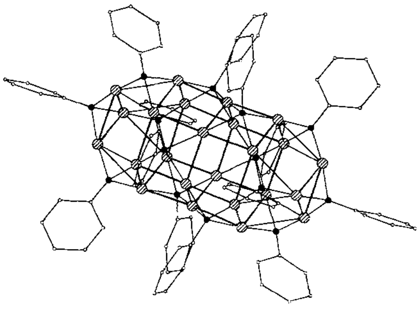
Self-assembly of functionally "inverse" zinc chlorins—3^1-hydroxy and 13^1-keto groups, which are functionally essential in the bacteriochlorophylls *c*, *d*, and *e*, have been interchanged—is possible in nonpolar solvents (see schematic representation below). This result sets structural conditions for the formation of large aggregates similar to those formed by bacteriochlorophylls in vitro and in light-harvesting antenna systems of photosynthetic bacteria.



A. Jesorka, T. S. Balaban,
A. R. Holzwarth,*
K. Schaffner 2861–2863

Aggregation of Modified Zinc Chlorins in Nonpolar Solvents–Bacteriochlorophyll *c* Mimics with Interchanged Hydroxy and Carbonyl Functions

Metal halide complexes and functionalized amines react to form imido-bridged transition metal clusters. This method can be used to synthesize imido clusters of electron-rich transition metals such as $[Li(thf)_4]_4[Cu_{24}(\mu_3\text{-}NPh)_8(\mu_4\text{-}NPh)_6]$ **1** (the structure of the anion of **1** is depicted on the right).



A. Decker, D. Fenske,*
K. Maczek 2863–2866

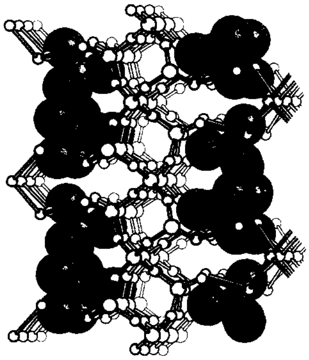
New Imido-Bridged Transition Metal Clusters: $[(C_5H_5)_4Ti_4(NSnMe_3)_4]$, $[Co_{11}(PPh_3)_3(NPh)_{12}]$, $[Ni_{11}Br_6(NtBu)_8]$, and $[Li(thf)_4]_4[Cu_{24}(NPh)_{14}]$

Laborious cleavage and isolation steps are avoided! The method of ^1H magic angle spinning (MAS) NMR spectroscopy can be used to monitor the course of the synthesis on a single resin particle in a suspended sample in the nanoliter detection range. This extremely useful technique for combinatorial chemistry was tested on a hydantoin reaction sequence.

M. Pursch, G. Schlotterbeck, L.-H. Tseng,
K. Albert,* W. Rapp 2867–2869

Monitoring the Reaction Progress in Combinatorial Chemistry: ^1H MAS NMR Investigations on Single Macro Beads in the Suspended State

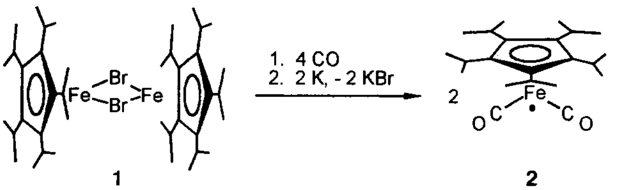
The missing link in the series clathrate hydrates, group silicate hydrates—layer silicate hydrates—porous framework silicas is provided by RUB-15, a new layer silicate hydrate with a three-dimensional bonding network composed of layerlike silicate ions and water molecules linked by hydrogen bonds. A section of the structure of is shown on the right. RUB-15 further illustrates the close relationship between crystalline compounds of water, silica, and mixtures thereof.



U. Oberhagemann, P. Bayat, B. Marler, H. Gies,* J. Rius 2869–2872

A Layer Silicate: Synthesis and Structure of the Zeolite Precursor RUB-15—$[N(CH_3)_4]_8[Si_{24}O_{52}(OH)_4] \cdot 20\,H_2O$

Monomeric in solution, dimeric in the crystal is the dicarbonyl(pentaisopropylcyclopentadienyl)iron(I) radical **2**, which is formed from the high-spin iron(II) complex **1** by carbonylation and reduction.

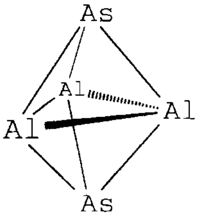


1 **2**

H. Sitzmann,* T. Dezember, W. Kaim, F. Baumann, D. Stalke, J. Kärcher, E. Dormann, H. Winter, C. Wachter, M. Kelemen 2872–2874

Synthesis and Characterization of the Stable Dicarbonyl(cyclopentadienyl)iron Radical $[(C_5R_5)Fe(CO)_2]$ (R = $CHMe_2$)

The bonding in heteropolyhedral compounds of the *closo*-borane type is discussed for $[As_2(AlCp^*)_3]$ clusters, whose molecular structure has been characterized by X-ray crystallography (framework shown on the right). Quantum chemical calculations on several trigonal-bipyramidal $E^V_2E^{III}_3$ structures revealed the mode of bonding for a variety of ligands ($Cp^* = C_5Me_5$; E^{III}: Group 13 element, E^V: Group 15 element).

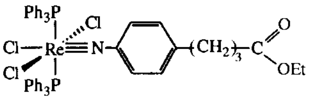


C. K. F. von Hänisch, C. Üffing, M. A. Junker, A. Ecker, B. O. Kneisel, H. Schnöckel* 2875–2877

$[As_2(AlCp^*)_3]$—A Compound with a Polyhedral As_2Al_3 Framework

---

Two important aspects, the synthesis of imido complexes of radioactive metal isotopes and the diversity that can be incorporated with this ligand, distinguish this communication. The multiply bonded organoimide ligand provides a new and powerful means of conjugating suitable radioisotopes of rhenium to biologically relevant molecules in the design of radiopharmaceuticals. Here stable isotope and ^{188}Re-labeled analogues (**1**) of the anticancer drug chlorambucil were synthesized.



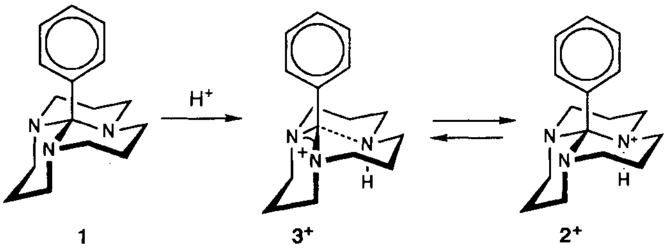
1

J. B. Arterburn,* I. M. Fogarty, K. A. Hall, K. C. Ott, J. C. Bryan 2877–2879

Functionalized Organoimidorhenium(v) Complexes as Potential Radiopharmaceuticals: Syntheses of Glycine Derivatives and the Structure Determination of a Rhenium Analogue of Chlorambucil

---

A bond stretch isomerism predicted over 30 years ago could exist in the organic cations 2^+ and 3^+, which arise from the protonation of **1** and have been characterized by X-ray crystallography. The two isomeric cations can be interconverted by changing the solvent polarity.



1 **3⁺** **2⁺**

R. D. Köhn,* G. Seifert, G. Kociok-Köhn 2879–2881

Solvent-Dependent C–N Bond Lengths in a Protonated Orthoamide

---

* Author to whom correspondence should be addressed

German versions of all reviews, communications, and highlights in this issue appear in the December issue of *Angewandte Chemie*. The appropriate page numbers can be found at the end of each article and are also included in the Author Index on p. 2883.

All the Tables of Contents from 1995 onwards may be found on the WWW under **http://www.vchgroup.de**

SERVICES

Deposition of Data from X-Ray Structure Analyses

In order to make life easier for authors and referees the Cambridge Crystallographic Data Centre (CCDC) and the Fachinformationszentrum Karlsruhe (FIZ) have unified their procedures for the deposition of data from single-crystal X-ray structure analyses.

From now on prior to submitting your manuscripts please deposit the data for your compound(s) **electronically** at the appropriate data base, that is, at the CCDC for organic and organometallic compounds and at the FIZ for inorganic compounds. Both data bases will be pleased to provide help (see our *Notice to Authors* in the first issue of this year). In general, you will receive a depository number from the data base within two working days after electronic deposition; please include this number with the appropriate standard text (see our *Notice to Authors*) in your manuscript. This will enable the referees to retrieve the structure data quickly and efficiently if they need this information to reach their decision.

This is now the uniform procedure for manuscripts submitted to the journals *Angewandte Chemie, Chemische Berichte, Chemistry—A European Journal*, and *Liebigs Annalen*.

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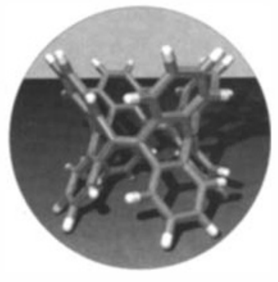
Pages 2549–2688

COVER PICTURE

The cover picture shows the first completely conjugated, tubelike hydrocarbon that is constructed by conventional chemical synthesis—a type of "picotube". It is synthesized in one step from tetradehydrodianthracene by photochemically induced metathesis reaction, which makes use of the strain energy as driving force. The highly symmetrical compound is characterized by exceptional stability. Ring-expanding metathesis—a new method for the construction of tubelike molecules—in conjunction with cyclization–dehydrogenation might point the way to interesting tube- and belt-shaped systems. The picture was generated by S. Kammermeier with the program POV-Ray on a Silicon Graphics Workstation. R. Herges et al. report on the synthesis and structure of the picotubes on p. 2669 ff.



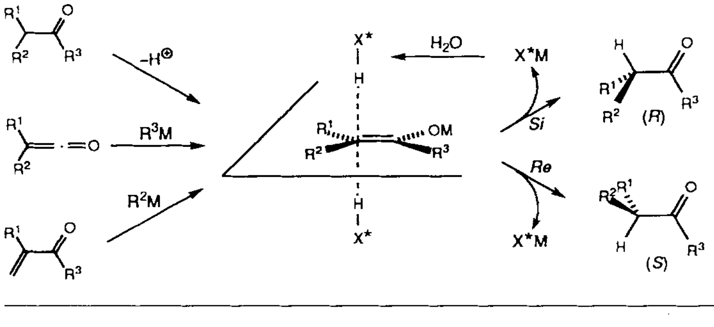
REVIEWS

Contents

The preferential transfer of a proton to one enantiotopic face of an enolate or enol derivative from a chiral proton donor HX* or from an achiral proton source in the presence of a chiral ligand is becoming increasingly important as a synthetic method. By judicious choice of reagents, both ketones and carboxylic acid derivatives can be obtained in almost enantiomerically pure form (see schematic overview below).

C. Fehr* 2566–2587

Enantioselective Protonation of Enolates and Enols



It's a great deal, but we still require additional information—that is the answer to the question in the title. How the knowledge of the three-dimensional structures of protein–ligand complexes and small organic molecules can be exploited for the development of computational tools for predicting binding affinities, molecular conformations, and binding modes is described herein. Evidence is also presented that care is needed—particularly for considerations based purely on structural arguments—since interactions such as hydrogen bonds and lipophilic contacts can lead to unexpected orientations of ligands in a protein pocket.

H.-J. Böhm,* G. Klebe* 2588–2614

What Can We Learn from Molecular Recognition in Protein–Ligand Complexes for the Design of New Drugs?

HIGHLIGHTS

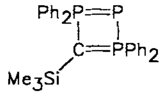
Electron transfer from a reducing agent to a fluorocarbon leads to cleavage of the strong and supposedly inert C–F bond. This process can be used to defluorinate perfluoroalkanes to produce perfluoroarenes or -alkenes catalytically under mild conditions. The transfer of two electrons from alkali metal oxalates to chlorofluorocarbons leads to complete degradation at relatively low temperatures [Eq. (a)].

$$C_nF_xCl_y + (x+y)e^- + (x+y)M^+ \longrightarrow nC + xMF + yMCl \qquad (a)$$

G. C. Saunders* 2615–2617

Defluorination of Perfluoroalkanes and Chlorofluorocarbons

In contrast to the antiaromatic and nonelusive mono- and oligophosphetes featuring only two-coordinate phosphorus atoms, unsaturated, four-membered phosphorus heterocycles with at least one η^5,σ^4-phosphorus atom such as triphosphete **1**, which was prepared by Karsch et al., are surprisingly stable compounds. These systems can undergo ring expansion to give five-membered heterocycles such as **2** (according to Bertrand et al.), react to form complexes, or undergo addition and substitution reactions.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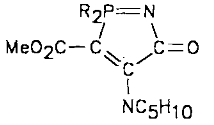
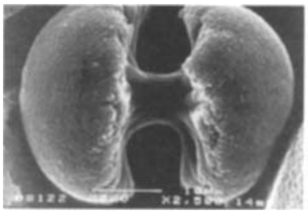

2

L. Weber* 2618–2621

Ylidic Four-Membered Rings with Four π-Electrons—Another Exciting Chapter in Phosphorus Chemistry

COMMUNICATIONS

Elongated, hexagonal-prismatic seed crystals are the starting point for the hierarchical growth of anisotropic spherical aggregates of fluorapatite in gelatin matrices. Discrete dumbbell-shaped aggregates (scanning electron microscope image shown on the right) are formed by self-similar, branched, needlelike upgrowths at both ends of the seeds. With successive generations, these aggregates close to give spheres with diameters of up to 400 µm. The system makes it possible to monitor the development of an abiotic information pattern into the macroscopic range.

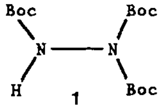


R. Kniep,* S. Busch 2624–2626

Biomimetic Growth and Self-Assembly of Fluorapatite Aggregates by Diffusion into Denatured Collagen Matrices

---

"Almost all possibilities have been exhausted", stated H. Wieland in 1913 in the preface to his monograph *Die Hydrazine* with regard to the synthesis of N,N′-substituted hydrazines. Even today suitable reagents and methods are lacking for the preparation of these compounds, which are important as precursors of pharmaceuticals, agrochemicals, and dyestuffs. The readily available, protected hydrazine **1** is a new reagent that may fill this gap.

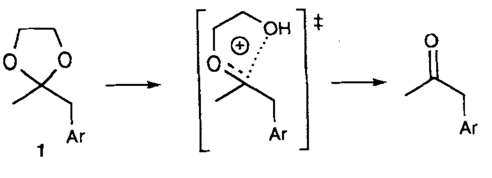

1

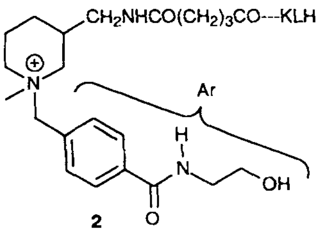
U. Mäeorg, L. Grehn,
U. Ragnarsson* 2626–2627

Prototypical Reagent for the Synthesis of Substituted Hydrazines

---

The hydrolysis of unactivated cyclic ketals such as **1** can be catalyzed by antibodies raised against the transition state analog **2**. This transformation is closely related to the cleavage of the glycosidic bond. The observed catalysis is triggered more by electrostatic complementarity to the transition state than by shape complementarity.

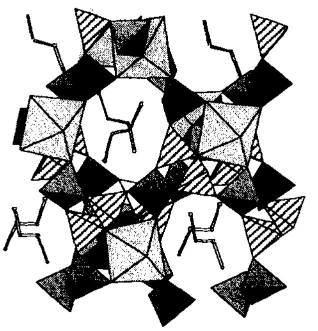



2

D. Shabat, S. C. Sinha,* J.-L. Reymond,*
E. Keinan* 2628–2630

Catalytic Antibodies as Probes of Evolution: Modeling of a Primordial Glycosidase

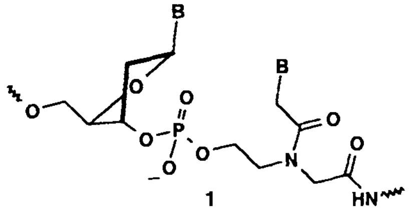
Channels measuring roughly 5.2 × 7.6 Å (O–O distances) are found in the first microporous borophosphate (a section of the structure is shown on the right). Ethylenediamine serves as a template in the hydrothermal synthesis. The framework is constructed from BO_4 and PO_4 tetrahedra and CoO_6 octahedra, and organic dications occupy the channels.



S. C. Sevov* 2630–2632

Synthesis and Structure of $CoB_2P_3O_{12}(OH)\cdot C_2H_{10}N_2$: The First Metal Borophosphate with an Open Framework Structure

Unambiguous binding to complementary DNA and RNA, stability toward 3′-exonucleases, and a similar uptake by cells as DNA oligomers characterize the PNA/DNA chimeras of type **1** described here. These chimeric oligomers are accessible in an automated synthesis sequence.

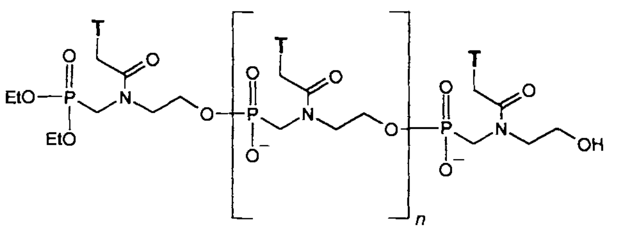


1

E. Uhlmann,* D. W. Will, G. Breipohl, D. Langner, A. Ryte 2632–2635

Synthesis and Properties of PNA/DNA Chimeras

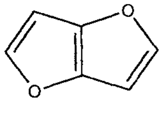
The water-solubility of PHONAs and their ability to bind complementary DNA make them interesting potential therapeutics. The nucleobases are attached to an achiral, charged backbone through a methylenecarbonyl linker, as in the case of PNAs (see below). PHONAs are synthesized in solution by block condensation.



A. Peyman,* E. Uhlmann, K. Wagner, S. Augustin, G. Breipohl, D. W. Will, A. Schäfer, H. Wallmeier 2636–2638

Phosphonic Ester Nucleic Acids (PHONAs): Oligonucleotide Analogues with an Achiral Phosphonic Acid Ester Backbone

The authors' answer to the question in the title is: No, the most stable positional isomers of the isoelectronic heteroatom analogues (**1** and **2**) of the pentalene dianion are not the most aromatic. Their arguments are based on the geometric and magnetic criteria (computed magnetic susceptibilities and anisotropies, ^1H NMR chemical shifts and nucleus-independent chemical shifts).



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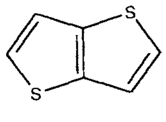
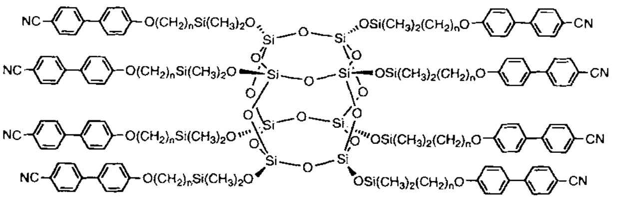


2

G. Subramanian, P. von R. Schleyer,* H. Jiao 2638–2641

Are the Most Stable Fused Heterobicycles the Most Aromatic?

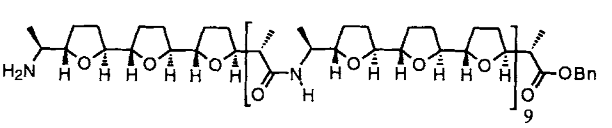
Cuboid silsesquioxanes with appropriate side chains (see below; n = 4, 6, 11) provide a means of structuring soft matter with inorganic cores. These compounds combine material characteristics of polymer and low molecular mass liquid crystals.



G. H. Mehl,* J. W. Goodby 2641–2643

Liquid-Crystalline, Substituted Octakis(dimethylsiloxy)octasilsesquioxanes: Oligomeric Supermolecular Materials with Defined Topology

Membrane-modifying and conductance-inducing, decapeptide **1** marks a new class of compounds, the oligo(tetrahydrofuranyl) peptides, which form artifical ion channels and can potentially contribute to a better understanding of the function and structure of their naturally occurring counterparts.



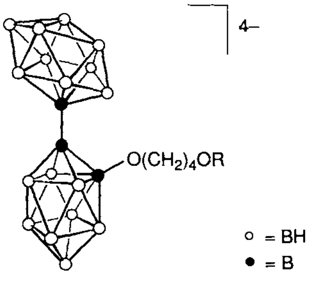
1

H. Wagner, K. Harms, U. Koert,*
S. Meder, G. Boheim* 2643–2646

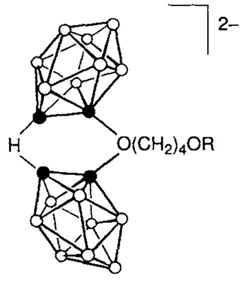
Oligo-THF Peptides: Synthesis, Membrane Insertion, and Studies of Ion Channel Activity

---

Completely unexpectedly, $[ae\text{-}B_{20}H_{17}O(CH_2)_4OR]^{2-}$ **1** is formed and not the expected $[ae\text{-}B_{20}H_{17}OR]^{4-}$ in the reaction of $[n\text{-}B_{20}H_{18}]^{2-}$ with alkoxides NaOR (R = methyl, isopentyl). The products result from the nucleophilic attack by an alkoxide ion on a THF solvent molecule that is associated with $[n\text{-}B_{20}H_{18}]^{2-}$. The anhydrous oxidation of **1** in ethanol produced the $[\mu\text{-}B_{20}H_{17}O(CH_2)_4OR]^{2-}$ ions (**2**), which can be hydrolyzed to produce the $[\mu\text{-}B_{20}H_{17}OH]^{2-}$ anion.



1



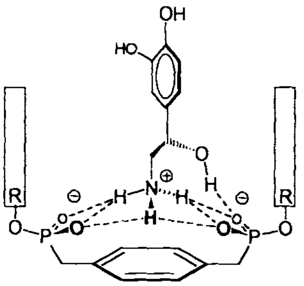
2

F. Li, K. Shelly, R. R. Kane,
C. B. Knobler,
M. F. Hawthorne* 2646–2649

The Novel, $[n\text{-}B_{20}H_{18}]^{2-}$-Induced Nucleophilic Ring Opening of Tetrahydrofuran by Alkoxide Anions

---

A new class of ammonium receptors binds especially strongly to biologically important amino alcohols such as glucosamine, norephedrine, and the β-blocker propranolol ($K_a > 50000$ in DMSO). The mechanism of molecular recognition (see the model on the right obtained from force-field calculations) imitates that of the natural adrenergic receptor.

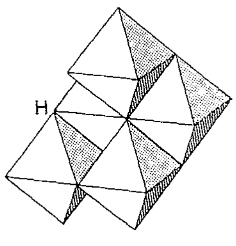


T. Schrader* 2649–2651

Towards Synthetic Adrenaline Receptors—Strong Binding of Amino Alcohols by Bisphosphonates

---

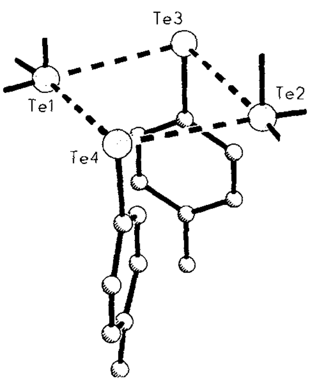
The anion $[\mathbf{HW_5O_{19}}]^{7-}$ (depicted on the right) could be an intermediate on the way to highly condensed polyoxotungstates(VI). The compound $K_7[HW_5O_{19}] \cdot 10H_2O$, which contains this anion, was obtained by fractional crystallization from an acidified K_2WO_4 solution.



J. Fuchs, R. Palm,
H. Hartl* 2651–2653

$K_7HW_5O_{19} \cdot 10H_2O$—A Novel Isopolyoxotungstate(VI)

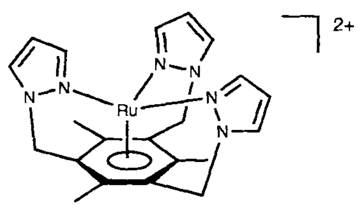
A description as pairs of ion pairs best suits the telluronium tellurolates $R^1_3TeTeR^2$ (R^1 = phenyl, R^2 = 4-methylphenyl for **1a**, R^2 = 4-methoxyphenyl for **1b**) and the corresponding selenolates, whose existence in the solid state is connected with cooperative chalcogen–chalcogen interactions. The central Te_4 ring of **1a** is shown on the right (phenyl substituents on Te1 and Te2 have been omitted for clarity).



J. Jeske, W.-W. du Mont,*
P. G. Jones 2653–2655

Dimeric Triaryltelluronium Arenetellurolates: New Metastable Tetramers of Diaryltellurium

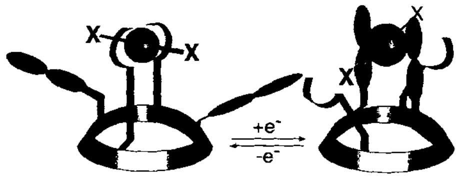
Half-sandwich coordination and tripodal chelation by one ligand is possible with the novel class of ligand, the coelenterands, described here. An example of a metal complex containing a coelenterand—the name is derived from the Greek words for hollow stomach—is shown on the right.



C. M. Hartshorn,
P. J. Steel* 2655–2657

Coelenterands: A New Class of Metal-Encapsulating Ligands

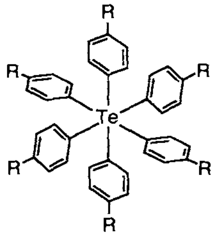
Simply by flipping up, suitable ligand units attached to the calix[4]arene–iron(III) complex represented schematically on the right can bind the "soft" iron(II) ion generated on reduction (X = coordinating buffer molecules). The calixarene bears two sets of ion-binding groups: one for "hard" and one for "soft" metal ions. The metal complex switches between the two states during redox reactions, and this switching process can be followed in real time by UV/Vis spectroscopy.



C. Canevet, J. Libman,
A. Shanzer* 2657–2660

Molecular Redox-Switches by Ligand Exchange

The highest possible oxidation state of +6 is displayed by the tellurium center in the hexaaryltellurium compounds **1a** and **1b**. Both are extremely thermally stable and, unlike other organotellurium compounds, not light-sensitive. X-ray crystallographic analyses of **1** revealed rare examples of approximate T_h molecular symmetry.



1a, R = CF_3
1b, R = H

M. Minoura, T. Sagami, K.-y. Akiba,*
C. Modrakowski, A. Sudau, K. Seppelt,*
S. Wallenhauer 2660–2662

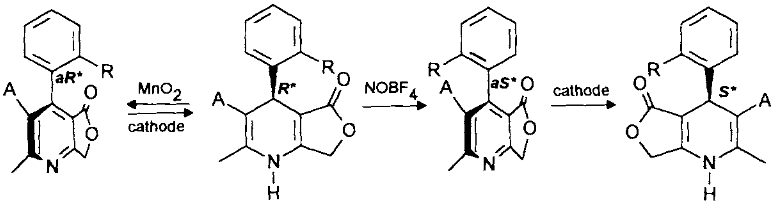
Hexaaryltellurium, the First Neutral Compounds Comprising Hexaarylated Elements

---

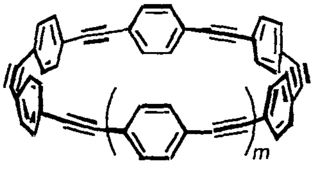
Stereoselective oxidation of optically active dihydropyridines with $NOBF_4$ or MnO_2 leads with either inversion or retention to axial chiral arylpyridines (see below), which can be converted by cathodic reduction into the corresponding dihydropyridines. This is the first report of the successful inversion of configuration for dihydropyridines.

A. Straub,* A. Goehrt 2662–2664

Inversion of Optically Active Dihydropyridines by Oxidation and Electroreduction



The belt-shaped, conjugated molecules 1 and 2 were synthesized by bromination–dehydrobromination of the corresponding hexaene and octaene. The air-sensitive but isolable compounds show appreciable strain in the triple bonds and large Stokes shifts in the emission spectra.

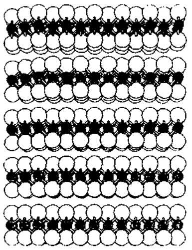


1: $m = 1$
2: $m = 3$

T. Kawase, H. R. Darabi,
M. Oda* 2664–2666

Cyclic [6]- and [8]Paraphenylacetylenes

Intergrown dichalcogenide layers with a predetermined modulation of composition can be prepared through controlled crystallization of reactants with superlattice structure. The resulting superlattice products (the picture shows the transition from one dichalcogenide component (black spheres) to the other (gray spheres)) are formed as polycrystalline thin films oriented with the dichalcogenide layers parallel to the substrate surface. We are thus a step closer to being able to tune physical and chemical properties through the design of superlattices.

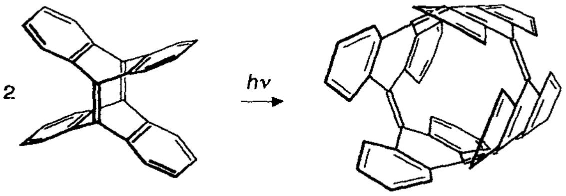


M. Noh, D. C. Johnson* 2666–2669

Designed Synthesis of $[TiSe_2]_m[NbSe_2]_n$ Superlattices from Modulated Reactants

---

A tubelike, fully conjugated hydrocarbon, a kind of "picotube", was prepared by ring-expanding metathesis (see below). This method may provide an approach for the chemical synthesis of a variety of other carbon tubes.

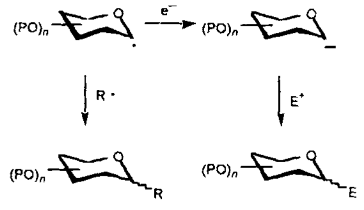


S. Kammermeier, P. G. Jones,
R. Herges* 2669–2671

Ring-Expanding Metathesis of Tetradehydroanthracene—Synthesis and Structure of a Tubelike, Fully Conjugated Hydrocarbon

---

Carbohydrate mimetics for the study of carbohydrate recognition in biological systems can be C-glycosides, which can now be prepared by the SmI_2-mediated coupling of glycosyl phosphates with carbon radical or carbon anion acceptors. The reaction proceeds by one-electron processes via the radical or the anion, respectively (see scheme on the right), and is complete within 15–30 min.

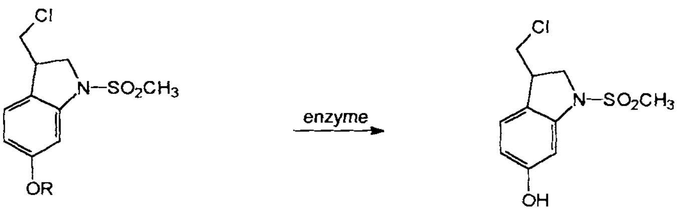


S.-C. Hung, C.-H. Wong* 2671–2674

Samarium Diiodide Mediated Coupling of Glycosyl Phosphates with Carbon Radical or Anion Acceptors—Synthesis of C-Glycosides

---

The O-glycosides 1 of the seco-CI derivative 2, which is the seco form of the simplified pharmacophoric group of the potent cytotoxic antibiotic CC-1065, show only very low toxicity. In tumor-selective cancer therapy they can be used in conjunction with conjugates of glycohydrolases and monoclonal antibodies that bind at tumor-associated antigens. The glycohydrolases cleave the prodrugs **1** and release the cytotoxic components **2**.



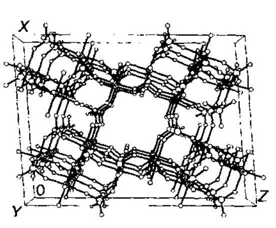
1a: R = β-D-Gal
1b: R = β-D-Glc
2

L. F. Tietze,* R. Hannemann, W. Buhr,
M. Lögers, P. Menningen, M. Lieb,
D. Starck, T. Grote, A. Döring,
I. Schuberth 2674–2677

Prodrugs of the Cytostatic CC-1065 That Can Be Activated in a Tumor-Selective Manner

---

Medium-sized channels pass through the structure of the first zinc fluoride phosphate (section of the structure is shown on the right). The framework is constructed from ZrO_6 and ZrO_5F octahedra and PO_4 and $PO_3(OH)$ tetrahedra. Further cavity-containing compounds of this type should be accessible by variation of the amine used as a template.



E. Kemnitz,* M. Wloka, S. Trojanov,
A. Stiewe 2677–2678

$[(enH_2)_{0.5}][Zr_2(PO_4)_2(HPO_4)F]\cdot H_2O$:
A Unique Zirconium Fluoride Phosphate with a Cavity Structure

---

* Author to whom correspondence should be addressed

BOOKS

German versions of all reviews, communications, and highlights in this issue appear in the second November issue of *Angewandte Chemie*. The appropriate page numbers can be found at the end of each article and are also included in the Author Index on p. 2686.

All the Tables of Contents from 1995 onwards may be found on the WWW under **http://www.vchgroup.de**

SERVICES

Deposition of Data from X-ray Structure Analyses

In order to make life easier for authors and referees the Cambridge Crystallographic Data Centre (CCDC) and the Fachinformationszentrum Karlsruhe (FIZ) have unified their procedures for the deposition of data from single-crystal X-ray structure analyses.

From now on prior to submitting your manuscripts please deposit the data for your compound(s) **electronically** at the appropriate data bank, that is, at the CCDC for organic and organometallic compounds and at the FIZ for inorganic compounds. Both data banks will be pleased to provide help (see our *Notice to Authors* in the first issue of this year). In general, you will receive a depository number from the data bank within one working day after electronic deposition; please include this number with the appropriate standard text (see our *Notice to Authors*) in your manuscript. This will enable the referees to retrieve the structure data quickly and efficiently if they need this information to reach their decision.

This is now the uniform procedure for manuscripts submitted to the journals *Angewandte Chemie, Chemische Berichte, Chemistry—A European Journal*, and *Liebigs Annalen.*

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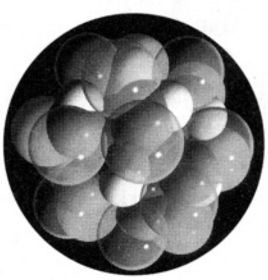
COVER PICTURE

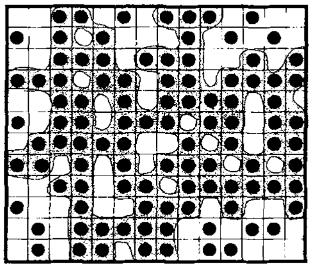


The cover picture shows a computer-generated space-filling representation of the product of photochemical chlorination of decamethyl-1,12-dicarba-*closo*-dodecaborane(12), decakis(dichloromethyl)-1,12-dicarba-*closo*-dodecaborane(12). The semitransparent Cl atoms (yellow) allow the visualization of the underlying and camouflaged icosahedral 1,12-dicarba-*closo*-dodecaborane framework, in which B is red, H is white, and C is gray. The CH vertices are buried in an array of five axially oriented Cl atoms arising from nearby $CHCl_2$ substituents. Apparent hydrocarbons of the type described here by M. F. Hawthorne et al. on p. 2536 ff. constitute a new class of carborane derivatives replete with unique chemistry and applications. The picture was produced by Darren M. Ricciardi, Imperative Images, Aurora, CO, USA, using the program Lightwave 3D by NEWTEK.

REVIEWS

Contents

The addition of diazonaphthoquinones to novolak resins controls the dissolution of solid films of these materials by perturbing their percolation field (shown on the right). This rather unexpected effect is the basis of a photolithographic resist (light-sensitive varnish) used in the manufacture of almost all of today's integrated circuits ("computer chips").



Continuous improvement of the McMurry reaction since its discovery in the 1970s has led to impressive applications in syntheses of natural products and pharmaceuticals. In addition, the exact mode of action of the titanium reagents has been scrutinized. In the latest variant the active titanium species is not generated before but during the reductive coupling of the carbonyl-containing substrate.

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HIGHLIGHTS

The subject of an exciting debate—does electron transfer play a role in bimolecular nucleophilic substitution (a)? How would this reaction differ from the classical S_N2 reaction (b)? A number of research groups have employed electrochemical and computational methods to determine if alternatives exist for one of the best known mechanisms in organic chemistry.

$$Nu^- + R\text{-}X \longrightarrow Nu^\bullet + R^\bullet + X^- \longrightarrow R\text{-}Nu + X^- \quad \text{(a)}$$

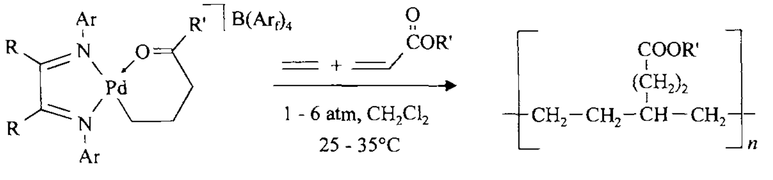
$$Nu^- + R\text{-}X \longrightarrow [Nu\cdots R\cdots X]^- \longrightarrow R\text{-}Nu + X^- \quad \text{(b)}$$

B. Speiser* 2471–2474

Electron Transfer and Chemical Reactions—Stepwise or Concerted? On the Competition between Nucleophilic Substitution and Electron Transfer

---

Long-chain-branched copolymers 2 can be prepared from ethene and acrylates (R′ = Me, *t*Bu, $CH_2(CF_2)_6CF_3$) with the Pd^{II} catalysts **1**. Copolymers of this type were previously produced exclusively by radical routes in high-pressure processes. Propene/carbon monoxide copolymers (polyketones) have been obtained with other Pd^{II} complexes.



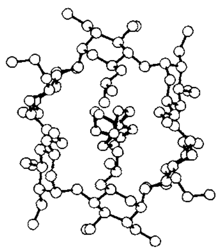
1 **2**

A. S. Abu-Surrah,
B. Rieger* 2475–2477

Late Transition Metal Complexes: Catalysts for a New Generation of Organic Polymers

COMMUNICATIONS

Even on a large scale an aqueous solution of 1,7-dioxaspiro[5.5]undecane and a tailored cyclodextrin selectively yields the inclusion complex with the (*R*) guest (shown on the right), the structure of which was studied both in the solid state and in solution. The yields are higher than would be expected for the racemate because the (*S*) enantiomer of the guest is transformed into the (*R*) enantiomer, which forms the more stable host–guest complex.

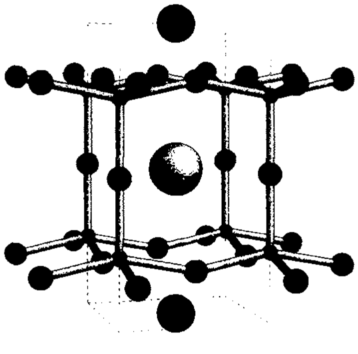


K. Yannakopoulou, D. Mentzafos,
I. M. Mavridis,*
K. Dandika 2480–2482

Chiral Recognition of (*R*)-(−)-1,7-Dioxaspiro[5.5]undecane by Hexakis(2,3,6-tri-*O*-methyl)-α-cyclodextrin

---

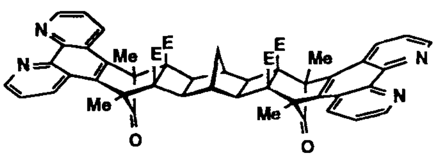
A structure reminiscent of the $YBa_2Cu_3O_7$ superconductor is shown by the novel reduced manganese perovskite $YBaMn_2O_5$ (on the right), in which double layers of MnO_5 square pyramids enclose the Ba^{2+} ions (large spheres), while Y^{3+} ions (medium-sized black spheres) lie between the layers. Unlike many oxidized Mn perovskites, $YBaMn_2O_5$ does not exhibit magnetoresistive effects. Instead a ferrimagnetic transition occurs at 167 K which may be due to Mn^{2+}/Mn^{3+} valence and spin ordering.

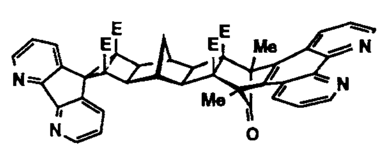


J. P. Chapman, J. P. Attfield,*
M. Molgg, C. M. Friend,
T. P. Beales 2482–2484

A Ferrimagnetic Manganese Oxide with a Layered Perovskite Structure: $YBaMn_2O_5$

In new bridging ligands the chelating groups listed in the title are fused to the termini of rigid molecular spacers. The resulting bisbidentate ligands such as those shown below have been prepared with matching and different terminal groups, and the coordination centers are arranged with varying separations and orientations. Selected bridging ligands and polypyridylruthenium(II) moieties were used to prepare dinuclear complexes, which were examined in electrochemical experiments. $E = CO_2CH_3$.



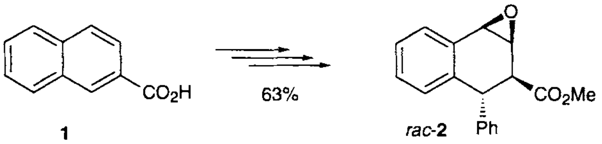


R. N. Warrener,* A. B. B. Ferreira,
A. C. Schultz, D. N. Butler,
F. R. Keene,* L. S. Kelso 2485–2487

Space-Separated 1,10-Phenanthroline, 4,5-Diazafluorene, or 3,6-Di(2-pyridyl)pyridazine Units as Ligands in Diruthenium Complexes: Preliminary Studies of Metal–Metal Interactions

---

Four stereogenic centers are generated with high diastereoselectivity in only a few steps starting from 2-naphthoic acid (**1**). Meyers oxazoline synthesis, nucleophilic addition of phenyllithium, and epoxidation afford *rac*-**2** in 63% overall yield. The stereochemical course of the reaction is directed by the phenyl group.



T. Linker,* K. Peters, E.-M. Peters,
F. Rebien 2487–2489

Highly Diastereoselective Synthesis and Epoxidation of Chiral 1,2-Dihydronaphthalenes

---

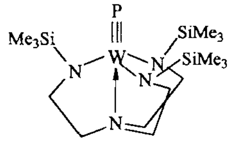
Remarkable news concerning the long-known and well-investigated reaction system naphthalene/sodium in THF is reported: At room temperature a reversible intermolecular transfer of hydrogen takes place both between naphthalene rings and also with THF molecules. In contrast, the corresponding lithium and potassium systems show no such behavior. In addition, alkanes and cycloalkanes as solvent additives effect a significant increase in the H/D exchange rate in the sodium system. Benzene, toluene, ethene, and even methane (!) also take part in the H/D exchange reactions in the naphthalene/sodium system.

S. Rummel,* M. A. Ilatovskaya,
E. I. Mysov, V. S. Lenenko,
H. Langguth, V. B. Shur 2489–2491

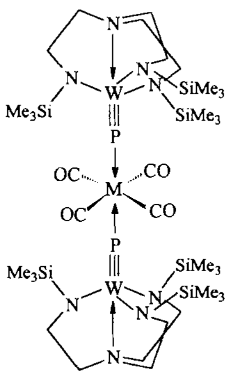
Catalytic Activation of C–H Bonds in Aromatic Hydrocarbons, Ethene, and Methane by the Naphthalene/Sodium System in Tetrahydrofuran

---

Complexes with terminal pnictide ligands are interesting in themselves and as ligands for the complexation of Lewis acids. Herein the syntheses of complexes such as **1** (E = P, As) and **2** (M = Cr, W) are described, and detailed theoretical studies on the relative thermodynamic stability of these and analogously constructed complexes are presented.



1



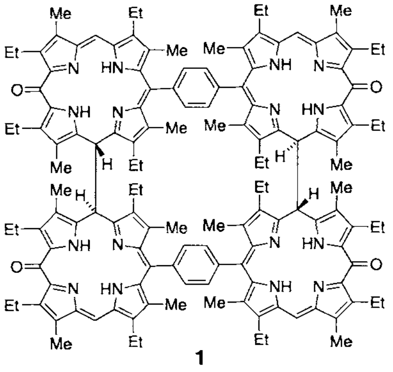
2

M. Scheer,* J. Müller,
M. Häser 2492–2496

Complexes Containing Phosphorus and Arsenic as Terminal Ligands

---

Oxidation at position 10 converts the title compounds into dimers. In an extension of this reaction a 15,15'-*p*-phenylene-linked bis(oxophlorin) produces the robust supramolecular array tetrakis(isooxophlorin) **1**. In the crystal **1** has an overall helical structure in which the groove is filled by molecules of *n*-hexane.

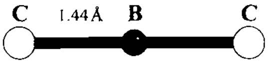


1

R. G. Khoury, L. Jaquinod, D. J. Nurco,
R. K. Pandey, M. O. Senge,
K. M. Smith* 2496–2499

Self-Assembling Covalently Linked Supramolecular Arrays of Defined Structure: The Remarkable Redox Reactivity of 15-*meso*-Substituted 5-Oxyporphyrins

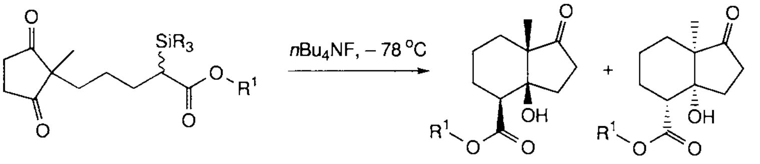
The highest negative charge of a 16-electron system known to date is shown by the CO_2-analogous anion $(C{=}B{=}C)^{5-}$ in Al_3BC_3. This has been confirmed by the vibrational spectroscopic and structural characterization of this compound, which revealed the linearity and bond lengths given below. Al_3BC_3 can be regarded as the first carbidecarbidoborate of aluminum the first.



H. Hillebrecht,*
F. D. Meyer 2499–2500

Synthesis, Structure, and Vibrational Spectra of Al_3BC_3, a Carbidecarboborate of Aluminum with Linear $(C{=}B{=}C)^{5-}$ Anions

Desilylations can trigger the intramolecular aldol reaction of alicyclic tricarbonyl compounds. Ester enolates are formed selectively and cyclize to give functionalized hydrindanones [Eq. (a); R^1 = (−)-menthyl, (−)- and (+)-phenylmenthyl; SiR_3 = $SiMe_3$, $SiPh_2Me$]. The cyclization products are extremely important and useful synthetic building blocks for the synthesis of steroids.

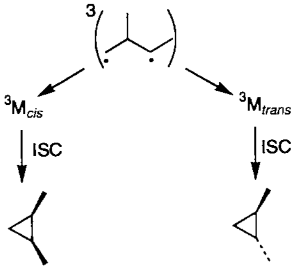


(a)

D. Schinzer,* T. Blume,
P. G. Jones 2500–2502

Asymmetric Cyclization of α-Silyl Esters to Give Functionalized Hydrindanones

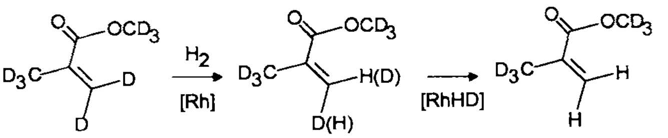
The mechanism of stereodifferentiation was elucidated for the triplet ring-closure reaction of 1,2-dimethyltrimethylene (shown schematically on the right). The combined analysis of potential energy surfaces and spin-orbit coupling surfaces indicated that stereodifferentiation reflects the energetic behavior of the triplet state. This could well be a general feature of triplet photoreactions. ISC = intersystem crossing.



M. Böckmann,
M. Klessinger* 2502–2504

Model Calculations on the Stereoselectivity of the Triplet Photoreaction of 1,2-Dimethyltrimethylene

Pairwise exchange of geminal protons in unsaturated carbonic acid derivatives of the type $H_2C{=}C(R)COOR'$ during the rhodium(I)-catalyzed hydrogenation [Eq. (a)] has been proven conclusively for the first time by using in situ NMR spectroscopy and parahydrogen (PHIP method). The most important conclusion is that the formation of the hydridoalkyl intermediates must be a reversible reaction.

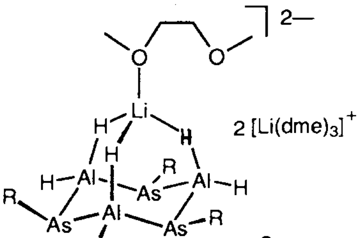


(a)

A. Harthun, R. Selke,*
J. Bargon* 2505–2507

Proof of a Reversible, Pairwise Hydrogen Transfer during the Homogeneously Rhodium(I)-Catalyzed Hydrogenation of α,β-Unsaturated Carbonic Acid Derivatives with In Situ NMR Spectroscopy and Parahydrogen

A considerable extension of the synthetic potential of lithium arsenides is likely through the alanates $[LiAl(AsHR)_4]$ (R = H, triorganosilyl), which can be synthesized from $LiAlH_4$ and H_2AsR. For example, the Zintl compound $[Li(tmeda)]_3As_7$ **1** was obtained by thermal decomposition in the presence of tmeda, and the first As_4Si_4 cubane was prepared by mild arsanylation of $RSiCl_3$ (R = 2,4,6-iPr$_3$C$_6$H$_2$). The novel complex **2** with an adamantane framework was formed from $RAsH_2$ (R = $Me_2C(i\text{Pr})SiMe_2$) and $LiAlH_4$. tmeda = $Me_2NCH_2CH_2NMe_2$, dme = $MeOCH_2CH_2OMe$.

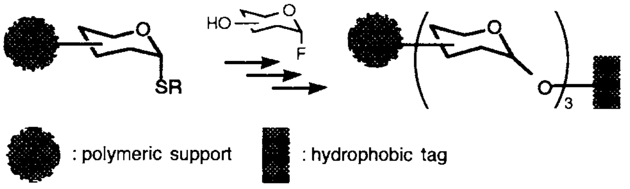


2

M. Driess,* K. Merz, H. Pritzkow,
R. Janoschek 2507–2510

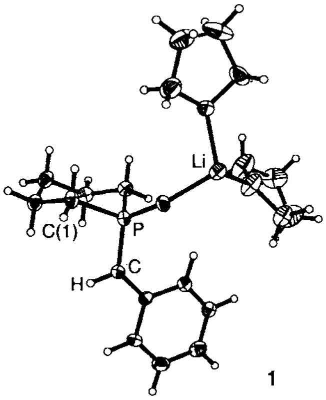
Lithium Arsanylalanates as Arsenide Sources: A Simple Route to the Zintl Anion As_7^{3-} and the Synthesis of a Tetraarsatetrasilacubane

Only a single purification step is required to isolate the glycoconjugate-related oligosaccharides prepared by a new strategy, which is shown schematically below. Prior to purification the support-bound oligosaccharide, which is labeled with a hydrophobic tag, is cleaved from the polymeric support and deprotected.

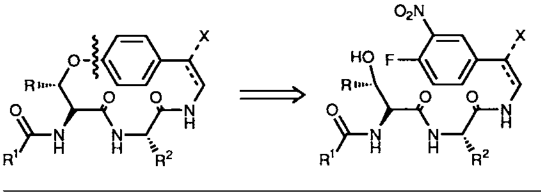


139 rotational lines of the ^{28}Si isotopomer of free silaethene $H_2C{=}SiH_2$ (**1**) have been observed in the gas phase by millimeter wave spectroscopy. The search was guided by ab initio calculations at the MP2, CCSD, and CCSD(T) levels with TZ2Pf basis sets. The rotational constants determined experimentally and by ab initio methods for **1** with a planar C_{2v}-symmetric structure agree within about 0.5%. Compound **1** was best produced by vacuum pyrolysis of 5,6-bis(trifluoromethyl)-2-silabicyclo[2.2.2]octa-5,7-diene in an Ar stream; **1** decomposes exponentially with a $1/e$ lifetime at ambient temperature of 30 ± 2 ms.

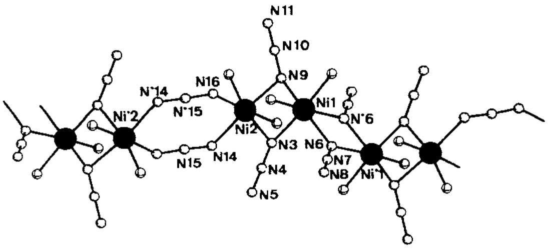
The anionic benzyl carbon atom is sp^2 hybridized in **1**, the first lithiated phosphane oxide that has been characterized by X-ray crystallography. In the solid state as well as in THF solution, **1** is shown to exist as a dimer with no Li–C contacts. Unlike related phosphonamides, **1** prefers an orthogonal conformation of the benzylic group in the solid state.



Macrocyclization by ether formation (retrosynthesis shown below), the key step in a conceptually novel approach to cyclopeptide alkaloids, relies on an intramolecular nucleophilic substitution reaction. This new strategy was demonstrated for the synthesis of model compounds for the 14-membered cyclopeptide alkaloids, an important class of natural products.



A complex sequence of ferro- and antiferromagnetic interactions occurs in the compound [Ni(N,N'-dmen)(μ-N_3)$_2$] (N,N'-dmen = N,N'-dimethylethylenediamine), which exists as a one-dimensional chain in the solid state (shown below; C atoms of the amine ligands are omitted). The magnetic behavior of this unusual spin system has been analyzed in detail.



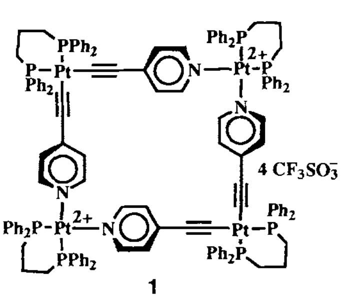
The simultaneous activation of carbon dioxide and benzene by SiF_3^+ in the gas phase has been investigated by FT-ICR spectrometry. The key step is the formation of a tightly bound $SiF_3^+-(CO_2)$ adduct, which converts the unreactive carbon dioxide into an electrophile able to carbonylate benzene efficiently. At low pressures the benzoyl cation is formed.

P. Cecchi, M. E. Crestoni, F. Grandinetti,*
V. Vinciguerra 2522–2524

Activation of Carbon Dioxide by Coordination with Cations in the Gas Phase: SiF_3^+-Mediated Coupling of CO_2 and Aromatic C–H Bonds

---

Even the metal–ligand coordination in the molecular square **1** is retained in the fragments generated by fast atom bombardment in the mass spectroscopic method described. In this example the $M-2\,OTf$ peak can be identified unequivocally owing to the peak separation of 0.5 m/z units in the isotopic distribution pattern.



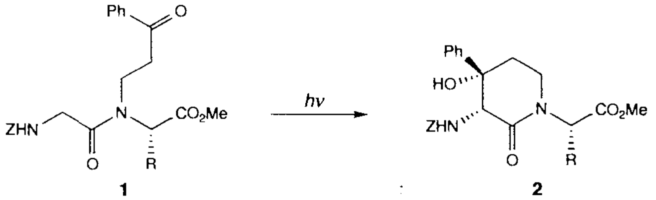
1

J. A. Whiteford, E. M. Rachlin,*
P. J. Stang* 2524–2529

Fast Atom Bombardment Mass Spectrometry for Characterizing Cationic Chelated Species

---

Never failing to surprise—radical reactions with amazing selectivity. Photocyclization of the modified dipeptides **1** proceeds via biradicals that cyclize to give the peptidomimetics **2**. Z = benzyloxycarbonyl.

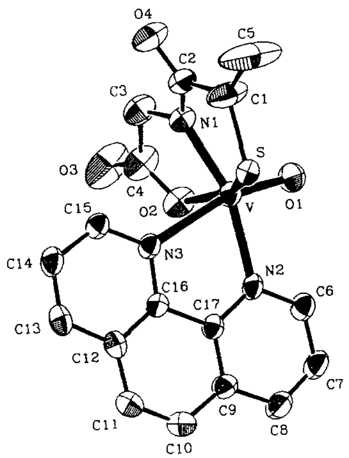


C. Wyss, R. Batra, C. Lehmann,
S. Sauer, B. Giese* 2529–2531

Selective Photocyclization of Glycine in Dipeptides

The sulfur atom, the nitrogen atom of the deprotonated amide functionality, and an oxygen atom of the carboxylate group are the ligating atoms of the dipeptide *N*-(2-mercaptopropionyl)glycine (H_3mpg) in its complex with the VO^{2+} center in the anion of **1** (shown on the right). This complex salt is accessible from $[VOCl_2(phen)]$ (phen = 1,10-phenanthroline) and H_3mpg in the presence of Et_3N. This study provides insight into the mode of binding of a dipeptide to an oxovanadium(IV) unit.

$Et_3NH[VO(mpg)(phen)]$ **1**

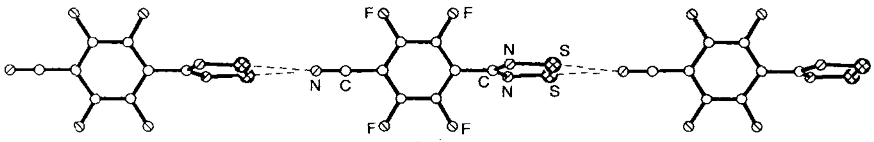


A. J. Tasiopoulos, A. T. Vlahos,
A. D. Keramidas, T. A. Kabanos,*
Y. G. Deligiannakis, C. P. Raptopoulou,
A. Terzis 2531–2533

Models of Oxovanadium(IV)–Protein Interactions: The First Oxovanadium(IV) Complexes with Dipeptides

---

Slow sublimation of the dithiadiazolyl radical 1 yields crystals of a new polymorph **1*β*** (orthorhombic, space group *Fdd*2). Below 36 K this new phase exhibits a spontaneous magnetic moment, which is described in terms of canted antiferromagnetism.

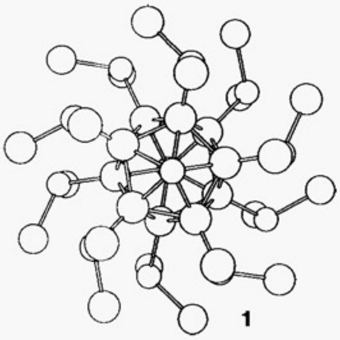


1

A. J. Banister, N. Bricklebank,
I. Lavender, J. M. Rawson,*
C. I. Gregory, B. K. Tanner,
W. Clegg, M. R. J. Elsegood,
F. Palacio 2533–2535

Spontaneous Magnetization in a Sulfur–Nitrogen Radical at 36 K

Complete halogenation of decamethyl-1,12-dicarba-*closo*-dodecaborane(12) under radical halogenation conditions affords the title compound **1** in high yields (structure shown along the C–C axis of the carborane framework). This molecule introduces an important new concept for the modular construction of structurally well-defined molecular systems.

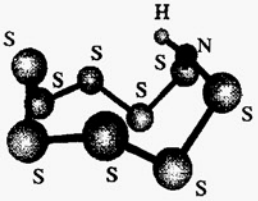

1

W. Jiang, C. B. Knobler,
M. F. Hawthorne* 2536–2537

Decakis(dichloromethyl)-1,12-dicarba-*closo*-dodecaborane(12): Camouflage of an Icosahedral Carborane by Using Bulky Functional Substituents

---

A surprisingly simple, systematic route to the title compounds is achieved by ligand transfer from [Cp_2TiS_7NH] to the difunctional sulfanes S_nCl_2 ($n = 1, 2$). This should provide new impetus to sulfur–nitrogen chemistry. Whereas the structure of S_9NH (shown on the right) is significantly different from that of S_{10}, the structure of S_8NH resembles that of S_9.



R. Steudel,* K. Bergemann,
J. Buschmann, P. Luger 2537–2539

Large Sulfur–Nitrogen Heterocycles: Preparation of the Sulfur Imides S_nNH ($n = 8, 9, 11$) and Structures of S_8NH and S_9NH

* Author to whom correspondence should be addressed

BOOKS

German versions of all reviews, communications, and highlights in this issue appear in the first November issue of *Angewandte Chemie*. The appropriate page numbers can be found at the end of each article and are also included in the Author Index on p. 2545.

All the Tables of Contents from 1995 onwards may be found on the WWW under **http://www.vchgroup.de**

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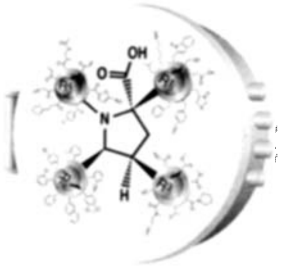
COVER PICTURE

The cover picture shows an everyday application of the combinatorial principle—the door of a safe! The four knobs of the combination lock are analogous to the four different groups R^1–R^4 attached to a small organic molecule. The illustration underlines the tremendous number of compounds possible by varying relatively few substituents. Combinatorial methods can provide access to every possible combination, and the correct solution provides access to a valuable target.



REVIEW

Contents

A numbers game or serious science? Many investigators are posing this question about the use of combinatorial chemistry in the search for new pharmaceuticals. It is undisputed, however, that this young and very rapidly developing area has attracted widespread international attention within a very short time. The authors give a comprehensive review and comment on current trends.

F. Balkenhohl,*
C. von dem Bussche-Hünnefeld,
A. Lansky, C. Zechel 2288–2337

Combinatorial Synthesis of Small Organic Molecules

CORRESPONDENCE

Contents

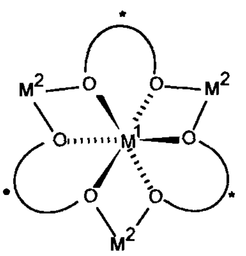
A coin with two sides: chemistry has both static and dynamic aspects. Yet in research in solid-state chemistry attention has focused almost exclusively on the former. Thus, the systematic investigation of the dynamic properties of materials such as the mechanisms of solid-state processes can be considered long overdue and essential for the development of strategies for rational synthesis and tailor-made materials.

R. Schöllhorn* 2338

Solid-State Chemistry: Restoring the Balance

HIGHLIGHT

In spite of relatively few examples, two-center catalysis is proving to be a clever and effective means of performing diverse reactions with both high regio- and enantioselectivity. A simple scheme allows classification of the efficient M^1-M^2–binol complexes **1** as well as the enzymes urease and carbon monoxide dehydrogenase. M^1 = La, Al,...; M^2 = Li, Na, K, ...



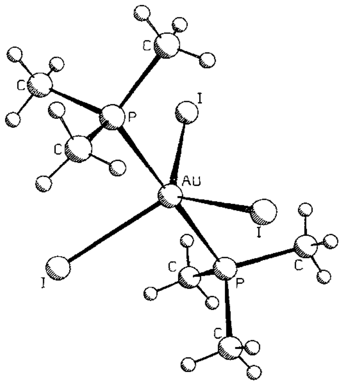
1

H. Steinhagen,
G. Helmchen* 2339–2342

Asymmetric Two-Center Catalysis—Learning from Nature

COMMUNICATIONS

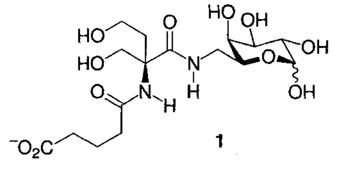
Unactivated gold powder readily reacts with Me_3EI_2 (E = P, As) in diethyl ether to form the planar complex $[AuI_3(AsMe_3)]$ and, surprisingly, the trigonal-bipyramidal complex $[AuI_3(PMe_3)_2]$ (structure shown on the right); the latter readily hydrolyzes to form $[(Me_3PO)_2H][AuI_2]$. The oxidation of this noble metal to Au^{3+} and the production of complexes of different stoichiometries and structures illustrates the oxidizing power and the subtlety of these Me_3EI_2 reagents.



S. M. Godfrey,* N. Ho, C. A. McAuliffe,*
R. G. Pritchard 2344–2346

The Oxidation of Gold Powder by Me_3EI_2 (E = P, As) under Ambient Conditions; Structures of $[AuI_3(PMe_3)_2]$, $[AuI_3(AsMe_3)]$, and $[(Me_3PO)_2H][AuI_2]$

Activities twice as good as those of sialyl Lewis^x are displayed by sialyl Lewis^x mimetics such as **1** which are made up of an amino acid, a galactose amine, and a carboxylate-bearing side chain.

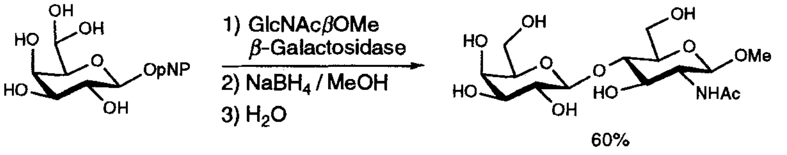


M. W. Cappi, W. J. Moree, L. Qiao,
T. G. Marron, G. Weitz-Schmidt,
C.-H. Wong* 2346–2348

The Synthesis of Novel 6-Amido-6-Deoxy-L-Galactose Derivatives as Potent Sialyl Lewis^x Mimetics

---

Two enzymes are used for the efficient synthesis of 6′-oxo-*N*-acetyl-D-lactosamine. Gal*β*OpNP, with the good *p*-nitrophenyl (pNP) leaving group, is first oxidized to the 6-oxo derivative with galactose oxidase. Subsequent transglycosylation with GlcNAc*β*OMe, catalyzed by *β*-galactosidase from *Bacillus circulans*, leads to the desired disaccharide in good yield [Eq. (a)].



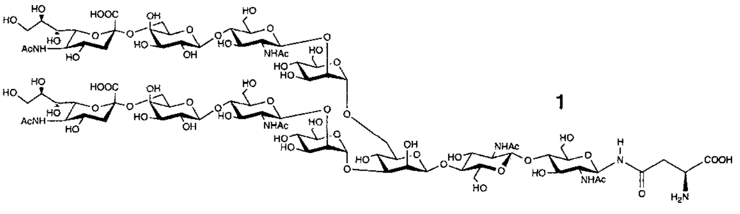
(a)

T. Kimura, S. Takayama, H. Huang,
C.-H. Wong* 2348–2350

A Practical Method for the Synthesis of *N*-Acetyl-D-lactosamine Derivatives by the Tandem Use of Galactose Oxidase and *β*-Galactosidase

---

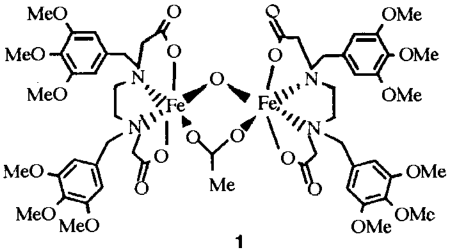
A partial structure of many glycoproteins, the complex undecasaccharide–asparagine conjugate **1** was obtained for the first time by total synthesis. Crucial to the synthesis was a combination of modern chemical and enzymatic methods, which reduced the overall number of steps and allowed efficient deprotonation.



C. Unverzagt* 2350–2353

Chemoenzymatic Synthesis of a Sialylated Undecasaccharide–Asparagine Conjugate

An excellent functionalized enzyme model for the active site of methane monooxygenase and ribonucleotide reductase is represented by the μ-acetato- and μ-oxo-bridged diiron complex **1**. Reaction with H_2O_2 or O_2 in the presence of ascorbate leads to hydroxylation of one phenyl ring to a phenol. This then coordindates to the metal center with formation of a mononuclear complex.



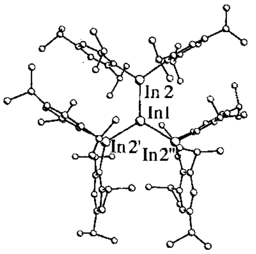
1

S. Ménage, J.-B. Galey, G. Hussler, M. Seité, M. Fontecave* 2353–2355

Aromatic Hydroxylation by H_2O_2 and O_2 Catalyzed by a μ-Oxo Diiron(III) Complex

---

Trigonal-planar coordination is seen for the indium center in $In(InTrip_2)_3$ (**1**) (Trip = 2,4,6-$i$$Pr_3C_6H_2$), the first indane with three unusually short bonds to indium substituents. The compound is obtained by the reduction of the diindane $Trip_2In{-}InTrip_2$ with lithium metal. In contrast, reduction of the aluminum and gallium analogs gives the $[Trip_2M{\cdots}MTrip_2]^-$ anions, which have a M–M π-bond order of 0.5.

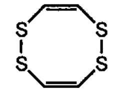


1

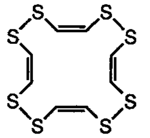
P. J. Brothers,* K. Hübler, U. Hübler, B. C. Noll, M. M. Olmstead, P. P. Power* 2355–2357

A New In_4 Cluster with Short In–In Bonds in Trigonal-Planar $In(InTrip_2)_3$

Tetrathiocin 1 and the tetramer 2 could be synthesized oxidatively from ethenedithiolate and were successfully characterized. Compound **2** with its cage structure can be considered as a new type of host molecule. It also forms from **1**, which has a twisted structure, in acetonitrile/chloroform.



1



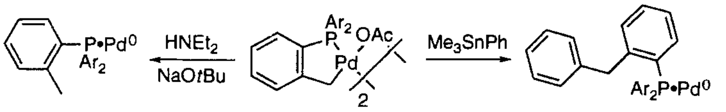
2

T. Shimizu, K. Iwata, N. Kamigata* 2357–2359

Crystal Structures and Properties of Cyclic Polyenes Possessing Disulfide Units

---

Pd^{II}/Pd^{IV} or Pd^{II}/Pd^0? The unusual Pd^{II} catalyst **1** was reduced to a Pd^0 complex by reaction with an amine and a base. β-Hydrogen elimination and subsequent C–H bond-forming reductive elmination generate a coordinated tris(o-tolyl)phosphane. The same palladium(II) metallacycle was reduced to Pd^0 in a cross-coupling reaction by C–C bond-forming reductive elimination to form coordinated $P(o\mathrm{Tol})_2(C_6H_4CH_2Ar)$. Thus, these compounds can react by a Pd^{II}/Pd^0-containing catalytic cycle.



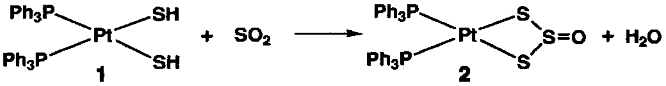
1

J. Louie, J. F. Hartwig* 2359–2361

A Route to Pd^0 from Pd^{II} Metallacycles in Amination and Cross-Coupling Chemistry

---

The platinium complex 1 is the first homogeneous catalyst that can be used in reactions that proceed analogously to the Claus process. The novel intermediate **2**, which contains a 2-oxotrisulfido chelating ligand, catalyzes the transformation of toxic H_2S into sulfur.

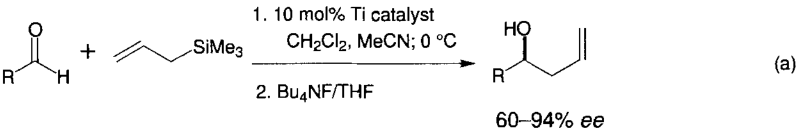


A. Shaver,* M. El-khateeb, A.-M. Lebuis 2362–2363

Homogeneous Catalysts for Claus Chemistry: The Preparation and Structure of *cis*-$[(PPh_3)_2PtS_3O]$, a Catalytically Active Intermediate

---

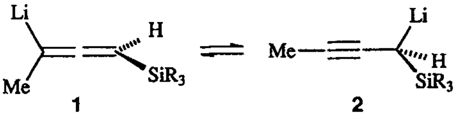
Unique reactivity is shown by the fluorotitanium complex obtained from TiF_4 and 1,1'-bi-2-naphthol. It is more reactive than the chloro-, bromo-, and alkoxytitanium complexes previously employed and catalyzes the enantioselective additions of allyltrimethylsilane to aldehydes [Eq. (a)], providing an alternative to known methods involving the corresponding organotin reagents.



D. R. Gauthier, Jr., E. M. Carreira* 2363–2365

Catalytic, Enantioselective Addition of Allylsilanes to Aldehydes: Generation of a Novel, Reactive Ti^{IV} Complex from TiF_4

Not one, but two structures are adopted by the metalation product of 1-triorganosilyl-2-butyne in solution. An equilibrium between the allenyllithium (**1**) and propargyllithium (**2**) reagents is rapidly established and has a free energy of activation ΔG^{+} of less than 4 kcal mol^{-1} at −150 °C.

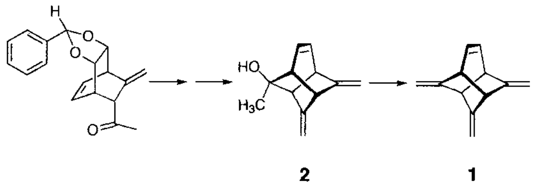


H. J. Reich,* J. E. Holladay 2365–2367

Structure of Silyl-Substituted Allenyl/Propargyllithium Reagents in Solution

---

The first $C_{12}H_{12}$ hydrocarbon with a central tricyclic skeleton and four double bonds (**1**) has been synthesized. In the most successful approach **2**, obtained from the corresponding ketone by treatment with MeLi, was transformed into the tetraene **1** by elimination of water under mild conditions with $(COCl)_2$/DMSO/NEt_3 (the Swern conditions).

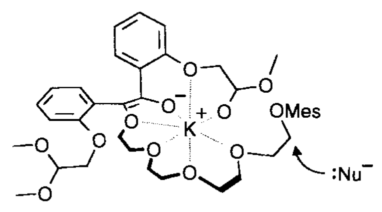


2 **1**

T. Herb, R. Gleiter* 2368–2369

2,7,9-Trimethylenetricyclo[4.3.0.0^{3,8}]-non-4-ene

Ring closure to the [15]crown-5 derivative is prevented in the reaction of an enediolate with tetraethyleneglycol dimesylate by participation of an acetal side chain (reaction intermediate depicted on the right). The attack of a second enediolate initiates the formation of the corresponding [30]crown-10 derivative in up to 50% yield.

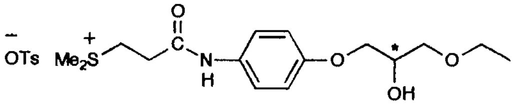


A. Merz,* O. Schneider,
L. Parkanyi 2369–2372

Side-Arm Participation in a Four-Component Template Synthesis of a [30]Crown-10 Derivative

---

Efficient enantiomeric resolution of the antiallergenic agent (±)-**ST**, which shows crystalline polymorphism, is accomplished by simple recrystallization. Both stable crystals of the racemic compound and metastable mixed crystals are formed, and the enantiomeric enrichment of the mother liquor virtually reaches 100% *ee*.



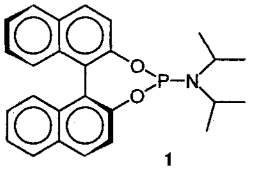
ST

T. Ushio, R. Tamura,* H. Takahashi,
N. Azuma, K. Yamamoto 2372–2374

Unusual Enantiomeric Resolution Phenomenon Observed upon Recrystallization of a Racemic Compound

---

Monodentate phosphorus amidites like 1 and $Cu(OTf)_2$ provide access to the first chiral complexes that catalyze the enantioselective conjugate addition of organozinc reagents to cyclic as well as acyclic enones. The ligand-accelerated process affords *β*-substituted ketones in excellent yields and with high *ee* values. Functional groups in the zinc reagent are tolerated.



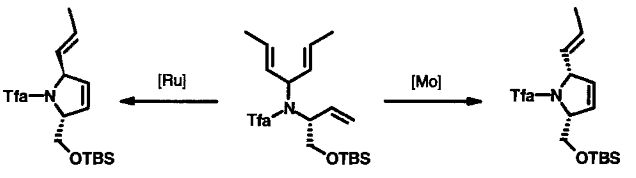
1

A. H. M. de Vries, A. Meetsma,
B. L. Feringa* 2374–2376

Enantioselective Conjugate Addition of Dialkylzinc Reagents to Cyclic and Acyclic Enones Catalyzed by Chiral Copper Complexes of New Phosphorus Amidites

---

The catalyst decides whether the *syn* or *anti* product is formed! In the cyclization of **1**, the ring-closing metathesis of two double bonds that are located at a chiral and a prochiral center leads to the α,α′-disubstituted pyrrolidine derivative **2** with viable diastereoselectivity. Tfa = trifluoroacetyl, [Ru] and [Mo] = Ru- and Mo-carbene complexes, respectively.

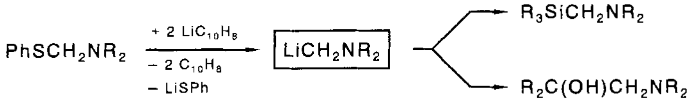


ent-anti-2* (88%, 92% *de*)** ***ent-1 ***ent-syn-2* (97%, 72% *de*)**

C. M. Huwe, J. Velder,
S. Blechert* 2376–2378

A Catalyst-Specific, Stereocontrolled Ring-Closing Metathesis

Compounds with the structural element -CH_2NR_2 are easily accessible from (phenylthiomethyl)amines by reductive C–S bond cleavage and subsequent addition or substitution (see below). One advantage of this shorter method than tin–lithium exchange is the ready availability of the starting materials, which need not be purified by chromatography.

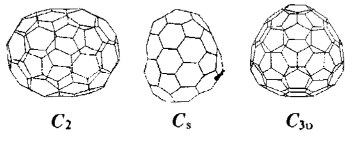


C. Strohmann,* B. C. Abele .. 2378–2380

Reductive Carbon–Sulfur Bond Cleavage: A Simple Pathway to Nonstabilized (Lithiomethyl)amines

---

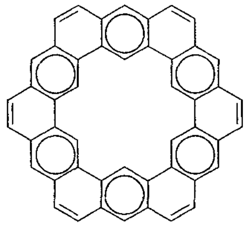
Endohedral fullerene compounds with isomeric carbon frameworks have been identified for the first time. The three stable isomers of $Tm^{2+}@C_{82}^{2-}$ were separated by HPLC, and characterized by cyclic voltammetry and by UV/Vis/NIR and ^{13}C NMR spectroscopy as probably having C_2, C_s, and C_{3v} symmetry (see picture).



U. Kirbach, L. Dunsch* 2380–2383

The Existence of Stable Tm@C_{82}-Isomers

Kekulene is indeed a "normal" aromatic molecule. This conclusion is reached in a theoretical study in which a number of calculated properties of kekulene and reference compounds such as benzene, phenanthrene, and 1,2:7,8-dibenzanthracene were compared. Structure **1** is the most apt description of this molecule, and claims of superaromaticity can finally be laid to rest.

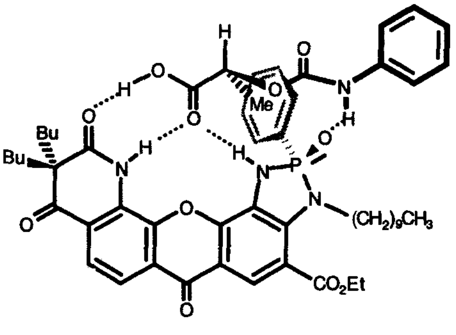


1 (benzenoid, D_{6h})

H. Jiao, P. von R. Schleyer* .. 2383–2386

Is Kekulene Really Superaromatic?

Simple chromatography using SiO_2 impregnated with (*S*)-4-chlorophenylcarbamoyllactic acid ((*S*)-**2**) can be used to separate the enantiomers of receptor **1** (R_f((*R*)-**1**/R_f((*S*)-**1**) = 0.8/0.1). The very large association constant of the more stable complex [(*R*)-**1**·(*S*)-**2**] (5.7×10^5 M^{-1}) was determined in a series of competitive NMR titrations with α-amino acid derivatives, which form less stable complexes with **1**.



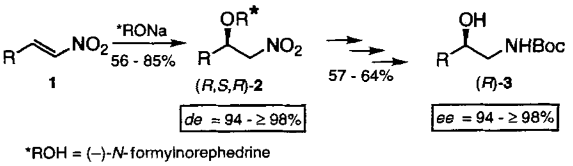
[(*R*)-**1**·(*S*)-**2**]

M. Martín, C. Raposo, M. Almaraz, M. Crego, C. Caballero, M. Grande, J. R. Morán* 2386–2388

Efficient Recognition of Chiral Carbamoyl-α-Hydroxyacids with a Cleft-Type Receptor

---

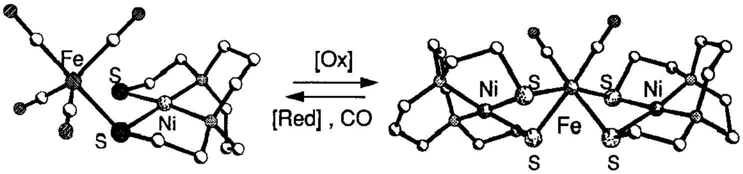
The asymmetric oxa-Michael addition of (−)-*N*-formylnorephedrine, a chiral oxygen nucleophile with a removable auxiliary, to (*E*)-nitroalkenes **1** permits the enantioselective synthesis of protected vicinal amino alcohols (*R*)-**3** with high enantiomeric excesses after reduction of the 1,4-adducts **2**. This new procedure opens an efficient entry to synthetic building blocks for natural products and drugs.



D. Enders,* A. Haertwig, G. Raabe, J. Runsink 2388–2390

Enantioselective Synthesis of Vicinal Amino Alcohols by Oxa-Michael Addition of (−)-*N*-Formylnorephedrine to Nitroalkenes

Stable and interconvertible are the Ni–Fe compounds **1** and **2** in which the *cis*-dithiolato sulfur atoms bind to the Fe^0–CO and Fe^{II}–CO complex fragments, respectively. Unlike the Ni–S distances, which are essentially independent of the oxidation state of the iron center and the denticity of the metallothiolato ligand, the Ni–Fe distances differ by 0.7 Å.



1 **2**

C.-H. Lai, J. H. Reibenspies,
M. Y. Darensbourg* 2390–2393

Thiolate-Bridged Nickel–Iron Complexes Containing both Iron(0) and Iron(II) Carbonyls

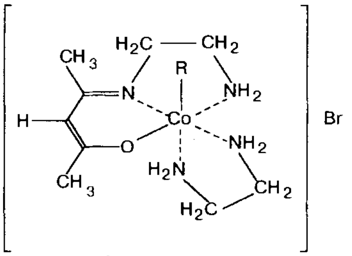
---

Activity comparable to that of noble metal catalysts is shown by the Mn-, Co-, or Fe-stabilized ZrO_2 catalysts for the low-temperature combustion of methane. The incorporation of the transition metal into the ZrO_2 bulk structure not only stabilizes the cubic (fluorite) modification, but also increases the reactivity of the lattice oxygen atoms drastically.

V. R. Choudhary,* B. S. Uphade,
S. G. Pataskar,
A. Keshavaraja 2393–2395

Low-Temperature Complete Combustion of Methane over Mn-, Co-, and Fe-Stabilized ZrO_2

Organocobalt(III) chelates with tridentate Schiff bases, in particular **1**, readily generate free radicals in mildly acidic (pH 5–7) solutions. These compounds display certain antitumor action and substantially enhance the efficacy of chemo-, radio-, and thermotherapy in cancer treatment.



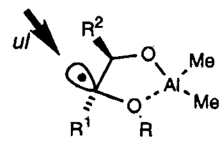
1, R = Et, *i*Pr

M. Vol'pin, I. Levitin,*
S. Osinsky 2395–2396

New Course in the Search for Antitumor Agents: The Use of pH-Dependent Sources of Reactive Radicals

---

The strong pyramidalization of the radical intermediates (shown on the right) is the reason why *anti* Cram chelation products are obtained in the reduction of 1,2-dialkyl-1,2-dioxy-substituted radicals, even though a chelate is formed. The main diastereoisomer results from an attack *syn* to the large substituent R^2. $R^1 = CH_2{-}CH{=}CH{-}CH_2SnBu_3$, R^2 = *t*Bu, R = *para*-methoxyphenyl.

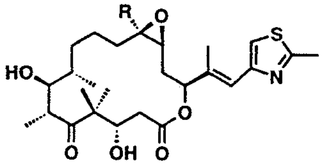


M. Gerster, K. Schenk,
P. Renaud* 2396–2399

Stereoselectivity in Reactions of 1,2-Dioxy-Substituted Radicals under Chelation Control: An Unexpected Result

---

The same mechanism as taxol but a completely different, simpler structure is displayed by the recently described epothilones A and B. These features immediately attracted the attention of synthetic chemists. An approach to the macrocyclic framework of the epothilones has now been devised through use of ring-closing metathesis with the Grubbs catalyst $[RuCl_2(CHPh)\{P(C_6H_{11})_3\}_2]$.



epothilone A (R = H)
epothilone B (R = CH_3)

K. C. Nicolaou,* Y. He, D. Vourloumis,
H. Vallberg, Z. Yang 2399–2401

An Approach to Epothilones Based on Olefin Metathesis

---

* Author to whom correspondence should be addressed

BOOKS

German versions of all reviews, communications, and highlights in this issue appear in the second October issue of *Angewandte Chemie*. The appropriate page numbers can be found at the end of each article and are also included in the Author Index on p. 2409.

All the Tables of Contents from 1995 onwards may be found on the WWW under **http://www.vchgroup.de**

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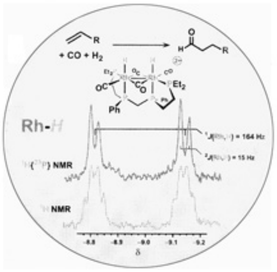
by H. tom Dieck
in CHEMISTRY

COVER PICTURE

The cover picture shows a novel rhodium(II) carbonyl hydrido complex, which is proposed as the active catalyst for regioselective hydroformylation, as well as sections from the 500 MHz ^{1}H NMR and $^{1}H\{^{31}P\}$ NMR spectrum of this compound in situ. The unusually large coupling constant of 164 Hz is not attributed to a *trans*-^{2}J(P,H) coupling, but to a ^{1}J(Rh,H) coupling. More about the behavior of this dinuclear rhodium complex is reported by Stanley et al. on p. 2253ff.



REVIEWS

Contents

Vertebrate genes can often be identified based on analogies to *Drosophila* genes. This homology has been important in advancing the understanding of vertebrate development on a genetic level, and indicates that a basic body plan is common to the vertebrates and arthropods. Comparisons of patterning in flies and vertebrates have been successful most recently in studies of zebra fish.

C. Nüsslein-Volhard* 2176–2187

The Identification of Genes Controlling Development in Flies and Fishes (Nobel Lecture)

Establishing inbred lines from single flies carrying mutagenized chromosomes was the strategy behind the mutagenesis experiments conducted by E. Wieschaus and C. Nüsslein-Volhard in Heidelberg. Within two generations, homozygous flies were obtained whose development was compared with that of their heterozygous siblings. The results from 27000 inbred lines led to first indications of the causes of early morphological changes in embryogenesis.

E. Wieschaus* 2188–2194

From Molecular Patterns to Morphogenesis—The Lessons from Studies on the Fruit Fly *Drosophila* (Nobel Lecture)

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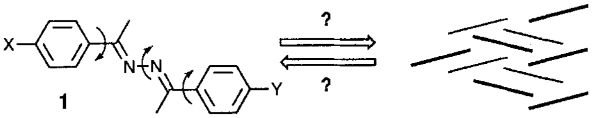
HIGHLIGHTS

Despite recent progress, true crystal engineering remains an elusive goal. Subtle differences in energy, as in the rotamers of **1**, may cause great differences in solid-state structures, and the influence of a crystalline environment on molecular parameters is even less well-understood. Successes and problems in the studies of the structures of molecular crystals are discussed.



J. J. Wolff* 2195–2197

Crystal Packing and Molecular Geometry

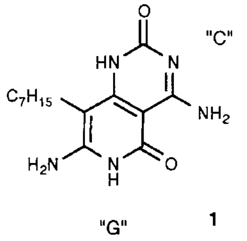
The two universally existing ribosomal elongation factors ET-Tu and EF-G are archetypes of the large family of G-proteins, which regulate a plethora of processes in the cell according to a basic scheme. In the past few years the crystal structures elucidated for various conformations of the elongation factors have provided exciting insights into the functions of G-proteins and into the mechanism of protein biosynthesis.

K. H. Nierhaus* 2198–2201

The Tricks of Ribosomal Elongation Factors

COMMUNICATIONS

Infinite channels with a diameter 10.5 Å are formed by the DNA-base hybrid **1** in the solid state. These channels arise because **1** specifically communicates the hydrogen bonding codes of the nucleobases cytosine and guanine ("C" and "G") to unambiguously assemble hexagonal, macrocyclic aggregates $\mathbf{1}_6$, which overlap in the crystal.



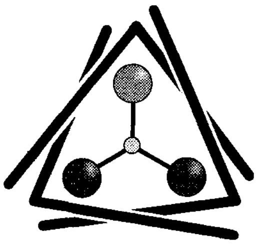
1

M. Mascal,* N. M. Hext,
R. Warmuth, M. H. Moore,
J. P. Turkenburg 2204–2206

Programming a Hydrogen-Bonding Code for the Specific Generation of a Supermacrocycle

---

Reminiscent of a windmill, the novel triple-helicate $[(Fe^{III})_2Fe^{II}OL_3]$ **1**, a neutral oxo-centered mixed-valence complex, is formed in a one-pot reaction by self-assembly. The pentadentate ligand L acts in a tritopic fashion and connects the three iron ions in a triangular plane. At the center of **1** lies a μ_3-O^{2-} ion. The structural similarity of **1** with trinuclear carboxylatoiron complexes is striking.



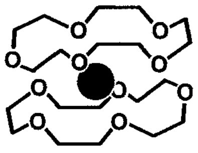
1

R. W. Saalfrank,* S. Trummer,
H. Krautscheid, V. Schünemann,
A. X. Trautwein, S. Hien,
C. Stadler, J. Daub 2206–2208

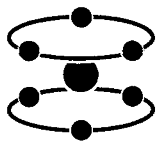
A Neutral, Triple-Helical, Trinuclear, Oxo-Centered Mixed-Valence Iron Complex

---

New blood for crown ether chemistry! Beside the well-known organocrown ether sandwich complexes **1** there now exist topologically equivalent metallacrown ether complexes **2**. These metallasandwich complexes are generated in a one-pot reaction by spontanous self-assembly and in one case have been unambiguously characterized by a crystallographic structure analysis.



1

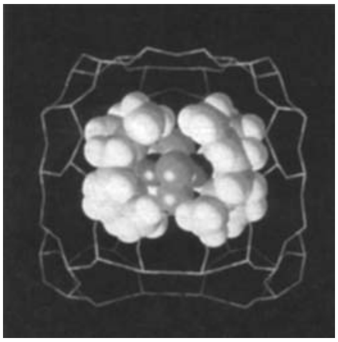


2

R. W. Saalfrank,* N. Löw, F. Hampel,
H.-D. Stachel 2209–2210

The First Metallacrown Ether Sandwich Complex

Adsorption of a cyclic amine ligand into a Mn-exchanged faujasite zeolite results in the formation of the corresponding amine–Mn complexes in the cavities of the zeolite. These "amine–Mn zeolites" are novel catalysts for the highly selective epoxidation of numerous olefins with H_2O_2. A computer model of a possible catalytically active species, a Mn^{III}/Mn^{IV} complex with bridging oxygen ligands, is shown on the right.

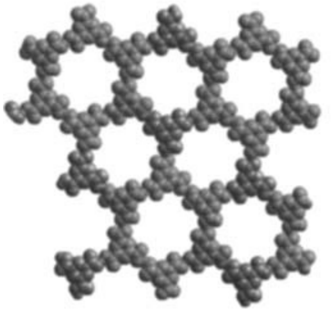


D. E. De Vos, J. L. Meinershagen, T. Bein* 2211–2213

Highly Selective Epoxidation Catalysts Derived from Intrazeolite Trimethyltriazacyclononane–Manganese Complexes

---

The trigonal symmetry of trimesic acid (1,3,5-benzenetricarboxylic acid) [H_3TMA] is exploited in the generation of honeycomb grid solids that eschew interpenetration. The structures of [*N*,*N*-dicyclohexylammonium]$_3$[TMA]·*x*MeOH and [*N*,*N*-dimethylammonium]$_{12}$[H_3TMA] · [H_2TMA^-]$_3$ · [$HTMA^{2-}$]$_3$ · [TMA^{3-}] reveal, relative to H_3TMA, expanded and contracted honeycomb grids having internal cavities with effective diameters of 12.7 and 10.4 Å, respectively.



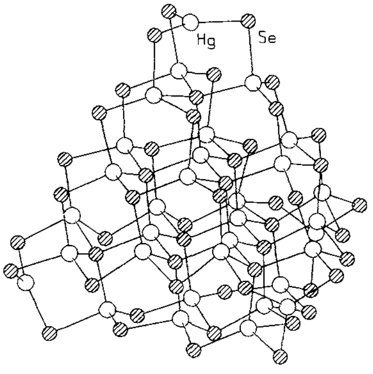
R. E. Melendez, C. V. K. Sharma, M. J. Zaworotko,* C. Bauer, R. D. Rogers 2213–2215

Toward the Design of Porous Organic Solids: Modular Honeycomb Grids Sustained by Anions of Trimesic Acid

---

Red crystals of **1** were obtained by treatment of Hg^{II} salts with PhSeSiMe$_3$ in organic solvents. Depending on the starting materials and conditions, **1** crystallizes either in the cubic space group *P*23 or in the trigonal space group *P*3$_2$. The diameter of the cluster that crystallizes in the cubic space group is about 2400 pm (the framework of the $Hg_{32}Se_{50}$ cluster is depicted on the right). In addition, the other title compounds were prepared and isolated in the form of colorless crystals.

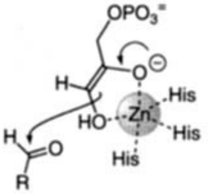
[$Hg_{32}Se_{14}(SePh)_{36}$] **1**



S. Behrens, M. Bettenhausen, A. C. Deveson, A. Eichhöfer, D. Fenske,* A. Lohde, U. Woggon 2215–2218

Synthesis and Structure of the Nanoclusters [$Hg_{32}Se_{14}(SePh)_{36}$], [$Cd_{32}Se_{14}(SePh)_{36}$-$(PPh_3)_4$], [$P(Et)_2(Ph)C_4H_8OSiMe_3$]$_5$-[$Cd_{18}I_{17}(PSiMe_3)_{12}$], and [$N(Et)_3C_4H_8OSiMe_3$]$_5$[$Cd_{18}I_{17}(PSiMe_3)_{12}$]

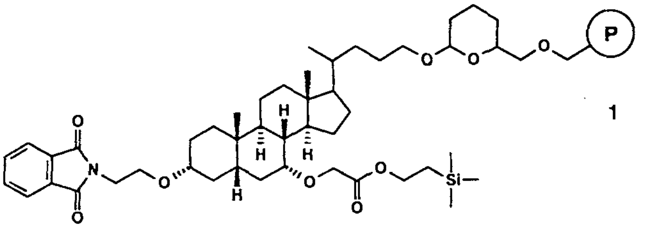
Chelation of the *cis*-enediolate form of dihydroxyacetone phosphate (see picture on the right) is the key step in the mechanism of action of Zn^{2+}-dependent aldolases. This proposal is derived from inhibition studies with model compounds for both ground and transition states and from an X-ray structure determination of a protein–ligand complex. The high degree of asymmetric induction occurring at both termini of the newly formed C–C bond can now be explained.



W.-D. Fessner,* A. Schneider, H. Held, G. Sinerius, C. Walter, M. Hixon, J. V. Schloss* 2219–2221

The Mechanism of Class II, Metal-Dependent Aldolases

A complete *β*-turn can be mimicked by the tetrapeptide mimetic **1**, which can thus be built into peptides with unambiguous directionality. Mimetic **1** was prepared from chenodeoxycholic acid, and is very interesting as a building block for compound libraries of *β*-turn mimics. Ⓟ = polymer support.

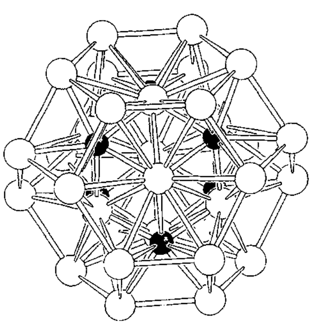


1

G. Wess,* K. Bock, H. Kleine, M. Kurz, W. Guba, H. Hemmerle, E. Lopez-Calle, K.-H. Baringhaus, H. Glombik, A. Enhsen, W. Kramer 2222–2224

The Design and Synthesis of a Scaffold for Combinatorial Chemistry Based on Bile Acid

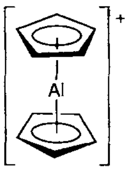
Delight from degradation and decomposition. The aesthetically pleasing $[Ni_{32}C_6(CO)_{36}]^{6-}$ carbide cluster was obtained by the degradation of $[Ni_{38}C_6(CO)_{42}]^{6-}$ under a CO atmosphere and by the thermal decomposition of $[Ni_{10}C_2(CO)_{16}]^{2-}$. Its structure, the metal–carbon core of which is shown on the right, consists of an extended fragment of the $Cr_{23}C_6$ lattice stabilized in a shell of edge-bridging carbonyl ligands.



F. Calderoni, F. Demartin, M. C. Iapalucci, G. Longoni* 2225–2226

Synthesis and Crystal Structure of the $[Ni_{32}C_6(CO)_{36}]^{6-}$ Hexaanion: An Extended Fragment of the $M_{23}C_6$ Lattice Stabilized in a Shell of Edge-Bridging Carbonyl Ligands

One of the last hitherto unknown simple metallocenes, the aluminocenium cation $[Al(\eta\text{-}C_5H_5)_2]^+$ **1**, is readily accessible from $[AlCp_2Me]$ and $B(C_6F_5)_3$. The spectroscopic data are consistent with a metallocene structure. The complex is a highly efficient initiator for the carbocationic polymerization of isobutene and the industrially important copolymerization of isobutene and isoprene.

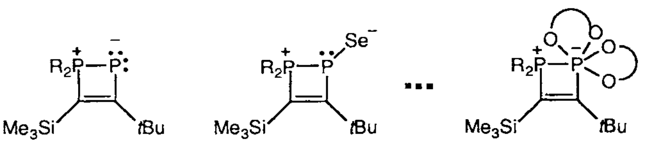


1

M. Bochmann,*
D. M. Dawson 2226–2228

The Aluminocenium Cation $[Al(C_5H_5)_2]^+$: A Highly Effective Initiator for the Cationic Polymerization of Isobutene

Without destruction of the four-membered ring skeleton, the σ^2-phosphorus atom of a $1\sigma^4,2\sigma^2$-diphosphete can extend its coordination number up to six (as the series below shows)!



M. Sanchez, R. Réau, F. Dahan,
M. Regitz, G. Bertrand* 2228–2230

From $1\sigma^4,2\sigma^2$ to $1\sigma^4,2\sigma^n$-Diphosphetes (n = 3–6): The Surprising Persistence of the P–P bond

The surface polarity can be regulated for amorphous, microporous Si/Ti mixed-oxide catalysts during their variable, single-step, preparation procedure (sol–gel). In contrast to zeolites the surface of these catalysts is thus tunable to the polarity of the substrate. Oxidations of various substrates can be catalyzed selectively not only with hydrogen peroxide but also with organic peroxides; the highest conversions are obtained with catalysts that have optimized surface polarity.

S. Klein, W. F. Maier* 2230–2233

Microporous Mixed Oxides—Catalysts with Tunable Surface Polarity

Purer than the driven snow. $Ce_2@C_{80}$ has been isolated with a purity of >99% by an efficient extraction procedure, followed by an HPLC separation. The X-ray photoelectron spectrum of $Ce_2@C_{80}$ suggests that both Ce atoms inside the cage occur as Ce^{3+}, in agreement with the results of a recent ab initio calculation.

J. Ding, S. Yang* 2234–2235

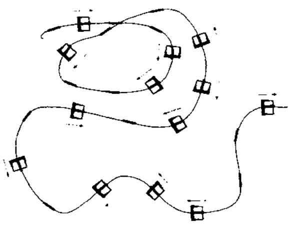
Isolation and Characterization of the Dimetallofullerene $Ce_2@C_{80}$

The inherent stabilizing effects of lone pair substituents from the first five rows of the periodic table on carbocations depend primarily on the *group* rather than on the *period*, judging from high-level ab initio computations (QCISD(T)/DZ++PP//MP2(fc)/DZ+P). When planarity is imposed on the pnictogen compounds, the stabilization energies from group 15 substituents are almost constant (ca. 95 kcal mol^{-1} from N to Sb, based on CH_3^+) and exceed the stabilization energies of chalcogens (60–66 kcal mol^{-1}, O<S≈Se<Te) and halogens (18–38 kcal mol^{-1}, F<Cl≈Br<I).

J. Kapp, C. Schade, A. M. El-Nahasa,
P. von R. Schleyer* 2236–2238

Heavy Element π Donation Is Not Less Effective

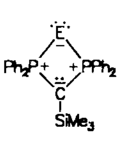
The movement of cyclophane rings along polymer chains may be appropriately described in terms of threading, passage along the thread, and unthreading (see picture). An NMR study of this shows that the molecules need to queue up in order to escape from the complexing polymer chain.



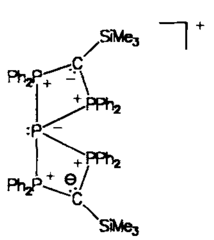
P. E. Mason, I. W. Parsons,*
M. S. Tolley 2238–2241

The First Demonstration of Molecular Queuing in Pseudo[*n*]polyrotaxanes: A Novel Variant of Supramolecular Motion

The first triphosphete 1a and its arsenic analog **1b** are the products of the reactions of PCl_3 and $AsCl_3$, respectively, with Li[C(PPh$_2$)$_2$(SiMe$_3$)]. The side product Ph$_2$(Cl)P=C(PPh$_2$)(SiMe$_3$) **2** reacts further with **1a** and $NaBPh_4$ by chloride abstraction to yield the spirocyclic ten-electron cation **3** with a pseudo-trigonal-bipyramidal PP_4 skeleton.



1a: E = P
1b: E = As

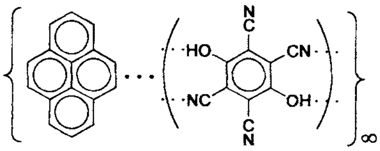


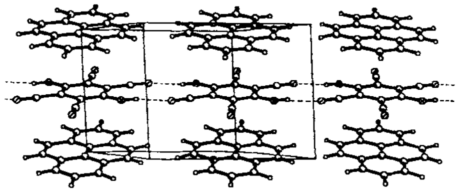
3

H. H. Karsch,* E. Witt,
F. E. Hahn 2242–2244

A Triphosphete and a Spirocyclic Cation with a PP_4 Skeleton and a 10e Spiro P Atom

Novel aspects for new materials are uncovered in the structures of donor/acceptor complexes in hydrogen-bonded networks. Three examples are presented: the herringbone pattern of mixed-stack donors and acceptors can be planarized, the hydrogen-bonded network can be stretched by included hydrate molecules to accommodate larger π-donors (see below), and the donor/acceptor function can be swapped by proton exchange.

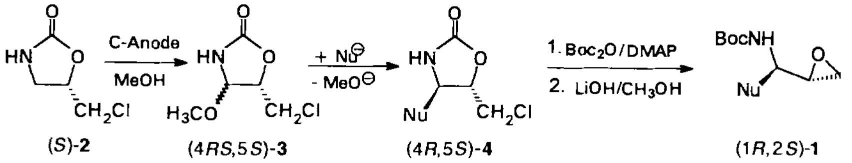




H. Bock* W. Seitz, M. Sievert,
M. Kleine, J. W. Bats 2244–2246

Donor/Acceptor Complexes in Hydrogen-Bonded Networks: pH-Dependent Self-Organization

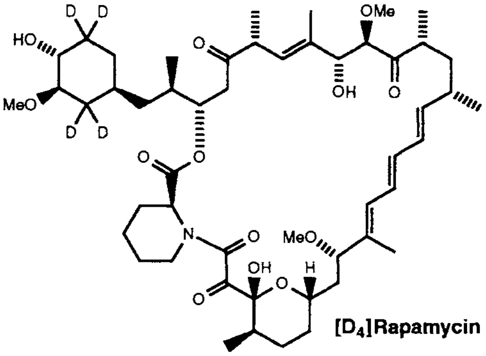
Anodic oxidation of (5*S*)- and (5*R*)-**2** provides (4*RS*,5*S*)- and (4*RS*,5*R*)-5-chloromethyl-4-methoxyoxazolidin-2-one **3**, respectively, in good yields. These are chiral cationic amidoalkylation reagents and, through diastereoselective nucleophilic methoxy group exchange, afford variably functionalized enantiomerically pure amino alcohols **4** as well as 1-substituted 2,3-epoxypropylamines **1**, which are precursors for peptidomimetics.



K. Danielmeier, K. Schierle,
E. Steckhan* 2247–2248

A New Chiral, Cationic β-Amino Alcohol Equivalent: A Variable Approach to Enantiomerically Pure Building Blocks for Hydroxyethylene Isosters

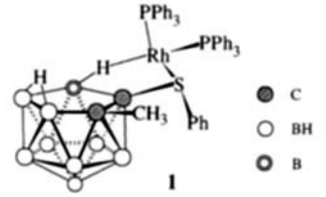
A remarkably high level of incorporation is observed when 2,2,5,5-tetradeutero-3,4-dihydroxycyclohexanecarboxylic acid is fed to the rapamycin-producing organism. Intriguingly, however, analysis of the gene sequence for the rapamycin polyketide synthase has suggested that the free acid may not normally be involved in rapamycin biosynthesis.



P. A. S. Lowden, G. A. Böhm,
J. Staunton,* P. F. Leadlay 2249–2251

The Nature of the Starter Unit for the Rapamycin Polyketide Synthase

Hydrogenation of 1-hexene is eight fimes faster with the rhodacarborane complex **1** than with [RhCl(PPh$_3$)$_3$]. The sulfur atom bound to the open face favors the interaction of the rhodium center with the more active B–H vertices situated on this face.

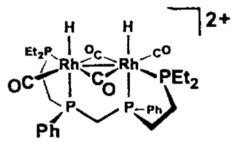


1

F. Teixidor, M. A. Flores, C. Viñas,*
R. Kivekäs, R. Sillanpää 2251–2253

[Rh(7-SPh-8-Me-7,8-$C_2B_9H_{10}$)(PPh$_3$)$_2$]: A New Rhodacarborane with Enhanced Activity in the Hydrogenation of 1-Alkenes

The catalytically active complex in the homogeneously catalyzed, regioselective hydroformylation is possibly the dinuclear complex dication **1**. The ^1J(Rh,H) coupling constant of 164 Hz is the largest such value ever reported and may be a distinctive marker for dinuclear Rh^{II} complexes with terminal hydrido ligands.

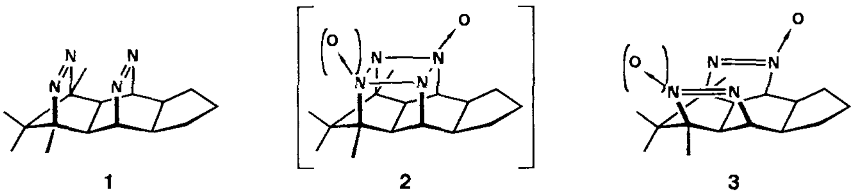


1

R. C. Matthews, D. K. Howell, W.-J. Peng, S. G. Train, W. D. Treleaven, G. G. Stanley* 2253–2256

Bimetallic Hydroformylation Catalysis: In Situ Characterization of a Dinuclear Rhodium(II) Dihydrido Complex with the Largest Rh–H NMR Coupling Constant

In the bisdiazene 1 and its N-oxides the two synperiplanar chromophores are fixed in so far the "best" stereochemical arrangement for $[2_\pi + 2_\pi]$ photocycloaddition. The formation of metathesis isomers **3** in the case of the oxides is taken as evidence for the intermediacy of the respective tetraazetidine oxides **2**.

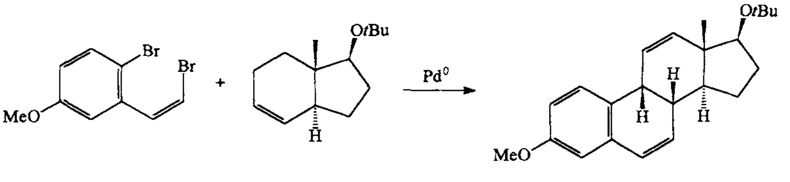


1 2 3

K. Exner, D. Hochstrate, M. Keller, F.-G. Klärner, H. Prinzbach* 2256–2259

Proximate, Synperiplanar Diazene/Diazene Substrates: N=N/N=NO and ON=N/N=NO Photometathesis Reactions

By means of a double Heck reaction the pharmacologically interesting estrapentaene **3** can be synthesized regio- and stereoselectively from (*Z*)-(2-bromoethenyl)-bromobenzene (**1**) and the indene derivative **2**. A variety of novel steroids can be obtained by variation of the benzene and indene components and subsequent functionalization.

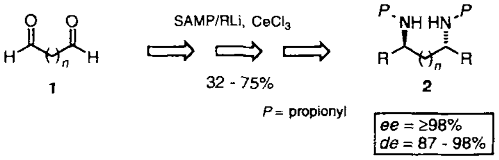


1 2 3

L. F. Tietze,* T. Nöbel, M. Spescha 2259–2261

Stereoselective Synthesis of Steroids with the Heck Reaction

The nucleophilic 1,2-addition of organocerium compounds to SAMP-hydrazones of dialdehydes **1** is the key step for the stereoselective synthesis of N-propionyl-protected, C_2-symmetric diamines **2**. Because the nucleophiles and dialdehydes can be varied, this method offers a flexible, highly diastereo- and enantioselective synthetic pathway to this important class of compounds.



D. Enders,* M. Meiers 2261–2263

Diastereo- and Enantioselective Synthesis of C_2-Symmetric, Protected 1,*n*-Diamines from Dialdehydes

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* Author to whom correspondence should be addressed

BOOKS

German versions of all reviews, communications, and highlights in this issue appear in the first October issue of *Angewandte Chemie*. The appropriate page numbers can be found at the end of each article and are also included in the Author Index on p. 2269.

SERVICES

All the Tables of Contents from 1995 onwards may be found on the WWW under **http://www.vchgroup.de**

The following reviews will appear in future issues:

Combinatorial Synthesis of Small Organic Molecules
F. Balkenhohl, C. von dem Bussche-Hünnefeld, A. Lansky, and C. Zechel

New Developments in the Chemistry of Low-Valent Titanium
A. Fürstner and B. Bogdanovic

Novolak-Diazoquinone Resists: The Imaging Systems of the Computer Chip
A. Reiser, H.-Y. Shih, T.-F. Yeh, and J.-P. Huang

What Can We Learn from Molecular Recognition in Protein–Ligand Complexes for the Design of New Drugs?
H.-J. Böhm and G. Klebe

Enantioselective Protonation of Enolates and Enols
C. Fehr

Self-Regeneration of Stereocenters (SRS)—Applications, Limitations, and Abandonment of a Synthetic Principle
D. Seebach, A. R. Sting, M. Hoffmann

Erich Hückel, Pioneer of Organic Quantum Chemistry: Reflections on Theory and Experiment
J. A. Berson

Biosynthesis of Vitamin B_1 (Thiamin): An Instance of Biochemical Diversity
I. D. Spenser, R. L. White

Chiral Recognition in π Complexes of Alkenes, Aldehydes, and Ketones with Transition Metal Lewis Acids; Development of a General Model for Enantioface Binding Selectivities
J. A. Gladysz, B. J. Boone

Selective Syntheses with Organocopper Reactions
N. Krause, A. Gerold

Unifying the Current Data on the Mechanism of Cleavage-Transesterification of RNA
E. V. Anslyn, D. M. Perreault

Chemical Applications of ZEKE Spectroscopy
K. Müller-Dethlefs, E. W. Schlag

On the Trail of Xanthates: Some New Chemistry from an Old Functional Group
S. Z. Zard

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CHEMISTRY

A EUROPEAN JOURNAL

1996
2/10

CEUJED 2 (10) 1189-1344 (1996) · ISSN 0947-6539 · Vol. 2 · No. 10 · October 1996

CONCEPTS

FULL PAPERS

Chemistry—A European Journal may be found after page 2270
with separate pagination and full details of its table of contents.

ANGEWANDTE CHEMIE

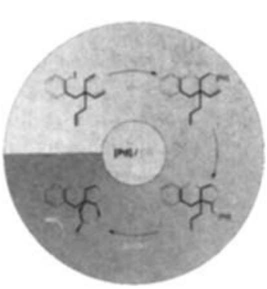
A Journal of the
Gesellschaft
Deutscher Chemiker

International Edition in English

1996
35/18
Pages 2005–2160

COVER PICTURE

The cover picture shows the palladium-catalyzed cyclization cascade of an iodotriene in the presence of CO in which "living" organopalladium species are formed as intermediates. Remarkably, this reaction succeeds with terminal alkenes that usually undergo β-dehydropalladation in the Heck reaction. E. Negishi et al. report more about this first cascade-type acylpalladation yielding polycycles with an angular mode of fusion on p. 2125ff. In the reaction shown seven C–C bonds are formed in one step.



REVIEWS

Contents

Two and sometimes even three metal ions are essential for the activity of many enzymes that catalyze the hydrolysis of phosphate ester and amide bonds. In addition to many mononuclear metallohydrolases, a number of metalloenzymes have been structurally characterized in which the active sites contain two adjacent metal ions that permit the transfer of phosphoryl and acyl groups. These studies provide detailed insight into the chemistry of two-metal ion catalysis—an important step towards the design of new artificial catalysts.

N. Sträter, W. N. Lipscomb,*
T. Klabunde, B. Krebs* 2024–2055

Two-Metal Ion Catalysis in Enzymatic Acyl- and Phosphoryl-Transfer Reactions

---

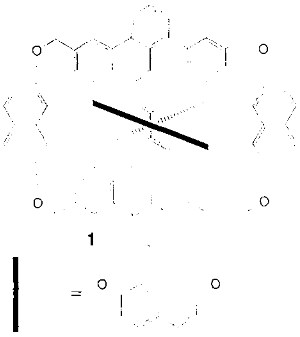
The efficiency of a demanding synthesis is often determined by the combination of protecting groups employed. Tried-and-true protecting groups are briefly presented here, including those that can be cleaved with acids, bases, fluoride ions, oxidation, reduction, light, and enzymes. Examples from published syntheses outline general themes and tactics for the development of successful protecting group strategies.

M. Schelhaas,
H. Waldmann* 2056–2083

Protecting Group Strategies in Organic Synthesis

HIGHLIGHTS

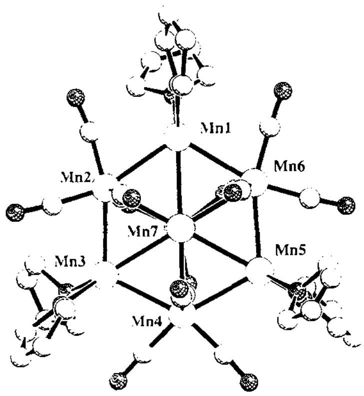
A cocktail of imaginative synthetic approaches, unique conformational behavior and analysis, unusual spectroscopic properties, and asymmetric synthesis, all liberally spiced with an assortment of intriguing structures (like **1**), is served up to illustrate recent advances in the diverse field of cyclophane chemistry. Cyclophanes can be auxiliaries in asymmetric synthesis and perhaps also starting materials for fullerenes.



G. J. Bodwell* 2085–2088

The New Inductees in the "Hall of Phane" No Phane, No Gain

Direct linkage of complex fragments of the classical Werner-type with metal carbonyl complex fragments characterizes a novel type of open-shell transition metal cluster, for which the term xenophilic has been proposed. These polynuclear complexes may display new metal frameworks with nonbridged metal–metal bonds; the structure of such a fragment ([Mn$_7$(thf)$_6$(CO)$_{12}$]$^-$) is depicted on the right.

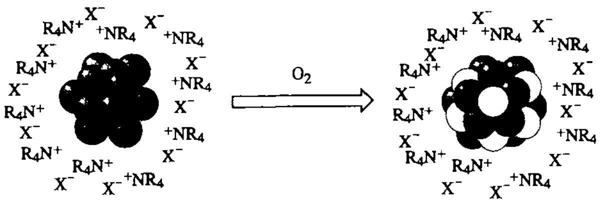


L. H. Gade* 2089–2090

"Strangelove" in Cluster Chemistry: A New Class of Open-Shell Transition Metal Clusters

COMMUNICATIONS

Complete oxidation without formation of bulk CoO results when cobalt clusters stabilized with R$_4$N$^+$X$^-$ are exposed to O$_2$. Since the resulting soluble, nanostructured cobalt(II) oxide clusters (idealized representation below; dark spheres: metal atoms; light spheres: oxygen atoms; R = C$_8$H$_{17}$) do not penetrate very far into the pores of Al$_2$O$_3$ pellets, unlike the Co clusters, these materials are potential shell catalysts.

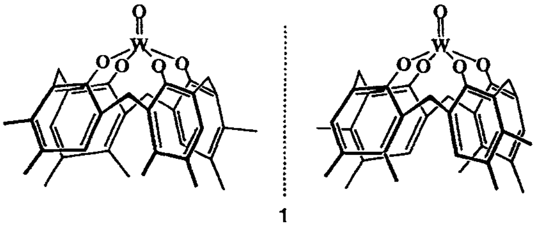


M. T. Reetz,* S. A. Quaiser, M. Winter, J. A. Becker, R. Schäfer, U. Stimming, A. Marmann, R. Vogel, T. Konno 2092–2094

Nanostructured Metal Oxide Clusters by Oxidation of Stabilized Metal Clusters with Air

---

Complexation with dichlorotungsten or oxotungsten groups locks chiral calix[4]arenes into rigid cone conformations. The resulting chiral metallocalix[4]arenes such as **1** (picture shows both enantiomers) have been resolved for the first time and are potential building blocks for new materials and supramolecular catalysts.

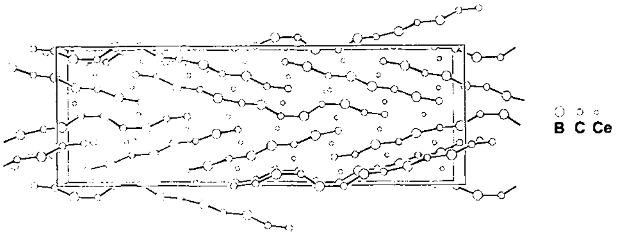


1

B. Xu, P. J. Carroll, T. M. Swager* 2094–2097

Chiral Metallocalix[4]arenes: Resolution by Diastereomeric Tungsten(VI) Alkoxides

B_xC_y cumulene-like chains with up to 13 atoms can be stabilized in compounds such as $Ce_{10}B_9C_{12}$ (see picture). In a first approximation the bonding between the metal and the nonmetal atoms can be considered as ionic (for instance, $(Ce^{1.7+})_{10}(B_4C_4)^{8-}(B_5C_8)^{9-}$).

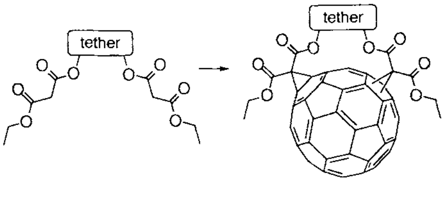


D. Ansel, J. Bauer,* F. Bonhomme,
G. Boucekkine, G. Frapper, P. Gougeon,
J.-F. Halet,* J.-Y. Saillard,*
B. Zouchoune 2098–2101

Boron–Carbon Chains Stabilized in Rare Earth Metallic Frameworks

---

A versatile and simple method provides access to covalent bisadducts of C_{60} with high regio- and diastereoselectivity. Starting from optically pure bis(malonate) derivatives and C_{60}, a double Bingel reaction afforded optically active *cis*-3 bisadducts (*ee* > 97%), whose chirality results exclusively from the addition pattern.

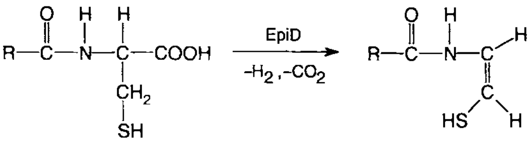


J.-F. Nierengarten, V. Gramlich,
F. Cardullo, F. Diederich* 2101–2103

Regio- and Diastereoselective Bisfunctionalization of C_{60} and Enantioselective Synthesis of a C_{60} Derivative with a Chiral Addition Pattern

---

A key player in the biosynthesis of epidermin, the novel enzyme EpiD converts peptidyl cysteines into thioenols [Eq. (a)]. The thioenols are unstable and decompose within hours. The oxidative decarboxylation of a ^{13}C-labeled peptide substrate was monitored by mass spectrometry and NMR spectroscopy, and the structure of the intermediate in the biosynthesis was determined. R = peptide residue.



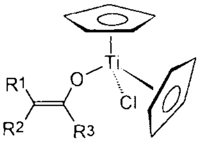
(a)

C. Kempter, T. Kupke, D. Kaiser,
J. W. Metzger, G. Jung* 2104–2107

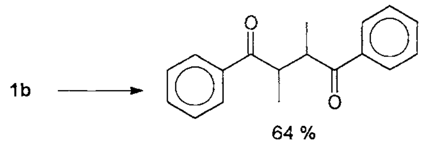
Thioenols from Peptidyl Cysteines: Oxidative Decarboxylation of a ^{13}C-Labeled Substrate

---

Unusually stable against hydrolysis is the titanium enolate **1a** (R^1, R^2 = Mes, R^3 = H), which can be stored in air for three months without any decomposition and leads, after one-electron oxidation, to the first titanium enolate radical cation characterized in solution. These novel electrophiles undergo Ti–O bond cleavage and C–C bond formation, for example in the synthesis of **2** from titanium enolate **1b** (R^1 = H, R^2 = Me, R^3 = Ph).



1a, 1b



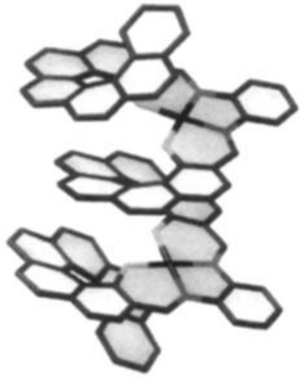
2

M. Schmittel,* R. Söllner 2107–2109

First Characterization of a Titanium Enolate Radical Cation in Solution: Carbon–Carbon Bond Formation and the Kinetics of the Mesolytic Ti–O Bond Cleavage

---

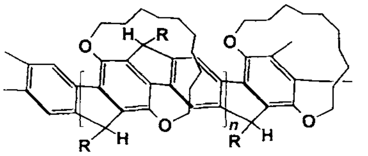
Coordinating the Schiff base of a helicenedicarbaldehyde to nickel centers resulted in the first ladder polymer that has an unbroken network of double bonds winding in one direction along a helix (see the representation on the right). Helicene and nickel salophen units alternate in the product, on average 8.3 times.



Y. Dai, T. J. Katz,*
D. A. Nichols 2109–2111

Synthesis of a Helical Conjugated Ladder Polymer

A chiroptically active compound without a helical structure has been constructed in the ladder polymer **1** (R = 3,4-$C_6H_3(OC_6H_{13})_2$), which has been synthesized from the corresponding enantiomerically pure $OC_{10}H_{20}O$-bridged diboronic acid. The molar ellipticity of **1** [2.2×10^6 rad cm^2 mol^{-1} (461 nm)] leads to an anisotropy factor of $g = 0.003$, which is thus only an order of magnitude less than the maximum value (0.02) for chiral conjugated polymers so far reported.



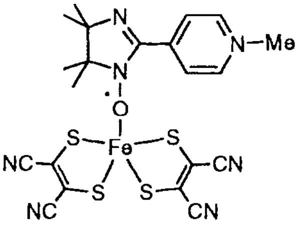
1

R. Fiesel, J. Huber, U. Scherf* 2111–2113

Synthesis of an Optically Active Poly(*para*-phenylene) Ladder Polymer

---

A novel combination of $S = 1/2$ and $S = 3/2$ spin crossover and magnetic interaction between ligand and central metal exists in the iron(III) complex **1**. Compound **1** is readily accessible from the corresponding dimeric thiolatoferrate(III) complex and the corresponding pyridinium salt, and offers a further example for the diversity of properties of molecular magnetic materials.



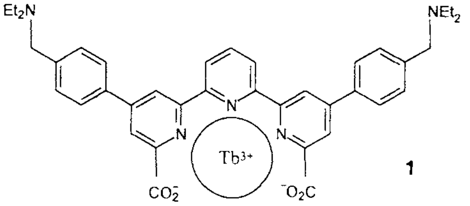
1

J.-P. Sutter, M. Fettouhi, L. Li, C. Michaut, L. Ouahab,* O. Kahn* 2113–2116

Synergy between Magnetic Interaction and Spin Crossover in an Iron(III) Complex with an Organic Radical as Ligand

---

The green luminescence of the terbium complex **1** is increased by a factor of 16 when the amino groups in the side chains are protonated. Because its luminescence has a lifetime of 0.62 ms, this complex can serve as an effective pH sensor in intrinsically fluorescent environments.

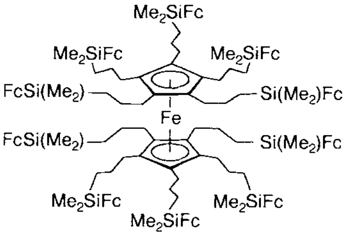


A. P. de Silva,* H. Q. N. Gunaratne, T. E. Rice 2116–2118

Proton-Controlled Switching of Luminescence in Lanthanide Complexes in Aqueous Solution: pH Sensors Based on Long-Lived Emission

---

The decaferrocenyl ferrocene 1, prepared readily from decaallylferrocene by hydrosilylation, is an ideal substrate for further ($n \times 10$)-fold functionalization. Highly functionalized compounds such as **1** are of interest as building blocks for redox-active polymers and as molecular electron reservoirs. Fc = ferrocenyl.



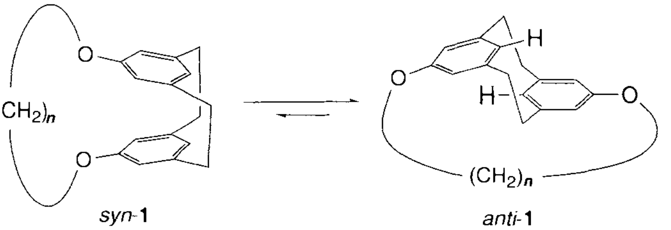
1

P. Jutzi,* C. Batz, B. Neumann, H.-G. Stammler 2118–2121

Maximum Functionalization of Metallocenes: Decaallylferrocene and Derivatives

---

The tether length determines the conformation of [2.2]metacyclophane **1**. The cyclophane with the 13-atom tether ($n = 11$) exists at room temperature as an equilibrium mixture of *syn* and *anti* isomers (ca. 5.9:1), whereas the next lower homologue ($n = 10$) in this series adopts only the *syn* conformation and the next higher homologue ($n = 12$) solely the *anti* conformation.



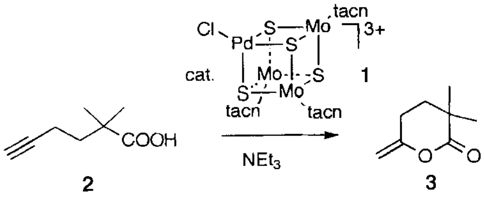
syn-**1** *anti*-**1**

G. J. Bodwell,* T. J. Houghton, J. W. J. Kennedy, M. R. Mannion* 2121–2123

First-Generation Tethered [2.2]Metacyclophanes-Prototypes of Molecular Devices

0570-0833/96/3518-2010 $ 15.00+.25/0

Catalytic activity remarkably higher than that of mononuclear palladium catalysts is exhibited by the cuboidal sulfide cluster **1** (tacn = 1,4,7-triazacyclononane) in the lactonization of alkynoic acids (**2** → **3**). The reaction can even be conducted in water owing to the good solubility and stability of the cluster in this medium.

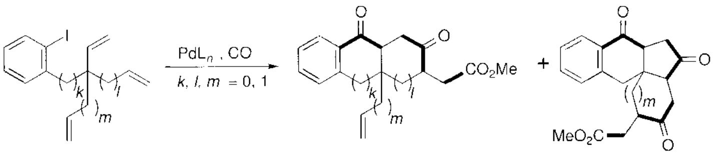


T. Wakabayashi, Y. Ishii, K. Ishikawa, M. Hidai* 2123–2124

A Novel Catalyst with a Cuboidal $PdMo_3S_4$ Core for the Cyclization of Alkynoic Acids to Enol Lactones

---

Up to seven C–C bonds are formed in an acylpalladation cyclization cascade that relies on the use of carbon monoxide as a one-carbon unit [Eq. (a)]. This reaction not only provides an efficient synthesis of polycycles but is also the first example of a carbometalation cascade giving products with an angular mode of ring fusion.

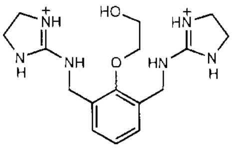


C. Copéret, S. Ma, E. Negishi* 2125–2126

Palladium-Catalyzed Carbonylative Cyclization Cascades with Iododienes and -trienes

---

A million times faster! The phosphorylation of **1**, in which the heterocyclic cations mimic the arginine residues at positions 35 and 87 in staphylococcal nuclease, is significantly faster than the analogous reaction of uncharged alcohols. Compound **1** is the most reactive mimetic of this enzyme.



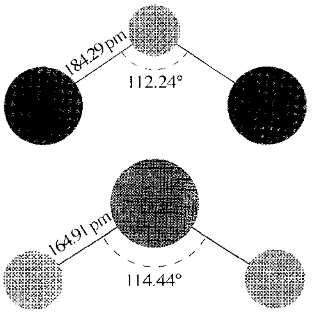
1

M.-S. Muche, M. W. Göbel* 2126–2129

Bis(guanidinium) Alcohols as Models of Staphylococcal Nuclease: Substrate Binding through Ion Pair Complexes and Fast Phosphoryl Transfer Reactions

---

Two bromine oxides with more than two atoms have been structurally characterized for the first time in the gas phase (see picture on the right; top: Br_2O, bottom: OBrO). Both molecules occur over a solid product formed in the reaction of O and Br_2. Under certain conditions BrO, OBrO, and Br_2O were obtained simultaneously.

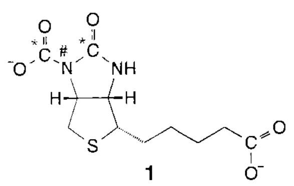


H. S. P. Müller,* C. E. Miller, E. A. Cohen 2129–2131

Dibromine Monoxide, Br_2O, and Bromine Dioxide, OBrO: Spectroscopic Properties, Molecular Structures, and Harmonic Force Fields

---

The enzymatic carboxylation of carboxybiotin (**1**) at the N-1′ nitrogen atom was proved unequivocally by the observation of ^1J(C,N) and ^2J(C,C) spin–spin coupling constants in NMR experiments. Essential to these studies was the use of the labeled substrates [1′-^{15}N]- and [2′-^{13}C]biotin along with [1,5-$^{13}C_2$]-glutaconate as the source of $^{13}CO_2$.

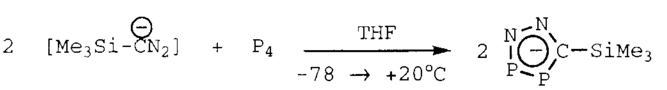


S. Berger,* A. Braune, W. Buckel,* U. Hertel, M.-L. Lee 2132–2133

Enzyme-Catalyzed Formation of Carboxybiotin as Proved by the Measurement of ^{15}N,^{13}C and ^{13}C,^{13}C Spin–Spin Coupling

---

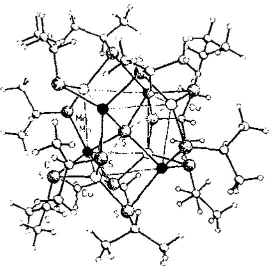
A formal [2+3]cycloaddition between |P≡P| and a diazomethyl anion affords the anionic, aromatic five-membered ring $[RCP_2N_2]^-$ (R = Me_3Si) [Eq. (a); counterion Li^+]. This reaction is a rare example of the use of P_4 in organic synthesis.



C. Charrier, N. Maigrot, L. Ricard, P. Le Floch, F. Mathey* 2133–2134

The Reaction of White Phosphorus with Lithium (Trimethylsilyl)diazomethanide: Direct Access to a New, Aromatic 1,2,3,4-Diazadiphosphole Ring

The cubane-like Mn_4Cu_4 framework with an interstitial μ_4-S ion is the outstanding feature of **1**, the octanuclear mixed-metal complex that is formed by the reaction of $(Me_4N)_2[Mn_2(S\textit{i}C_3H_7)_6]$ with CuCl in acetonitrile. The Mn_4S_{13} core of **1** can be considered as a minimal fragment of the sphalerite-type structure.



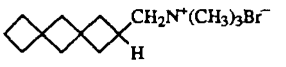
1

H.-O. Stephan, M. G. Kanatzidis, G. Henkel* 2135–2137

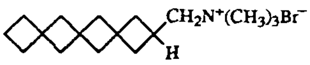
$[Cu_4Mn_4(S\textit{i}C_3H_7)_{12}S]^{2-}$, a Novel Octanuclear Heterometallic Complex Consisting of a Metal Cube with an Interstitial μ_4-Sulfide Ion and Edge-Bridging Thiolate Ligands

---

Micelles are usually highly disorganized. But how do surfactants with rigid linear hydrophobic chains behave? The linear spiro-surfactants **1** and **2**, which were prepared in multistep syntheses, display very different relationships between surface tension and surfactant concentration. Spiro-phospholipids were also prepared and found to have exceptionally high transition temperatures.



1



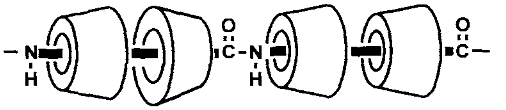
2

F. M. Menger,* J. Ding 2137–2139

Spiro-Surfactants and -Phospholipids: Synthesis and Properties

---

Molecular nylon threads that are completely encased by cyclodextrin molecules (see sketch below) can be synthesized by solid-state polycondensation of α,ω-amino acids in channellike cyclodextrin inclusion compounds. Since the polyamide chains are covered with cyclodextrins, they are soluble in water, but only for a limited time, because the rings tend to slowly unthread to some extent.

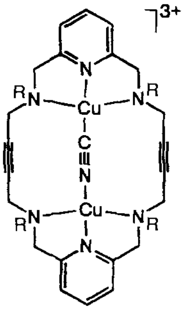


M. B. Steinbrunn, G. Wenz* 2139–2141

Synthesis of Water-Soluble Inclusion Compounds from Polyamides and Cyclodextrins by Solid-State Polycondensation

---

A highly selective response of a microelectrode to cyanide ions is induced by the lipophilic dicopper(II) macrocyclic complex $[(L)Cu_2(NO_3)_4]$ (L = polyazamacrocycle; see structural formula on the right) embedded in a PVC liquid membrane. The complex is the first example of a new type of anion-selective ionophore. The target anion is efficiently incorporated by a molecular recognition process. R = $C_{16}H_{33}$.

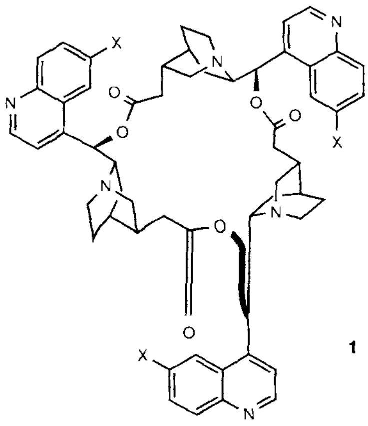


B. Ahlers, K. Cammann,* S. Warzeska, R. Krämer* 2141–2143

Molecular Recognition of Cyanide by a Dicopper(II) Macrocyclic Ionophore: Construction of a Cyanide-Selective Liquid-Membrane Electrode

---

A remarkably narrow product distribution is observed in the thermodynamic cyclization of modified Cinchona alkaloids to yield predominantly the trimer **1** (X = H, OMe); this is a representative of a new class of macrocycle. The reaction was proved to be reversible by resubmitting the cinchonidine (X = H) and quinine (X = OMe) to the reaction conditions: a statistical mixture of all four possible trimers was obtained.

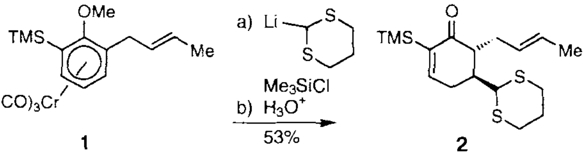


1

S. J. Rowan, P. A. Brady, J. K. M. Sanders* 2143–2145

Structure-Directed Synthesis under Thermodynamic Control: Macrocyclic Trimers from Cinchona Alkaloids

Chlorotrimethylsilane is the reagent of choice to trap the ionic intermediate that arises on nucleophilic addition to *ortho*-substituted anisoletricarbonylchromium complexes and to suppress its tendency toward *tele*-substitution (relative to the methoxy group). Thus the planar-chiral complex **1** can be transformed into the cyclohexenone **2** with complete retention of the stereochemical information in greater than 95% *ee*. Compound **2** is a promising precursor for the total synthesis of (+)-ptilocaulin.



H.-G. Schmalz,*
K. Schellhaas 2146–2148

Controlling the Course of Nucleophilic Additions to *ortho*-Substituted (η^6-Anisole)tricarbonylchromium Complexes: Dienol Ether Formation versus *tele*-Substitution

---

Complex libraries composed of more than five thousand cyclopeptides can act as chiral selectors when added to the mobile phase in capillary electrophoresis. Cyclohexapeptide sublibraries (such as those listed below) were used to achieve baseline separations of enantiomers of N^α-dinitrophenyl (DNP) and 9-fluorenylmethoxycarbonyl (FMOC) amino acids and Tröger's base. This approach can be used to identify selectors for difficult-to-separate racemates.

c[DFXXXa] c[RKXXXa] c[OOXXXO]

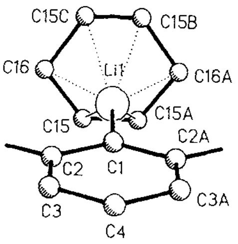
G. Jung,* H. Hofstetter, S. Feiertag,
D. Stoll, O. Hofstetter,
K.-H. Wiesmüller,
V. Schurig* 2148–2150

Cyclopeptide Libraries as New Chiral Selectors in Capillary Electrophoresis

---

Stabilized only by steric effects and weak solvation by benzene, the aryllithium compound **1** exists as a monomeric benzene adduct. The unique structure of **1** in the solid state is shown on the right; the *ortho* substituents on the η^1-bound phenyl ring have been omitted for clarity.

$C_6H_6 \cdot LiC_6H_3$-2,6-(2,4,6-iPr$_3C_6H_2)_2$ **1**



B. Schiemenz, P. P. Power* ... 2150–2152

Synthesis and Structure of a Unique Monomeric σ-Bonded Aryllithium Compound Stabilized by a Weak Li–Benzene π Interaction

---

* Author to whom correspondence should be addressed

BOOKS

German versions of all reviews, communications, and highlights in this issue appear in the second September issue of *Angewandte Chemie*. The appropriate page numbers can be found at the end of each article and are also included in the Author Index on p. 2157.

SERVICES

All the Tables of Contents from 1995 may be found on the WWW under **http://www.vchgroup.de**

COVER PICTURE

Contents

The cover picture shows a polyhedral representation of the structure of the nitridosilicate $BaYbSi_4N_7$. The overall SiN network structure in this compound consists of star-shaped $[N(SiN_3)_4]$ building blocks (blue). Here for the first time nitrogen atoms (red) that covalently bridge four silicon atoms were discovered. The nitridosilicates thus have significantly more possibilities for forming different structures than the oxosilicates. More about these fascinating results in solid-state chemistry is reported by H. Huppertz and W. Schnick on pages 1983–1984.

REVIEWS

Contents

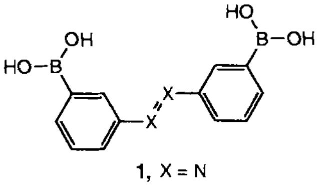
Improved binding properties for hybridization with RNA and increased stability towards nucleases—DNA and RNA analogues composed of modified nucleic acids must display these key features for application as potential antisense therapeutics. Although much data has been accumulated on the chemical stability of numerous synthetic analogues, as well as on their cell permeation and RNA hybridization properties, the structural origins of the altered selectivity and stability are often only poorly understood. X-ray crystallography can yield insight, and interpretation of the thermodynamic data on the basis of the 3D structures may be helpful in the development of new and improved nucleic acid analogues.

M. Egli* 1894–1909

Structural Aspects of Nucleic Acid Analogs and Antisense Oligonucleotides

---

Molecular saccharide receptors based on boronic acid are just as important for the selective recognition of monosaccharides (for example, **1** and **2**) as for the design of dye and fluorescence sensors (for example, **2**), the determination of the configuration of saccharides, or for the active transport of saccharide-like drugs through cell membranes.



1, X = N
2, X = CH

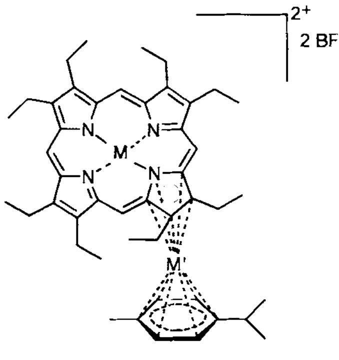
T. D. James, K. R. A. S. Sandanayake, S. Shinkai* 1910–1922

Saccharide Sensing with Molecular Receptors Based on Boronic Acid

HIGHLIGHTS

Contents

Metal–porphyrin π bonds such as those in 1 and 2 were hitherto unknown modes of coordination in porphyrin complexes. However, arene complexes of this kind were recently synthesized by Rauchfuss et al. (*Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1833). Metal–porphyrin interactions of this type may also play a role in reactions catalyzed by metalloporphyrins.



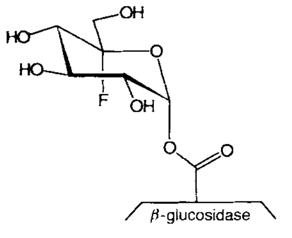
1 M = Ni, M' = Ru
2 M = Zn, M' = Os

M. O. Senge* 1923–1925

π-Pyrrole–Metal Complexes—The Missing Coordination Mode for Metal–Porphyrin Interactions

---

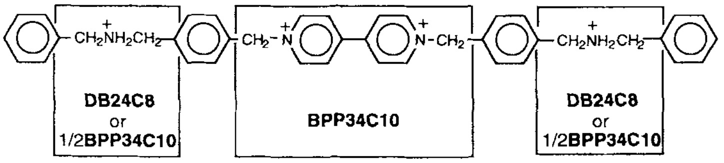
Excellent inhibitors of retaining α- and β-glucosidases, the recently synthesized 5-fluoroglucopyranosyl fluorides form stable enzyme–inhibitor complexes (shown schematically on the right), which were characterized by electrospray mass spectrometry. The results obtained in studies with these fluoro sugars provide fuel for the long-standing discussion on the mechanism of enzyme-catalyzed glycoside hydrolysis.



A. E. Stütz* 1926–1928

A Novel Approach for Clarifying the Reaction Mechanism of Retaining Glycoside Hydrolases

Three recognition sites—a bipyridinium unit and two secondary dibenzylammonium centers—within the tetracation **1** can be differentiated by two simple macrocyclic receptors, bis-*para*-phenylene[34]crown-10 (**BPP34C10**) and dibenzo[24]crown-8 (**DB24C8**). Strict self-assembly processes under thermodynamic control yielded either [(**DB24C8**)$_2$·**BPP34C10**·**1**] in a selective manner or the pseudopolyrotaxane [(**BPP34C10**)$_2$·**1**]$_n$.



1

P. R. Ashton, P. T. Glink,
M.-V. Martinez-Diaz,
J. F. Stoddart,* A. J. P. White,
D. J. Williams 1930–1933

Thermodynamically Controlled Self-Assembly of Pseudorotaxanes and Pseudopolyrotaxanes with Different Recognition Motifs Operating Self-Selectively

---

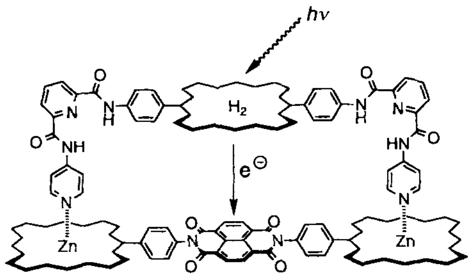
A flux is essential for the synthesis of Hf_7P_4, which has been obtained by the reaction of Hf with Fe and HfP. The compound proved to be thermodynamically stable and iron-free, but could not be synthesized without the addition of iron as a flux material. Hf_7P_4 is surprisingly isostructural with Zr_7P_4, and a possible explanation for this is given based on COOP calculations.

H. Kleinke,
H. F. Franzen* 1934–1936

Hf_7P_4: A New Binary Phosphide Synthesized by a Surprising Route

---

Zinc porphyrin/pyridine coordination interactions have been used to assemble complexes containing two different chromophore arrays. These undergo photoinduced electron transfer (see picture) and energy transfer reactions, which mimic some of the primary events in photosynthesis.

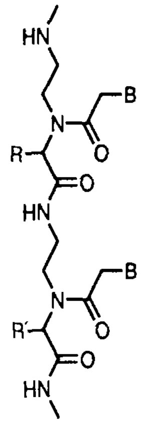


C. A. Hunter,*
R. K. Hyde 1936–1939

Photoinduced Energy and Electron Transfer in Supramolecular Porphyrin Assemblies

---

Functionalized chiral D- and L-amino acids in peptide nucleic acids (PNAs; backbone of a PNA shown on the right) affect their solubility properties as well as their hybridization with DNA and RNA. Mismatched base pairs are discriminated by these new PNAs better than by glycine PNAs. Monomers may find application in amide-based combinatorial chemistry, PNAs in the pharmokinetic field and in the synthesis of DNA conjugates.



G. Haaima, A. Lohse, O. Buchardt,
P. E. Nielsen* 1939–1942

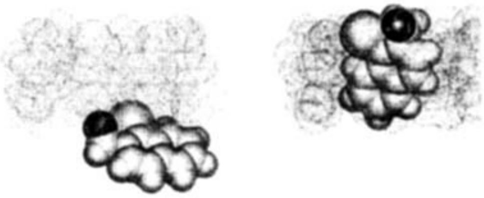
Peptide Nucleic Acids (PNAs) Containing Thymine Monomers Derived from Chiral Amino Acids: Hybridization and Solubility Properties of D-Lysine PNA

The initiation step in a deprotonation of CH-acidic compounds could be the formation of a complex between the organic precursor and the metalation reagent. This is the conclusion drawn from the reaction of $Ph_2P(=O)CH_3$ with $(Me_3Si)_2NLi$, which yielded a stable dimeric adduct $[(Me_3Si)_2NLi \cdot O{=}P(CH_3)Ph_2]_2$ with a central Li_2N_2 ring. MO calculations on the model system $H_2LiNLi \cdot O{=}P(CH_3)_2$ support these experimental findings.

D. R. Armstrong, M. G. Davidson,
R. P. Davies, H. J. Mitchell,
R. M. Oakley, P. R. Raithby,
R. Snaith,* S. Warren............ 1942–1944

A Stable Methyl Phosphane Oxide/Lithium Amide Complex: a Structural and MO Calculational Investigation of the Mechanism of Proton Abstraction by Alkali Metal Reagents

An extraordinarily large difference in the photochemical behavior of the regioisomers is observed when the bromonaphthalene lumophore is appended to the primary or the secondary OH groups of β-cyclodextrin. In the first case when this lumophore lies outside the cavity (bottom left, oxygen of ether linkage shown in black), no phosphorescence is observed. In the second case, however, the lumophore shows bright phosphorescence even in the presence of air, which strongly suggests that it is included within the cavity (bottom right).

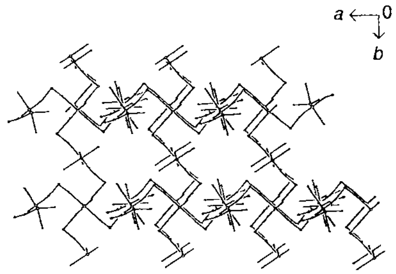


M. A. Mortellaro, W. K. Hartmann, D. G. Nocera* 1945–1946

Regioisomeric Effects on the Excited State Processes of a Cyclodextrin Modified with a Lumophore

---

Fine tuning of the magnetic properties can be achieved in $[Ni(tren)]_3[Fe(CN)_6]_2 \cdot 6H_2O$ (**1**, section of structure shown on the right; tren = tris(2-aminoethyl)amine), the first example of a three-dimensional bimetallic network of a Prussian blue analogue containing organic groups. The compound orders as a bulk ferrimagnet at about 8 K.

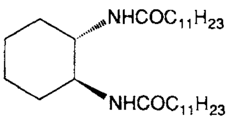


M. S. El Fallah, E. Rentschler, A. Caneschi, R. Sessoli, D. Gatteschi* 1947–1949

A Three-Dimensional Molecular Ferrimagnet Based on Ferricyanide and $[Ni(tren)]^{2+}$ Building Blocks

---

Between 2 and 44 g L⁻¹ of the diamide **1** are necessary to obtain stable gels with a wide variety of organic solvents. The circular dichroism of the gels can be attributed to the formation of chiral aggregates from **1**, which are held together by hydrogen bonds and van der Waals interactions.



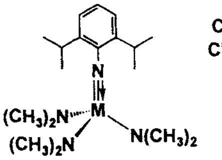
1

K. Hanabusa,* M. Yamada, M. Kimura, H. Shirai 1949–1951

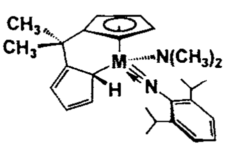
Prominent Gelation and Chiral Aggregation of Alkylamides Derived from *trans*-1,2-Diaminocyclohexane

---

Two of the three dimethylamido ligands in **1** (M = Nb, Ta) can be readily replaced by doubly deprotonated 2,2-bis(cyclopentadienyl)propane to give **2**, which undergoes an $\eta^1:\eta^5 \rightleftharpoons \eta^5:\eta^1$ coordination exchange equilibrium with a rather low activation barrier, leading to the (*S*,*R*)/(*R*,*S*) racemate.



1



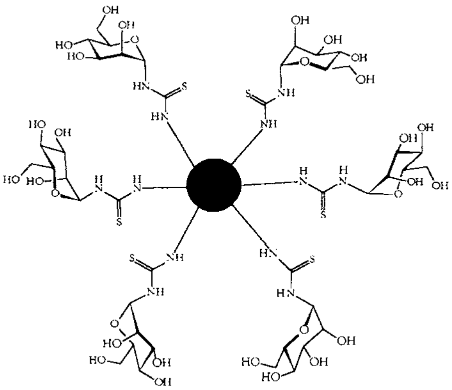
rac-**2**

W. A. Herrmann,* W. Baratta, E. Herdtweck 1951–1953

Structure Dynamics in Novel *ansa*-Metallocenes of Niobium and Tantalum

---

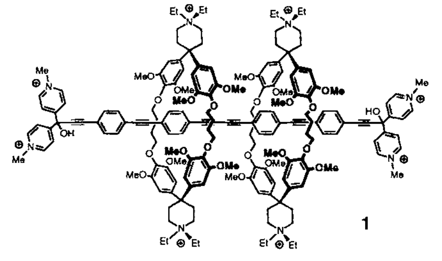
Sugar coating for dendrimers! Glycosyl isothiocyanates react with polyamidoamine dendrimers as core units to form glycoconjugates containing many sugar moieties (schematic representation of clustering of mannose residues shown on the right), which function as antiadhesives in cell–cell recognition. This flexible, speedy preparation can generate diverse cluster glycosides on a gram scale.



T. K. Lindhorst,* C. Kieburg 1953–1956

Glycocoating of Oligovalent Amines: Synthesis of Thiourea-Bridged Cluster Glycosides from Glycosyl Isothiocyanates

Hydrophobic binding and Glaser coupling enable the synthesis of [3]rotaxane **1** in 30% yield. The conjugated dumbbell component fluoresces six times more brightly when encased in cyclophane rings than when "naked" in solution. Counterion: Cl^-.

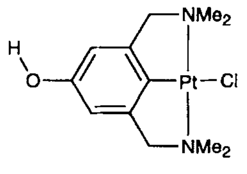


1

S. Anderson,*
H. L. Anderson* 1956–1959

Synthesis of a Water-Soluble Conjugated [3]Rotaxane

Strong hydrogen bonds (Cl···H–O 161(15)°; Cl···O 3.127(8) Å) lead to self-assembly of the *para*-hydroxyaryldiamineplatinum complex **1** to form linear, one-dimensional organometallic polymeric chains. The molecular building blocks in the polymer chain are oriented as a result of the directionality of the hydrogen bonds.



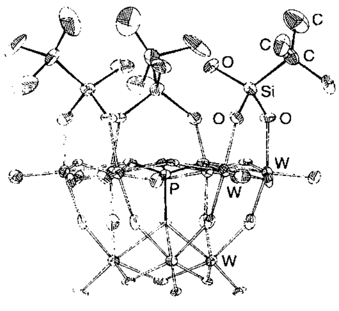
1

P. J. Davies, N. Veldman, D. M. Grove,
A. L. Spek, B. T. G. Lutz,
G. van Koten* 1959–1961

Organoplatinum Building Blocks for One-Dimensional Hydrogen-Bonded Polymeric Structures

---

Trivacant polyoxotungstates such as α-A-$[PW_9O_{34}]^{9-}$ ions react with tBuSiCl$_3$ to afford the anion **1**. This can react further with other trichlorosilanes to give α-A-$[PW_9O_{34}$-$(t\text{BuSiO})_3(\text{RSi})]^{3-}$ ions (R = H, Me, Et, $CH{=}CH_2$, $CH_2CH_2CH_2Cl$). Similar arsenic compounds are also reported.

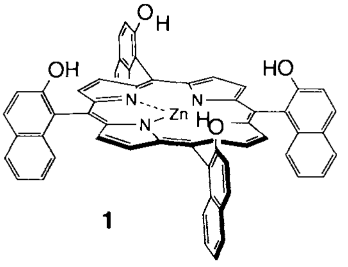


1

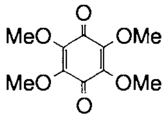
A. Mazeaud, N. Ammari,
F. Robert,
R. Thouvenot* 1961–1964

Coordination Chemistry of Polyoxometalates: Rational Synthesis of the Mixed Organosilyl Derivatives of Trivacant Polyoxotungstates α-A-$[PW_9O_{34}(t\text{BuSiO})_3$-$(\text{RSi})]^{3-}$ and α-B-$[AsW_9O_{33}(t\text{BuSiO})_3$-$(\text{HSi})]^{3-}$

In only a few picoseconds the photoinduced electron transfer in the noncovalently linked complex between zinc porphyrin **1** and the quinone **2** is complete. Transient absorption spectra show the zinc porphyrin cation radical as typical intermediate of the electron transfer.



1



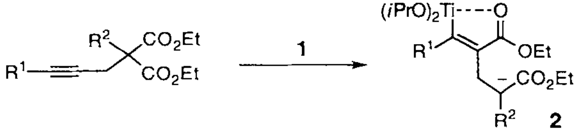
2

T. Hayashi,* T. Miyahara,
S. Kumazaki, H. Ogoshi,*
K. Yoshihara 1964–1966

Photoinduced Electron Transfer between Multifunctional Porphyrin and Ubiquinone Analogues Linked by Several Hydrogen-Bonding Interactions

---

Two unprecedented reactions of $[(\eta^2\text{-}CH_3CHCH_2)Ti(OiPr)_2]$ (**1**) are described here: its reactions with diethyl propargylmalonates to afford the titanated α-alkylideneglutarates **2** (see below), and with β,γ- and γ,δ-unsaturated esters to afford the acyltitanium compounds.

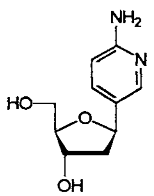


A. Kasatkin, T. Yamazaki,
F. Sato* 1966–1968

Reactions of β,γ- and γ,δ-Unsaturated Esters with the Reagent $Ti(OiPr)_4/2\,i$PrMgCl: Formation of β-Titanated Esters, β-Titanated Cyclobutanones, and Acyltitanium Compounds

---

DNA triple helices in the parallel binding motif can efficiently be stabilized at neutral pH by replacing deoxycytidine in the third strand by the C-nucleoside **1**. The increase in stability is due to the higher pK_a of the base in **1**, rendering its protonation, required for base pair formation, more favorable at physiological pH.

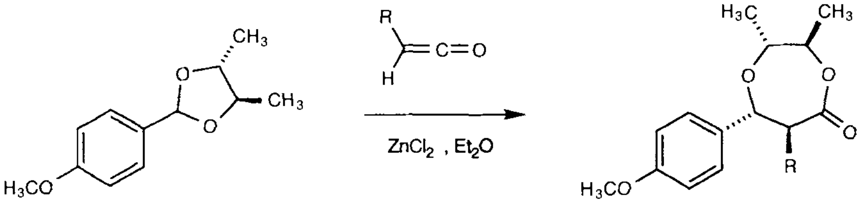


1

S. Hildbrand,
C. Leumann* 1968–1970

Enhancing DNA Triple Helix Stability at Neutral pH by the Use of Oligonucleotides Containing a More Basic Deoxycytidine Analog

High stereoselectivity earmarks the Lewis acid catalyzed insertion of ketenes in chiral acetals. The *anti*-configurated aldol products **2** are formed from **1** with more than 95% stereoselectivity. A wide range of ketenes and acetals can be used, which enables the synthesis of interesting heterocycles.



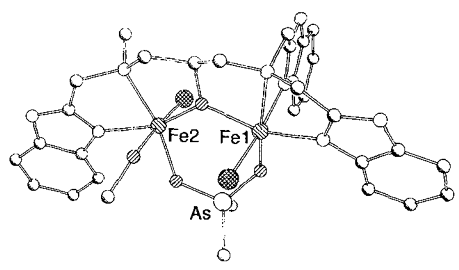
1 R = Cl, CH$_3$, C$_6$H$_5$ **2**

J. Mulzer,* D. Trauner,
J. W. Bats 1970–1972

Stereoselective Insertion of Ketenes into O,O-Acetals: Synthesis of β-Alkoxy Esters and 1,4-Dioxepan-5-ones

---

A considerably stable adduct is formed by the reaction of **1** with hydrogen peroxide. Complex **1** is the first X-ray crystallographically characterized unsymmetrical diiron(III) complex with a μ-alkoxo bridging ligand (the structure of the complex cation is depicted on the right) and catalyzes the oxidation of the peroxidase substrate diammonium 2,2′-azinobis-(3-ethylbenzothiazolin-6-sulfonate) with H_2O_2.



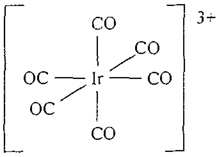
[Fe$_2$(mtbpo){O$_2$As(CH$_3$)$_2$}Cl$_2$(CH$_3$OH)](ClO$_4$)$_2$·4CH$_3$OH **1**

B. Eulering, M. Schmidt,
U. Pinkernell, U. Karst,
B. Krebs* 1973–1974

An Unsymmetrical Dinuclear Iron(III) Complex with Peroxidase Properties

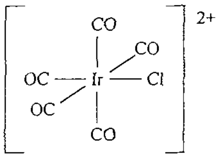
---

The first homoleptic carbonyl cation of a tripositive metal, [Ir(CO)$_6$]$^{3+}$ (**1**), has been obtained as a thermally stable [Sb$_2$F$_{11}$]$^-$ salt. The existence of **1** permits a comparison of the spectroscopic properties in the 5d series of isoelectronic hexacarbonyl species ranging from [Hf(CO)$_6$]$^{2-}$ to [Ir(CO)$_6$]$^{3+}$. In addition the molecular structure of the related cation [Ir(CO)$_5$Cl]$^{2+}$ (**2**) is reported.



$[Ir(CO)_6]^{3+}$

1



$[Ir(CO)_5Cl]^{2+}$

2

C. Bach, H. Willner,* C. Wang,
S. J. Rettig, J. Trotter,
F. Aubke* 1974–1976

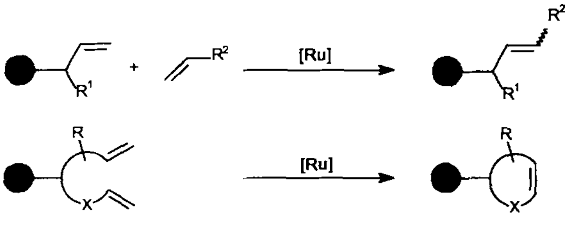
Cationic Iridium(III) Carbonyl Complexes: [Ir(CO)$_6$]$^{3+}$ and [Ir(CO)$_5$Cl]$^{2+}$

Dispersing water in a fluorocarbon seems against nature, since two more antipathetic types of liquids, in terms of intermolecular interactions, just do not exist. Every single characteristic relevant to water-in-fluorocarbon reverse emulsion stability (solubility and diffusivity parameters, interfacial tension and densities) is unfavorable. Yet stable emulsions of this type can be prepared with an appropriate fluorinated surfactant. Such reverse emulsions have potential as a new class of pulmonary drug-delivery system.

V. M. Sadtler, M. P. Krafft,
J. G. Riess* 1976–1978

Achieving Stable, Reverse Water-in-Fluorocarbon Emulsions

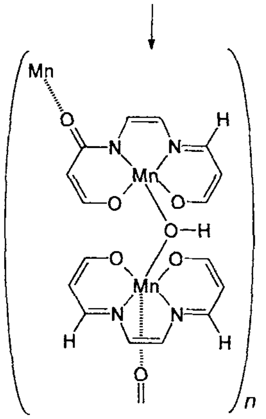
Cross metathesis between carrier-bound and dissolved olefins enable the simple construction of disubstituted double bonds on the solid phase (see below). As expected, ring-closing metathesis of immobilized diolefins can also be achieved in good yields by this method. The olefin metathesis can thus also be applied in topical solid-phase syntheses.



M. Schuster, J. Pernerstorfer,
S. Blechert* 1979–1980

Ruthenium-Catalyzed Metathesis of Polymer-Bound Olefins

The formation of a hydroperoxo ligand that bridges two Mn^{II} centers can be discussed as the first step in the reaction of dioxygen with [Mn(salophen)] complexes. This oxygenation leads to the selective oxidation of an imino group to an amido group and thus finally to a hydroxy-bridged Mn^{III}-polymer (see picture on the right). H_2salophen = *N,N-o*-phenylenebis(salicylidenimine).



E. Gallo, E. Solari, N. Re,
C. Floriani,* A. Chiesi-Villa,
C. Rizzoli 1981–1983

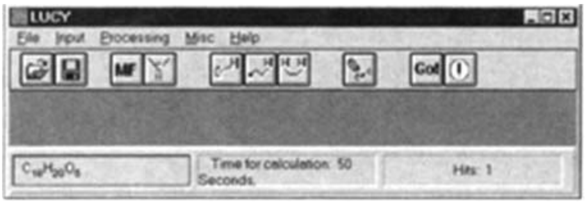
Dioxygen Activation by a Manganese Complex Containing a Schiff Base: Selective Oxidation of an Imino to an Amido Group within the Salophen Ligand and Formation of a Hydroxy-Bridged Mn^{III}-Polymer

Four silicon atoms have been connected to one central nitrogen atom for the first time in $BaYbSi_4N_7$. These $N^{[4]}$ bridges significantly extend the spectrum of possible linkages in Si–N network structures of nitridosilicates. While oxosilicates are built up by SiO_4 tetrahedra with either terminal oxygen atoms or simply bridging $O^{[2]}$ atoms, the $N^{[2]}$, $N^{[3]}$, and $N^{[4]}$ linkages in nitridosilicates enable novel highly cross-linked Si–N network structures.

H. Huppertz, W. Schnick* 1983–1984

$BaYbSi_4N_7$—Unexpected Structural Possibilities in Nitridosilicates

To test all possible interpretations of the ambiguous information from an HMBC diagram is a task that for a person is at best tedious and at worst impossible, but that is straightforward for a computer. That effective structure elucidation can be conducted in this manner is shown by the program LUCY, the user interface of which is shown below.



$C_{16}H_{20}O_5$

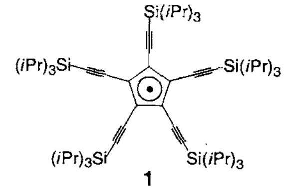
Time for calculation: 50 Seconds

Hits: 1

C. Steinbeck* 1984–1986

LUCY—A Program for Structure Elucidation from NMR Correlation Experiments

Stable in air for weeks as a solid and for days in solution, the blue-green pentaethynylcyclopentadienyl radical **1** is readily formed from ethynylated cyclopentadiene derivatives, which were prepared as potential precursors to decaethynyl metallocenes. The stability of **1** contrasts strikingly with that of previously described pentaaryl- and pentaisopropylcyclopentadienyl radicals, which, although stable at 25 °C, are highly sensitive to oxygen.

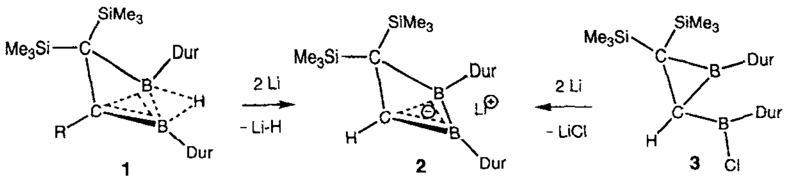


1

N. Jux, K. Holczer,*
Y. Rubin* 1986–1990

An Unusually Stable Pentaethynylcyclopentadienyl Radical

The 1,2-diboretanide ring inversion barrier for **2** (19.5 kcal mol^{-1} determined by ^{1}H NMR) is the largest among all the known isoelectronic 2π-electron homoaromatic analogues. The X-ray structure analysis of **2**, which was synthesized from **1** (R = H) or **3** (Dur = 2,3,5,6-tetramethylphenyl), reveals a short central C–B bond (171.1 pm).



D. Steiner, H.-J. Winkler,
C. Balzereit, T. Happel,
M. Hofmann, G. Subramanian,
P. von R. Schleyer, W. Massa,
A. Berndt* 1990–1992

1,2-Diboretanides: Homoaromatic 2π-Electron Compounds with High Inversion Barriers

* Author to whom correspondence should be addressed

BOOKS

German versions of all reviews, communications, and highlights in this issue appear in the first September issue of *Angewandte Chemie*. The appropriate page numbers can be found at the end of each article and are also included in the Author Index on p. 1873.

All the Tables of Contents from 1995 onwards may be found on the WWW under **http://www.vchgroup.de**

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Deutscher Chemiker

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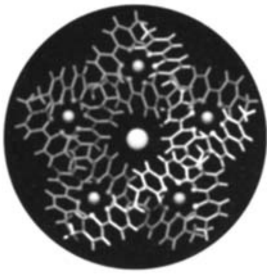
1996
35/16
Pages 1745–1876

COVER PICTURE



The cover picture shows the crystal structure of a unique supramolecular architecture consisting of five tris(bispyridine) ligands (shown in different colors) wrapped around five Fe^{II} ions (purple) in a double-helical fashion and closed to form a torus around a central chloride ion (green). This circular helicate is an analogue of circular DNA. Its formation also points to the possibility of designing self-assembling systems that generate receptors for specific substrates from a collection of suitable ligands and metal ions. More about the circular helicate and the concept of "virtual combinatorial libraries" is reported by J.-M. Lehn et al. on p. 1838ff.

REVIEWS

Contents

The ozone hole, a nuclear winter, and the greenhouse effect are some of the themes that concerned Paul Crutzen in his work, for which he was awarded the Nobel Prize in 1995. Here he reports on his path to his results and his plans for the future.

P. J. Crutzen* 1758–1777

My Life with O_3, NO_x, and Other YZO_x Compounds (Nobel Lecture)

Cause and result can be geographically widely separated. This fact is corroborated by the finding that the annually recurring ozone hole over Antarctica, which has been steadily increasing in size since 1985, is predominantly due to anthropogenic emissions from the Northern Hemisphere. How the realization dawned that it is primarily the chlorine atoms released by photochemical reactions of CFCs in the upper stratosphere that destroy the ozone shield is described by M. J. Molina in his Nobel Lecture.

M. J. Molina* 1778–1785

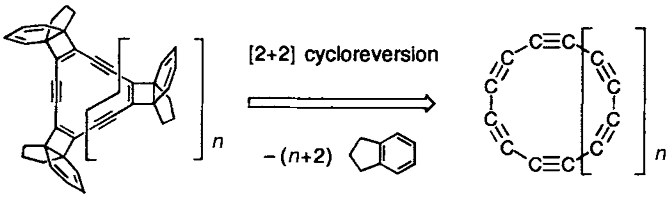
Polar Ozone Depletion (Nobel Lecture)

Hope for the atmosphere is the cautiously worded resumé of F. S. Rowland based on his knowledge of the developments in recent years about the influence of the CFCs on the ozone budget. Thanks to the restrictions that came into effect in the 1990s, the concentrations of some CFCs in the atmosphere have already reached their maximum value; for others this point will be reached in the near future. Nevertheless, large ozone losses are expected in the Antarctic spring until the middle of the 21st century.

F. S. Rowland* 1786–1798

Stratospheric Ozone Depletion by Chlorofluorocarbons (Nobel Lecture)

The smallest C_n clusters produced to date by [2+2]cycloreversion (*cyclo*-C_{12} and *cyclo*-C_{16}) as well as *cyclo*-C_{20} can be synthesized from propellane-annelated dehydroannulenes (**1**–**3**). Spectroscopic data indicate that the dehydroannulenes have either a planar (**2**) or a puckered (**3**) conformation.



1, *n*=1
2, *n*=2
3, *n*=3

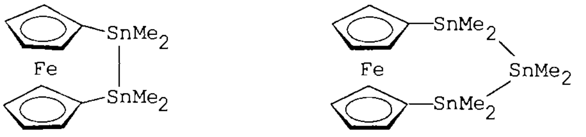
cyclo-C_{12} (*n*=1)
cyclo-C_{16} (*n*=2)
cyclo-C_{20} (*n*=3)

Y. Tobe,* H. Matsumoto, K. Naemura,
Y. Achiba,* T. Wakabayashi .. 1800–1802

Generation of Cyclocarbons with 4*n* Carbon Atoms (C_{12}, C_{16}, and C_{20}) by [2+2] Cycloreversion of Propellane-Annelated Dehydroannulenes

---

A convenient route to the stanna[*n*]ferrocenophanes **1** and **2** is presented. The series of homologous hetero[2]ferrocenophanes of the type $[Fe(C_5H_4EMe_2)_2]$ (E = C, Si, Sn) is thus supplemented by **1**. A comparison of the molecular structures (for E = C, Si, Sn) reveals that as the E–E bond length increases, the strain in the [2]ferrocenophane molecule decreases.

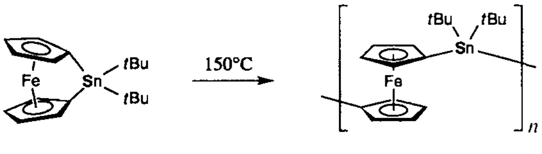


1 **2**

M. Herberhold,* U. Steffl, W. Milius,
B. Wrackmeyer 1803–1804

1,2-Distanna[2]- and 1,2,3-Tristanna-[3]ferrocenophanes

What is the smallest tilt angle necessary for an [*n*]metallocenophane to undergo ring-opening polymerization (ROP)? In previous work [*n*]metallocenophanes with tilt angles of up to 13° were found to be resistant to thermally induced ROP. The stanna[1]ferrocenophane **1**, the first [*n*]metallocenophane containing a heavy main group element in the bridge, has a tilt angle of only 14° but still polymerizes to yield novel high molecular weight poly(ferrocenylstannane)s **2**.



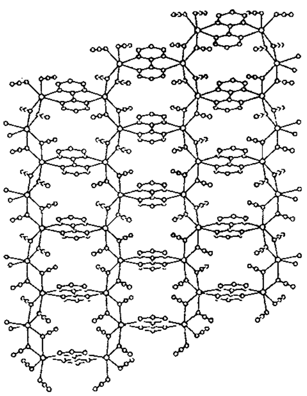
1 **2**

R. Rulkens, A. J. Lough,
I. Manners* 1805–1807

Synthesis and Ring-Opening Polymerization of a Tin-Bridged [1]Ferrocenophane

---

Same composition but different structures characterize the manganese complexes **1** and **2** of the formula $[Mn_2(bpym)(N_3)_4]$, which are obtained by the reaction of manganese(II) nitrate with 2,2'-bipyrimidine (bpym) and sodium azide in aqueous solution. Compound **1** has a honeycomb layered structure (shown on the right) and exhibits overall ferromagnetic interactions; **2** has a three-dimensional polymeric structure and shows overall antiferromagnetic interactions.



G. De Munno,* M. Julve,* G. Viau,
F. Lloret, J. Faus, D. Viterbo . 1807–1810

Azido and 2,2'-Bipyrimidine Ligands as Useful Tools in Designing Two- and Three-Dimensional Manganese(II) Networks

---

Manganese(II) nitrate, sodium azide, and 2,2'-bipyrimidine (bpym) react to give **1** in which the azido groups function as end-on bridging ligands and the bpym as a bis(bidentate) ligand. The structure of **1** can be described as a honeycomb sheet formed by Mn_6 hexagons. Magnetic susceptibility data reveals the existence of ferro- and antiferromagnetic interactions that are mediated by the azido ligands and the bpym ligands, respectively.

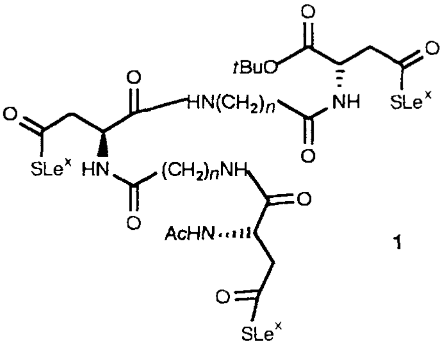
$[Mn_2(bpym)(N_3)_4]$ **1**

R. Cortés,* L. Lezama, J. L. Pizarro,
M. I. Arriortua, T. Rojo* 1810–1812

Alternating Ferro- and Antiferromagnetic Interactions in Honeycomb-Like Layers of an Azidomanganese(II) Compound

0570-0833/96/3516-1748 $ 15.00+.25/0

Glycosyl transferases provide rapid access to defined oligovalent sialyl Lewis^x structures (SLe^x) attached to a peptide backbone such as compound **1**. MALDI-TOF mass spectrometry proved to be an elegant, reliable method for monitoring the individual glycosylation steps.

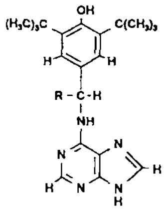


1

G. Baisch, R. Öhrlein* 1812–1815

Chemoenzymatic Synthesis of Sialyl Lewis^x Glycopeptides

Dynamic systems consisting of heterocyclic substrates like 1 and a model receptor can be resolved by EPR and ENDOR spectroscopy because of the difference in time resolution of these techniques. Intermolecular interactions in these lock-and-key complexation equilibria influence the intramolecular flexibilities. R = CH_3.



1

M. Jäger, H. B. Stegmann 1815–1818

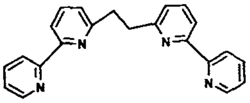
Molecular Recognition Analyzed by EPR, ENDOR, and NMR Spectroscopy

---

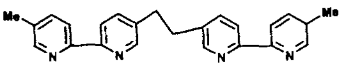
Self-assembly of new tetranuclear (1) and octanuclear (2) manganese carboxylate clusters is controlled by the bis(bipyridine) ligands L1 and L2, respectively, which are shown on the right. The cation **1** consists of two Mn_2O complex fragments, each of which contains one Mn^{II} and one Mn^{III} center; **2** contains two butterfly-like Mn_4O_2 cores linked by bis(bipyridine) bridges. Counterion: ClO_4^-.

$[Mn_4O_2(O_2CMe)_4(L1)_2]^{2+}$ **1**

$[Mn_8O_4(O_2CEt)_{14}(L2)_2]^{2+}$ **2**



L1



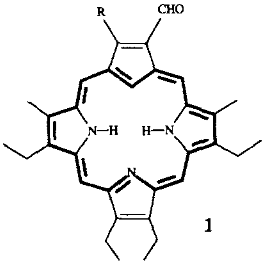
L2

V. A. Grillo, M. J. Knapp, J. C. Bollinger, D. N. Hendrickson,*
G. Christou* 1818–1820

Bis(bipyridine) Ligands in Manganese Carboxylate Cluster Chemistry:
Self-Assembly of a Cluster Complex with Two Butterfly-Like $[Mn_4(\mu_3\text{-}O)_2]^{8+}$ Cores

---

A link has been forged between porphyrins and annulenes by carbaporphyrins **1** (R = H and CH_3), in which one nitrogen atom of the porphyrin framework is replaced by a carbon atom. These novel compounds are 18π arenes like porphyrins and have similar spectroscopic properties.

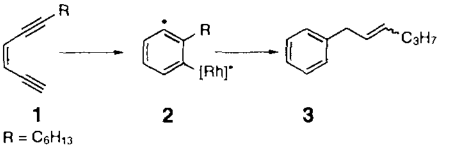


1

K. Berlin* 1820–1822

Carbaporphyrins

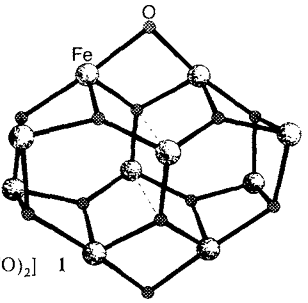
A transition metal catalyst can trigger the cycloaromatization of an enediyne. A coordinatively unsaturated rhodium complex catalyzes the cyclization of the acyclic enediyne **1** to produce **3**. The cyclization, which is similar to the Myers reaction, proceeds via a vinylidene–rhodium intermediate and the 1,4-organorhodium diradical **2**. Rh = $[RhCl(iPr_3P)_2]$.



K. Ohe,* M.-a. Kojima, K. Yonehara, S. Uemura* 1823–1825

Rhodium(I)-Catalyzed Cycloaromatization of Acyclic 3-Ene-1,5-diynes

Two distorted Fe_6O_6 hexagonal prisms with a common rectangular face form the core (shown on the right) of the decanuclear iron complex **1**. Magnetic studies indicate a high-spin ground state of around $S = 11$ or 12. Hchp = 6-chloro-2-pyridone.

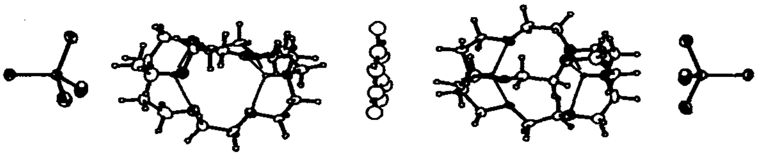


$[Fe_{10}Na_2(\mu_4\text{-}O)_2(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(O_2CPh)_{10}(chp)_6(H_2O)_2(Me_2CO)_2]$ **1**

C. Benelli, S. Parsons, G. A. Solan,
R. E. P. Winpenny* 1825–1828

Ferric Wheels and Cages: Decanuclear Iron Complexes with Carboxylato and Pyridonato Ligands

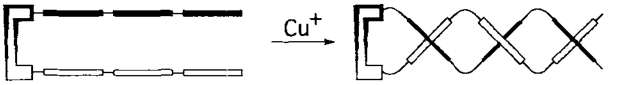
From an arene-rich liquid clathrate medium the title compound can be isolated in crystalline form. It is the first example of a compound in which an ionophore is stabilized by NH_4^+–π interaction. The crystal contains a linear supramolecular complex comprising five components (see picture) in which the cryptate molecules are elongated along their long axes.



L. R. MacGillivray,
J. L. Atwood* 1828–1830

Structural Reorganization of the Doubly Protonated [222]Cryptand through Cation–π and Charge–Charge Interactions: Synthesis and Structure of Its $[CoCl_4]\cdot 0.5\,C_6H_5CH_3$ Salt

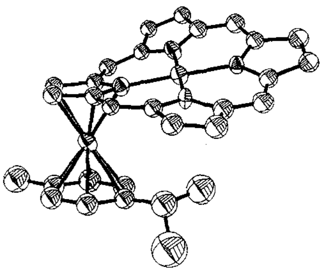
The handedness of helical polybipyridine metal complexes can be induced by a template, as shown schematically below. Introduction of one linking stereoelement at one end of the strands sets the trend of the complexation, and the stereochemical information is transmitted over nanometer distances.



C. R. Woods, M. Benaglia, F. Cozzi,
J. S. Siegel* 1830–1833

Enantioselective Synthesis of Copper(I) Bipyridine Based Helicates by Chiral Templating of Secondary Structure: Transmission of Stereochemistry on the Nanometer Scale

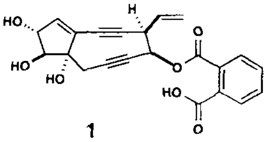
A new bonding mode is present in the title compound, in which a metalloporphyrin serves as a π ligand. The results of an X-ray crystal structure analysis (shown on the right) and spectroscopic studies clearly show that the metalloporphyrin is strongly affected by the complexation.



K. K. Dailey, G. P. A. Yap,
A. L. Rheingold,
T. B. Rauchfuss* 1833–1835

Metalloporphyrins as Ligands: Synthesis and Characterization of $[(\eta^6\text{-cymene})Ru\{\eta^5\text{-Ni(OEP)}\}]^{2+}$

A phthalate group serves as the trigger for controlling the stability of the enediyne precursor **1**. β-Elimination of this trigger generates the corresponding enediyne and the DNA-cleaving biradical. The highly strained nine-membered ring in **1**, an analogue of the kedarcidin chromophore, was constructed by a transannular [2,3]Wittig rearrangement. Incubation of supercoiled DNA with **1** (1 mM) leads to double strand cleavage without the addition of a reducing agent, which is required for other DNA cleaving systems.

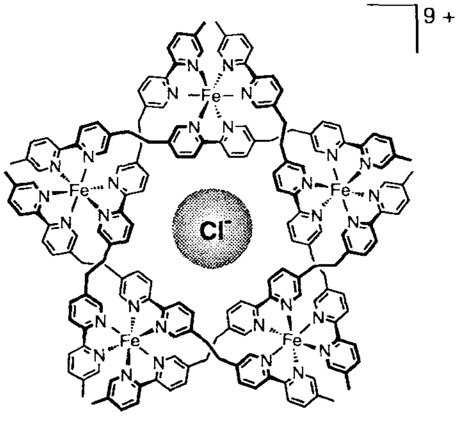


1

T. Takahashi,* H. Tanaka, H. Yamada,
T. Matsumoto, Y. Sugiura 1835–1837

DNA Cleavage by a Nine-Membered Masked Enediyne, an Analogue of the Kedarcidin and C-1027 Chromophores

The simple reaction of a tris-bpy ligand strand with $FeCl_2$ leads to the self-assembly of the unique cation **1**, which consists of a torus formed by five ligands wrapped around five Fe^{II} ions in a double-helical fashion and closed around a central chloride ion. This structure, a fivefold circular helicate, is a helicate analogue of circular DNA.

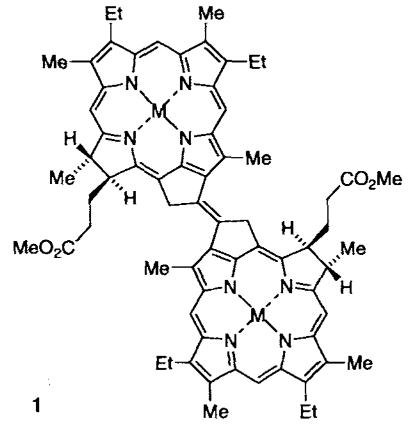


1

B. Hasenknopf, J.-M. Lehn,* B. O. Kneisel, G. Baum, D. Fenske 1838–1840

Self-Assembly of a Circular Double Helicate

The titanium-mediated coupling of Ni^{II} and Zn^{II} pyrophaeophorbides results in formation of planar ethene-fused bisphaeophorbides **1**, M = Ni, Zn. Absorption spectroscopy indicates that the two chlorin units are highly conjugated, and the X-ray crystal structure shows the two phaeophorbide rings to be almost coplanar.



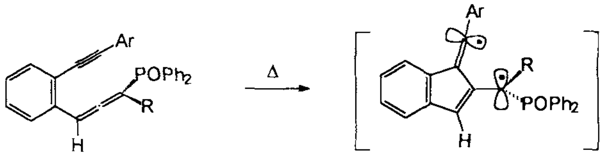
1

L. Jaquinod, M. O. Senge, R. K. Pandey, T. P. Forsyth, K. M. Smith* .. 1840–1842

Planar Bischlorophyll Derivatives with a Completely Conjugated π-System: Model Compounds for the Special Pair in Photosynthesis

---

Tales of the Unexpected. The thermal reaction of aryl-substituted enyne allenes **1** does not proceed by the expected Myers–Saito cycloaromatization. Instead a novel cyclization *via* intermediate benzofulvene biradicals **2** takes place.



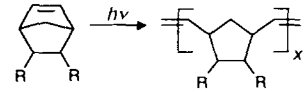
1 2

M. Schmittel,* M. Strittmatter, S. Kiau 1843–1845

An Unprecedented Biradical Cyclization as an Alternative Pathway to the Myers–Saito Cycloaromatization in the Thermal Reactions of Enyne Allenes

---

A new type of photopolymerization (depicted on the right) relies on well-defined, early transition metal complexes. Schrock-type catalysts are photochemically generated from di- or trialkyl tungsten complexes. The photoactivity and latency of the new catalysts are demonstrated by photo-differential scanning calorimetric and viscosimetric measurements.

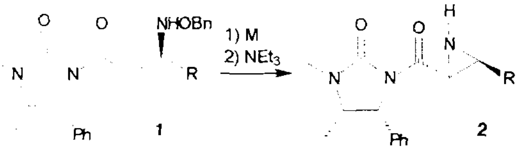


P. A. van der Schaaf,* A. Hafner, A. Mühlebach 1845–1847

Photoinduced Ring-Opening Metathesis Polymerization (PROMP) with Photochemically Generated Schrock-Type Catalysts

---

Diastereoselectivities at previously unattained levels. Aziridines **2** can be prepared from precursors **1** via the Ti or Al enolates in >99% *de*. Further advantages of this approach are the easy access to **1** by $AlMe_2Cl$-catalyzed 1,4-addition of *O*-benzylhydroxylamine to α,β-unsaturated chiral imides, and the straightforward recovery of the chiral auxiliary by treatment with lithium benzyloxide. R = Me, Et, *n*Pr; M = $TiCl_4$, $AlMe_2Cl$.

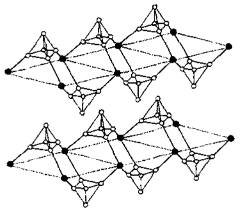


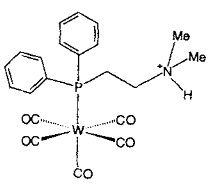
1 2

G. Cardillo,* S. Casolari, L. Gentilucci, C. Tomasini 1848–1849

Asymmetric Synthesis of Alkyl Aziridine-2-Carboxylates from Chiral 3′-Benzyloxyaminoimides

Functionalization of a phosphane ligand facilitates intercalation of the free ligand and its tungsten pentacarbonyl complex (example shown bottom right) in α-zirconium phosphate (section of structure shown bottom left). Syntheses of intercalated products with the stoichiometry [Zr(HPO$_4$)$_2$(Q)$_x$·yH$_2$O] (Q = Ph$_2$PCH$_2$CH$_2$NMe$_2$, $x = 0.46$, $y = 1.1$; Q = (OC)$_5$W(Ph$_2$PCH$_2$CH$_2$NMe$_2$), $x = 0.51$, $y = 1.5$) are reported.





J. S. Bone, D. G. Evans,* J. J. Perriam, R. C. T. Slade 1850–1852

Synthesis of New Hybrid Materials by Intercalation of a Bifunctional Aminophosphane and Its Tungsten Pentacarbonyl Complex in α-Zirconium Phosphate

---

Displaced intermolecular and intramolecular equilibria, which lead to a nonlinear change in the concentration ratios of intermediates, are possibly the cause for the experimentally long-known nonlinear temperature dependence of logarithmic product ratios in selection processes (isoinversion principle). This interpretation takes into account a change in dominance of differences in the activation enthalpy and entropy for the overall selection process, as well as a change in the rate-determining step with variation of the temperature.

D. Heller,* H. Buschmann, H.-D. Scharf 1852–1854

Nonlinear Temperature Behavior of Product Ratios in Selection Processes

---

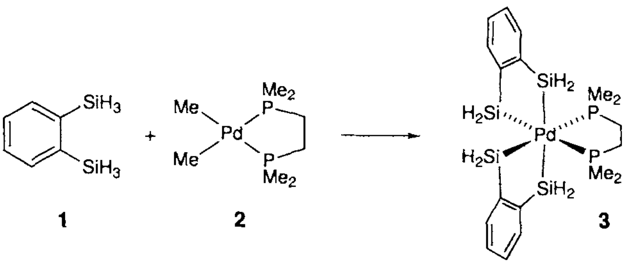
Useful intermediates for the synthesis of functionalized, linear alkyl chains by classical Grignard reactions or reactants for the synthesis of biblock copolymers by further reaction with polar monomers—the dialkylmagnesium compounds described herein are accessible in a living transfer polymerization under very mild conditions with [Cp$^*_2$LnCl$_2$Li(OEt$_2$)$_2$] (Ln = Nd, Sm) as catalysts and simple dialkylmagnesium compounds RMgR′ (R = Et, R′ = Bu or R = R′ = n-hexyl) using ethylene as substrate.

J.-F. Pelletier, A. Mortreux,* X. Olonde, K. Bujadoux 1854–1856

Synthesis of New Dialkylmagnesium Compounds by Living Transfer Ethylene Oligo- and Polymerization with Lanthanocene Catalysts

---

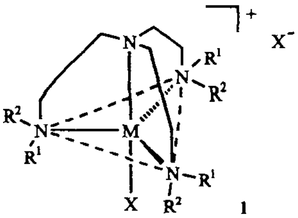
Smoothly and in good yield, the reaction of 1,2-disilylbenzene **1** and the palladium complex **2** affords the silylpalladium(IV) complex **3**. Compounds like this might be intermediates in catalytic transformations of silanes.



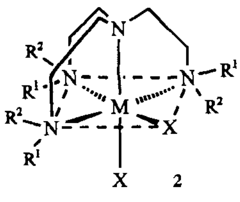
S. Shimada, M. Tanaka,* M. Shiro 1856–1858

The First Silylpalladium(IV) Complex

Trigonal-bipyramidal and octahedral coordination is found in transition metal complexes **1** and **2** (M = Co, Ni, Cu, Zn; X = Cl, NO$_3$, NCS (or SCN)) with dendrimeric ethyleneimine ligands of the first (R^1 = H; R^2 = CH$_2$-3,4-C$_6$H$_3$[O(CH$_2$)$_9$CH$_3$]$_2$) and second generation (R^1 = R^2 = CH$_2$CH$_2$NHCO-3,4-C$_6$H$_3$[O(CH$_2$)$_9$CH$_3$]$_2$). These complexes form a novel class of metallomesogens. With a second generation dendrimer as the ligand or with Zn^{II} as the central atom, a hexagonal-columnar phase is formed. Otherwise, lamellar mesophases are obtained.



1

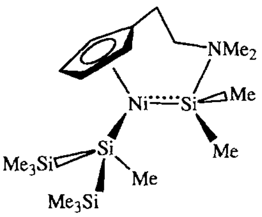


2

U. Stebani, G. Lattermann,* M. Wittenberg, J. H. Wendorff 1858–1861

Metallomesogens with Branched, Dendrimeric Amino Ligands

In the absence of strong π acceptors or soft Lewis bases (PR_3) acting as competing ligands, the aminoalkyl-functionalized Cp ligand unfolds its full potential in coordination chemistry. This is exemplified by the synthesis of the unusual silanediyl(silyl) complex **1**.



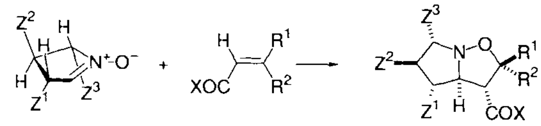
1

S. Nlate, E. Herdtweck,
R. A. Fischer* 1861–1863

An Intermolecularly Donor-Stabilized Silanediyl(silyl)nickel Complex: Combined Si–Si Bond Cleavage and Methyl Migration between Silicon Centers

---

Only the convex face of the chiral, cyclic nitrone **1** is accessible to dipolarophiles **2** in [3 + 2]cycloadditions. Since in addition Z^2 dictates the orientation of the dipolarophiles by directing the smallest substituent (H) of **2** into the most demanding space, the cycloadducts **3** are obtained with almost perfect stereocontrol.



1 **2** **3**

$Z^1 = Z^2 = t\text{BuMe}_2\text{Si}$ >99 %*de*

$Z^3 = CH(Me)CO_2Me$

T. Ishikawa, Y. Tajima, M. Fukui,
S. Saito* 1863–1864

Synthesis and Asymmetric [3 + 2] Cycloaddition Reactions of Chiral Cyclic Nitrone: A Novel System Providing Maximal Facial Bias for both Nitrone and Dipolarophile

* Author to whom correspondence should be addressed

BOOKS

German versions of all reviews, communications, and highlights in this issue appear in the second August issue of *Angewandte Chemie*. The appropriate page numbers can be found at the end of each article and are also included in the Author Index on p. 1873.

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ANGEWANDTE CHEMIE

A Journal of the
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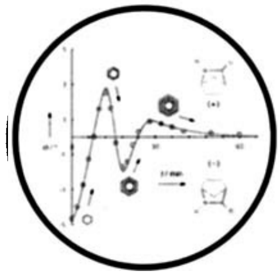
International Edition in English

1996
35/15
Pages 1585–1744

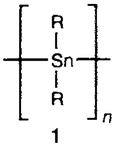
COVER PICTURE

The cover picture shows the time dependence of the optical rotation of a solution of a mixture of the bicyclic lactam 2-azabicyclo[2.2.2]hept-5-en-3-one enantiomers, which depicts oscillations during resolution by the preferential crystallization method. This phenomenon arises because layers of the (–)- and (+)-enantiomers (depicted as red and green hexagons, respectively) crystallize alternately from solution to form each crystal. The results on this apparently bizarre and unprecedented oscillating behavior are described in the communication by A. Collet et al. on p. 1666.



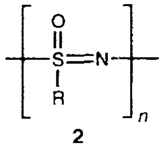
REVIEWS

The incorporation of inorganic elements in the main chain of polymers is an attractive method for accessing processable materials with novel properties. In this article, recent advances in the inorganic polymer field are surveyed, with emphasis on the new polymer systems prepared over the last decade such as **1**–**3**.



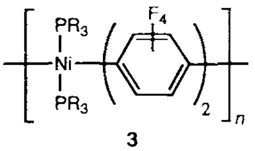
$[\mathrm{SnR_2}]_n$

1



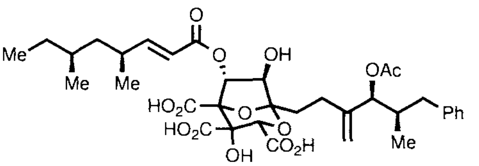
$[\mathrm{S(=O)(R)=N}]_n$

2



3

Novel structures and profound biological activity are the prerequisites for exciting, multifaceted projects in natural products chemistry. Zaragozic acids such as compound **1** are excellent examples. Their unusual, heavily oxygenated core structure and effectiveness in lowering serum cholesterol levels have motivated tremendous research activity since their discovery in 1991/1992.



1

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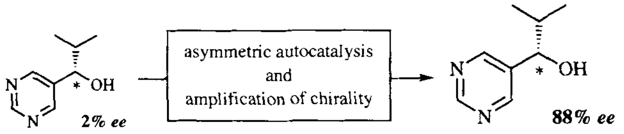
HIGHLIGHTS

A Darwinistic principle in catalysis? The term for the catalysis of an asymmetric, catalyzed reaction by its product is "asymmetric autocatalysis". The enantiomeric excess of a self-replicating system such as that described by Soai et al. can be amplified enormously in several reaction cycles [Eq. (a)].

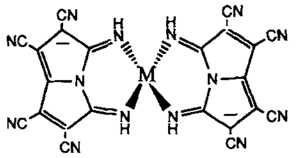


(a)

C. Bolm,* F. Bienewald,
A. Seger 1657–1659

Asymmetric Autocatalysis with Amplification of Chirality

Metallic or ferromagnetic properties are displayed by Cu complexes with the dicyanoquinodiimine (DCNQI) anion and a V complex with the tetracyanoethyletylene (TCNE) anion. These exceptional properties arise from pπ–dπ ligand–metal interactions. An entire field based on the coordination chemistry of organocyanides is emerging, aided by the discoveries of unusual molecules such as **1** (M = Fe, Ni, Cu, Zn) that involve coupling of two TCNE ligands on a metal center.



1

K. R. Dunbar* 1659–1661

Organocyanide Acceptor Molecules as Novel Ligands

COMMUNICATIONS

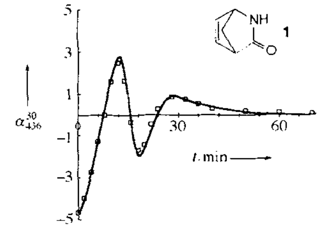
A linear arrangement of guest molecules in perhydrotriphenylene inclusion compounds can lead to supramolecular materials with optimized physical properties. Through cocrystallization, different guests displaying pronounced nonlinear optical properties were incorporated within the channels of the host species (shown on the right) to give a high yield of polar single crystals.

R. Hoss, O. König, V. Kramer-Hoss,
U. Berger, P. Rogin,
J. Hulliger* 1664–1666

Crystallization of Supramolecular Materials: Perhydrotriphenylene (PHTP) Inclusion Compounds with Nonlinear Optical Properties

---

Lamellar twinning of opposite enantiomers explains why the enantiomeric composition of a supersaturated solution oscillates during resolution by preferential crystallization of the bicyclic lactam (**1**; see diagram on the right).

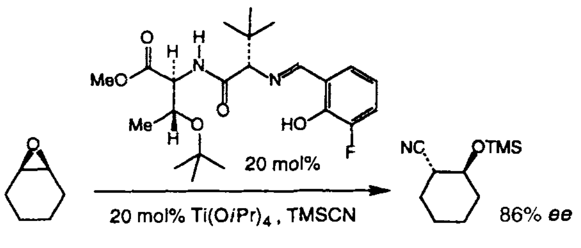


G. A. Potter, C. Garcia, R. McCague,
B. Adger, A. Collet* 1666–1668

Oscillating Crystallization of (+) and (+) Enantiomers during Resolution by Entrainment of 2-Azabicyclo[2.2.1]hept-5-en-3-one

---

The first catalytic and enantioselective opening of *meso* epoxides with trimethylsilylcyanide (TMSCN) [Eq. (a)] is reported. Combinatorial strategies and solid-phase techniques were used for optimization of asymmetric induction through parallel synthesis and screening of peptide-derived ligands. A dipeptide Schiff base that affords high enantioselectivities was identified through iterative modification of the modular ligand structure.

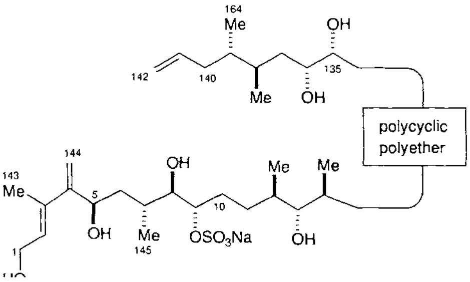


(a)

B. M. Cole, K. D. Shimizu,
C. A. Krueger, J. P. A. Harrity,
M. L. Snapper,*
A. H. Hoveyda* 1668–1671

The Discovery of Chiral Catalysts through Ligand Diversity: Ti-Catalyzed Enantioselective Addition of TMSCN to *meso* Epoxides

All's well that ends well! The complete assignment of the structure of the largest known natural product that is not a biopolymer (maitotoxin) has concluded with the determination of the configurations of the stereogenic centers in its two acyclic side chains. The results of NMR studies were confirmed by comparison with synthesized model compounds. The absolute configuration was determined by analysis of a fragment of the natural product and a corresponding synthesized unit by GC with a chiral column. In the contracted structure below, the acyclic side chains are attached to the termini of a polycyclic polyether.



T. Nonomura, M. Sasaki, N. Matsumori, M. Murata, K. Tachibana,* T. Yasumoto 1672–1675

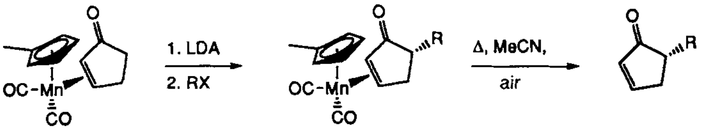
The Complete Structure of Maitotoxin, Part II: Configuration of the C135–C142 Side Chain and Absolute Configuration of the Entire Molecule

M. Sasaki, N. Matsumori, T. Maruyama, T. Nonomura, M. Murata, K. Tachibana,* T. Yasumoto 1675–1678

The Complete Structure of Maitotoxin, Part I: Configuration of the C1–C14 Side Chain

---

Asymmetric alkylations and kinetically controlled aldol reactions are possible with the planar-chiral η^2-manganese complexes of cyclopent-2-enone that can now be prepared in enantiomerically pure form [Eq. (a); LDA = lithium diisopropylamide; R = Me, allyl, Bn or RX = R'CHO, R' = *i*Pr, Ph]. After mild demetalation the chiral cyclopentenone derivatives, which are difficult to prepare by other means, are obtained with good enantiomeric excesses.



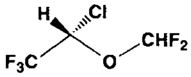
(a)

D. Schinzer,* H. Bärmann 1678–1680

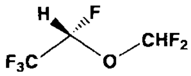
Diastereoselective C–C Bond Formation with Nonracemic Planar-Chiral η^2-Manganese Complexes

---

A controversial assignment has been revisited by the determination of the absolute configurations of (+)-isoflurane [(+)-**1**] and (+)-desflurane [(+)-**2**] by anomalous X-ray dispersion at −180 °C. The dextrorotatory isomers should have the (*S*) configuration, in agreement with other findings. The consequences of this assignment are particularly important for the stereochemical course of certain enantioselective reactions.



(+)-(*S*)-**1**



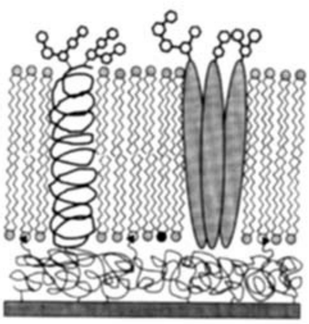
(+)-(*S*)-**2**

V. Schurig,* M. Juza, B. S. Green, J. Horakh, A. Simon* 1680–1682

Absolute Configurations of the Inhalation Anesthetics Isoflurane and Desflurane

---

Polymer-supported lipid bilayers on solid substrates are of particular interest for the investigation of membrane proteins. A great improvement in the homogeneity of such lipid bilayers can be obtained by the introduction of "anchor lipids" into the monolayer facing the substrate. The resulting attached lipid bilayers (tethered supported bilayers) like that shown schematically on the right are interesting biomembrane models.



D. Beyer, G. Elender, W. Knoll, M. Kühner, S. Maus, H. Ringsdorf,* E. Sackmann 1682–1685

Influence of Anchor Lipids on the Homogeneity and Mobility of Lipid Bilayers on Thin Polymer Films

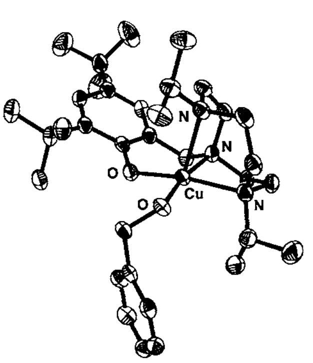
---

A "fingerprint" that we believe to be an essential condition for superconductivity is shown by the electronic band structure of the novel phase $Ce_9Br_5(CBC)_3$. Although the magnetic moment of the Ce^{3+} ion quenches superconductivity, the isostructural lanthanum compound is a superconductor at 6 K.

H. Mattausch, A. Simon,* C. Felser, R. Dronskowski 1685–1687

$La_9Br_5(CBC)_3$: A New Superconductor

Sterically hindered triazacyclononane derivatives bearing one alkyl-substituted phenolato group have enabled the synthesis of copper complexes that mimic key intermediates in the postulated catalysis cycle of galactose oxidase. For example, one-electron oxidation of the copper(II) complex pictured on the right yields benzaldehyde, probably with participation of a Cu^{II} complex containing a phenoxyl radical. A similar mechanism has been proposed for the active enzyme.

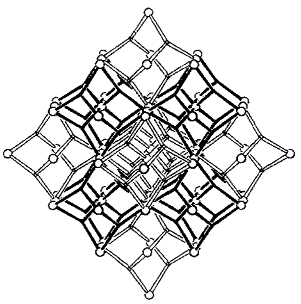


J. A. Halfen, V. G. Young, Jr., W. B. Tolman* 1687–1690

Modeling of the Chemistry of the Active Site of Galactose Oxidase

---

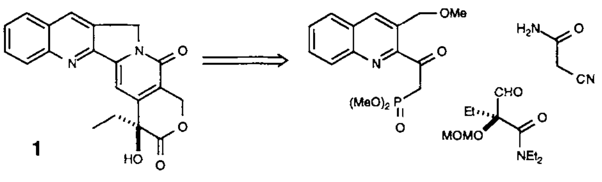
Two independent and identical interpenetrating three-dimensional networks of a highly symmetrical type in which tpt ligands act as trigonal building blocks and Cu^{I} ions as tetrahedral 4-connecting units are contained in cubic crystals of the title compound. Tpt units appear in centrosymmetrically related pairs within which triazine rings make close π–π contacts.



B. F. Abrahams, S. R. Batten, H. Hamit, B. F. Hoskins, R. Robson* 1690–1692

A Cubic (3,4)-Connected Net with Large Cavities in Solvated $[Cu_3(tpt)_4](ClO_4)_3$ (tpt = 2,4,6-Tri(4-pyridyl)-1,3,5-triazine)

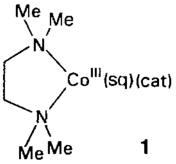
A quinoline, a chiral aldehyde, and cyanoacetamide are the three components (see retrosynthesis below) merged in five steps to afford the antitumor agent (+)-camptothecin (CPT, **1**). The overall yield of CPT is 30% over ten steps from dimethyl 2-ethylmalonate (the precursor of the aldehyde component). MOM = methoxymethyl.

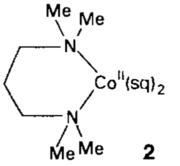


M. A. Ciufolini,* F. Roschangar 1692–1694

Total Synthesis of (+)-Camptothecin

The length of the carbon chain between the N-donor centers of the bidentate amine ligand N–N (= $Me_2N(CH_2)_nNMe_2$) determines the charge distribution in the redox isomers of cobalt complexes of the type $[Co^{III}(N-N)(sq)(cat)]$ and $[Co^{II}(N-N)(sq)_2]$ with semiquinone (sq) and catecholate (cat) as additional ligands. Complexes with tmmda ($n = 1$) and tmeda ($n = 2$; **1**) exist as Co^{III} isomers at temperatures below 350 K. The addition of a third methylene group (tmpda, $n = 3$; **2**) to the chelate ring results in a dramatic drop in the Co^{III}/Co^{II} transition temperature of 200 K.





O.-S. Jung,* D. H. Jo, Y.-A. Lee, Y. S. Sohn, C. G. Pierpont* ... 1694–1695

Ancillary Ligand Dependent Shifts in Charge Distribution for Cobalt–Quinone Complexes

---

Sure diisocyanate (1) exists! Those who believed that of the many conceivable $C_2N_2O_2$ isomers only cyanogendi-*N*-oxide (**1**) could be synthesized were mistaken. It is possible to generate diisocyanate by means of matrix-isolation techniques, to characterize it spectroscopically, and to compile data on its stability.

$O{=}C{=}N{-}N{=}C{=}O$

1

$O{\leftarrow}N{\equiv}C{-}C{\equiv}N{\rightarrow}O$

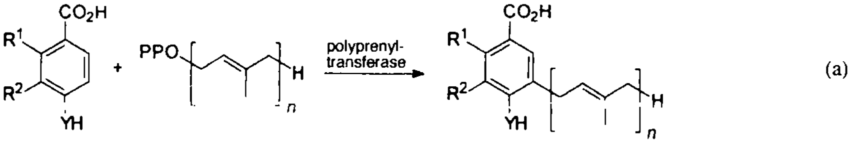
2

G. Maier,* M. Naumann, H. P. Reisenauer, J. Eckwert 1696–1697

Diisocyanate

0570-0833/96/3515-1591 $ 15.00+.25/0

The enzymatic Friedel–Crafts alkylation for the synthesis of up to fivefold ring-substituted 3-polyprenylbenzoic acid derivatives can be accomplished regiospecifically with a polyprenyl-transferase, which exhibits a surprisingly broad substrate spectrum ([Eq. (a)]; OPP = pyrophosphate). Although a membrane enzyme, its simple production and enrichment, and good shelf life provide an excellent basis for general use in organic synthesis.



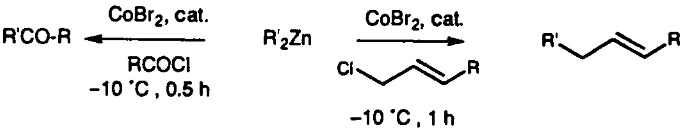
(a)

L. Wessjohann,* B. Sontag 1697–1699

Prenylation of Benzoic Acid Derivatives Catalyzed by a Transferase from *Escherichia coli* Overproduction: Method Development and Substrate Specificity

---

A wide range of polyfunctional ketones and allylic compounds is accessible under mild reaction conditions through an efficient Co^{II}-catalyzed acylation or allylation of diorganozinc compounds (see below). The remarkable stability of the intermediate σ-alkyl transition metal complexes is crucial for the success of the reactions.

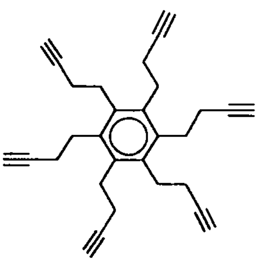


C. K. Reddy, P. Knochel* 1700–1701

New Cobalt- and Iron-Catalyzed Reactions of Organozinc compounds

---

The twelvefold dehydrobromination provides the title compound 1 in a straightforward, easily reproducible synthesis. In the solid state 1 displays a well-defined structure with C_i symmetry, in which four of the the six branches assume *trans* and two assume *gauche* arrangements. Compound 1, which can be stannylated, deprotonated, and complexed, should be a useful intermediate in the preparation of dendritic structures.

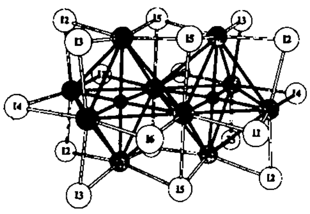


1

H.-W. Marx, F. Moulines, T. Wagner, D. Astruc* 1701–1704

Hexakis(but-3-ynyl)benzene

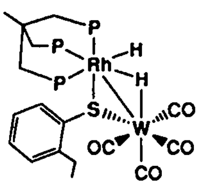
A missing link in the chemistry of rare earth metal cluster compounds stabilized by interstitial transition metals is the new $La_{10}Co_2$ dimeric cluster shown on the right with its iodine environment. The most remarkable structural features of this cluster are the two edge-sharing La octahedra, each centered by a Co atom.



M. Lulei, P. A. Maggard, J. D. Corbett* 1704–1706

The Novel Encapsulation of Transition Metals in a Bioctahedral Rare Earth Metal Cluster: $Cs_2La_{10}I_{17}Co_2$

The heterobimetallic complex 1 is the species that occurs immediately prior to hydrodesulfurization of benzo[*b*]thiophene. The Rh component is responsible for the initial C–S bond scission, and the W component, after addition of hydrogen, for the desulfurization.

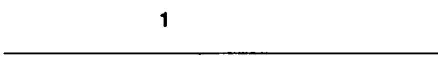


1

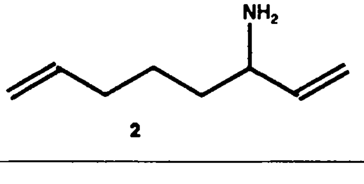
C. Bianchini,* M. V. Jiménez, C. Mealli, A. Meli, S. Moneti, V. Patinec, F. Vizza 1706–1708

Like on Heterogeneous Hydrodesulfurization (HDS) Catalysts, the Homogeneous HDS of Benzo[*b*]thiophene Is Achieved by the Concomitant Action of a Metal Promoter (Rh) and an Active HDS Component (W)

The industrially interesting primary octadienylamines 1 and **2** can be synthesized selectively for the first time from 1,3-butadiene and ammonia. The use of an aqueous catalyst phase together with an organic solvent as a second phase are the key to the success of this process. Consecutive reactions of the primary amines 1 and 2, which are more nucleophilic than ammonia, can thus be avoided.



1

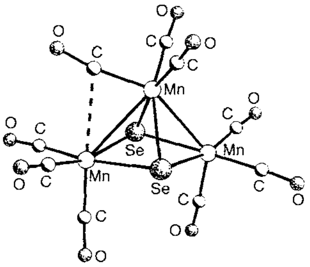


2

T. Prinz, W. Keim, B. Driessen-Hölscher* 1708–1710

Two-Phase Catalysis: A Strategy for Avoiding Consecutive Reactions as Exemplified in the Telomerization of Butadiene and Ammonia

$[Mn_2(CO)_{10}]$ disproportionates in the reaction with Na_2Se in THF leading to $[Mn(CO)_5]^-$ and $[Mn_3Se_2(CO)_9]^{2-}$ ions. In the crystal the former has a square-pyramidal geometry, whereas the latter contains a novel asymmetric carbonyl bridge (see picture on the right), which is also present in the "King complex" $[Fe_3S_2(CO)_9][Fe_2(S_2)(CO)_6]$.

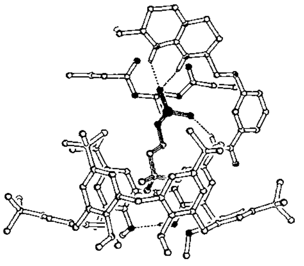


R. Seidel, B. Schnautz, G. Henkel* 1710–1712

$[Mn(CO)_5]^-$, the First Square-Pyramidal Pentacarbonyl Complex in the Complex Salt $[Ph_4P][Mn(CO)_5]$, and $[Mn_3Se_2(CO)_9]^{2-}$, the First Mixed Carbonyl-Selenido Complex of Manganese

---

The two key interactions in the binding of phosphorylcholine by the antibody McPC603 are utilized in the complexation of dioctanoyl-L-α-phosphatidylcholine (DOPC) and a novel non-peptidic abiotic receptor. These interactions are drawn as dotted lines in the structure of the complex shown on the right: hydrogen bonds between the choline phosphate and the guanidinium unit of the receptor, and cation–π interactions between the ammonium group of DOPC and the calixarene unit of the receptor.

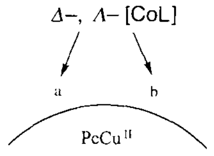


J. O. Magrans, A. R. Ortiz, M. A. Molins, P. H. P. Lebouille, J. Sánchez-Quesada, P. Prados, M. Pons, F. Gago, J. de Mendoza* 1712–1715

A Designed Non-Peptidic Receptor that Mimics the Phosphocholine Binding Site of the McPC603 Antibody

---

Different binding sites a and b on the protein surface (see the schematic diagram on the right) can be selected by enantiomeric metal complexes for electron transfer reactions. This was the result of circular dichroism studies of the products of the reaction between the Cu^{II}-containing plastocyanin ($PcCu^{II}$) and chiral Co^{II} complexes [CoL].



K. Bernauer,* L. Verardo 1716–1717

Selection of Different Reactive Sites by Enantiomers in Electron-Transfer Reactions Involving Metalloproteins

---

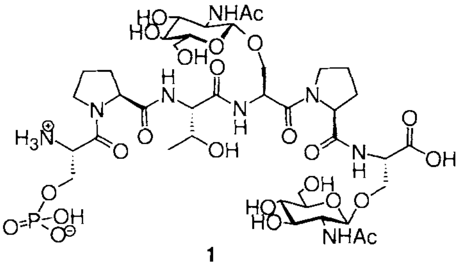
In situ electrophoresis is combined with the selectivity of NMR spectroscopy in electrophoretic NMR (ENMR). In a simple new ENMR experiment the signals of ions and electrically charged molecules or aggregates are filtered from the 1D NMR spectrum of a complex liquid mixture. Only the signals of charged species remain in a phase difference spectrum, facilitating the detection and identification of these particles, even when 2D ENMR methods fail.

S. R. Heil, M. Holz* 1717–1720

Mobility Filter for the Detection and Identification of Charged Species in Complex Liquid Mixtures by ENMR Phase Difference Spectroscopy

---

The application of different enzymatic protecting group techniques has allowed the first synthesis of a complex and sensitive phosphoglycohexapeptides like **1** under very mild conditions. This process makes repeated use of the *p*-phenylacetoxybenzyloxycarbonyl protecting group, which can be cleaved selectively with penicillin G acylase.

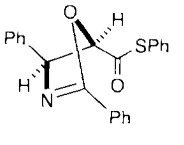


1

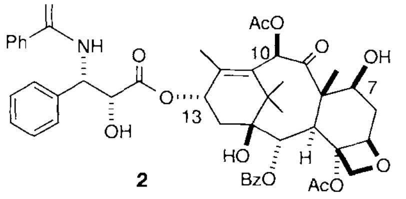
T. Pohl, H. Waldmann* 1720–1723

Enzymatic Synthesis of a Characteristic Phosphorylated and Glycosylated Peptide Fragment of the Large Subunit of Mammalian RNA Polymerase II

The production of Paclitaxel (taxol, 2) on an industrial scale may be possible with a novel semisynthesis relying on the readily accessible 10-deacetylbaccatin III and the side-chain unit **1**. The crucial factor is the remarkably high yield for the 13-O-acylation of the terpene framework, which is usually very difficult. Thioester **1** can be prepared fairly directly with the desired relative and absolute configuration by addition of the appropriate boron enolate to an imine.



1

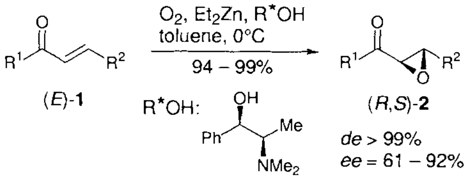


2

C. Gennari,* A. Vulpetti, M. Donghi, N. Mongelli, E. Vanotti 1723–1725

Semisynthesis of Taxol: A Highly Enantio- and Diastereoselective Synthesis of the Side Chain and a New Method for Ester Formation at C13 Using Thioesters

An efficient method for the asymmetric epoxidation of α,β-unsaturated ketones **1** is embodied in their reaction with oxygen in the presence of diethylzinc and (*R*,*R*)-*N*-methylpseudoephedrine. It affords epoxides **2** in excellent yields, with complete diastereoselectivity, and with enantiomeric excesses of up to 92% *ee*. The enantiomerically pure amino alcohol employed can be recovered virtually quantitatively with unchanged optical purity.

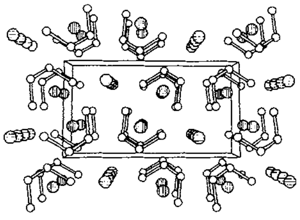


D. Enders,* J. Zhu, G. Raabe 1725–1728

Asymmetric Epoxidation of Enones With Oxygen in the Presence of Diethylzinc and (*R*,*R*)-*N*-Methylpseudoephedrine

---

A reaction of laughing gas and Na_2O at 360 °C provides the title compound. In the crystal the planar $N_2O_2^{2-}$ ions form channels in which the Na cations are lined up like linear strings (picture right; ⊜ Na; o N,O). The Na cations are thus surrounded in a pseudo octahedral manner by the almost planar anions.

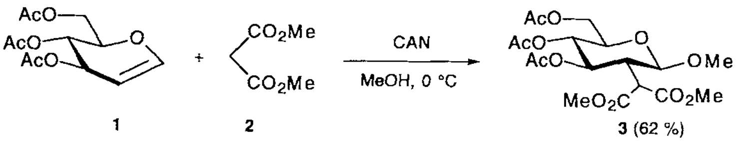


C. Feldmann, M. Jansen* 1728–1730

cis-Sodium Hyponitrite—A New Preparative Route and a Crystal Structure Analysis

---

Mild reaction conditions and high stereoselectivities characterize the addition of dimethyl malonate (**2**) to tri-*O*-acetyl-D-glucal (**1**) in the presence of cerium(IV) ammonium nitrate (CAN). Thus, the glucose C-analogue **3** can be synthesized in only one step in 62% yield.

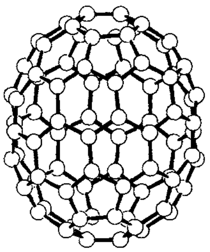


T. Linker,* K. Hartmann, F. Sommermann, D. Scheutzow, E. Ruckdeschel 1730–1732

Transition-Metal-Mediated Radical Reactions as an Easy Route to 2-C-Analogoues of Carbohydrates

---

One isomer of C_{80} with D_2 symmetry (shown on the right) is isolated from carbon soot generated by graphite arc discharge in helium. A comparison of the experimentally determined ^{13}C NMR shifts with those obtained from ab initio calculations indicates that this isomer corresponds to the most stable D_2 form.



F. H. Hennrich, R. H. Michel, A. Fischer, S. Richard-Schneider, S. Gilb, M. M. Kappes,* D. Fuchs, M. Bürk, K. Kobayashi, S. Nagase 1732–1734

Isolation and Characterization of C_{80}

* Author to whom correspondence should be addressed

BOOKS

0570-0833/96/3515-1594 $ 15.00+.25/0

German versions of all reviews, communications, and highlights in this issue appear in the first August issue of *Angewandte Chemie*. The appropriate page numbers can be found at the end of each article and are also included in the Author Index on p. 1741.

All the Tables of Contents from 1995 may be found on the WWW under **http://www.vchgroup.de**

SERVICES

The following reviews will appear in future issues:

Saccharide Sensing with Boronic Acid-Based Molecular Receptors
K. R. A. Samankumara Sandanayake, Tony D. James, and Seiji Shinkai

Structural Aspects of Nucleic Acid Analogs and Antisense Oligonucleotides
Martin Egli

My Life with O_3, NO_x, and Other YZO Compounds (Nobel Lecture)
P. J. Crutzen

Polar Ozone Depletion (Nobel Lecture)
M. J. Molina

Stratospheric Ozone Depletion by Chlorofluorocarbons (Nobel Lecture)
F. S. Rowland

Two-Metal Ion Catalysis in Enzymatic Acyl and Phorphoryl Transfer Reactions
B. Krebs

Protecting Group Strategies in Organic Synthesis
H. Waldmann

From Molecular Pattern of Morphogenesis. The Lessons Learned from Drosophila
E. F. Wieschaus

The Identification of Genes Controlling Development
C. Nusslein-Vollhard

What Can We Learn from Molecular Recognition in Protein—
Ligand Complexes for the Design of New Drugs?
Hans-Joachim Böhm and Gerhard Klebe

Enantioselective Protonation of Enolates and Enols
C. Fehr

Chiral Recognition in π Complexes of Alkenes, Aldehydes, and Ketones with Transition Metal Lewis Acids;
Development of a General Model for Enantioface Binding Selectivities
J. A. Gladysz, B. J. Boone

ANGEWANDTE CHEMIE

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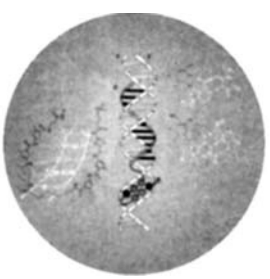
Gesellschaft
Deutscher Chemiker

International Edition in English

1996/35
13/14
Pages 1357–1584

COVER PICTURE

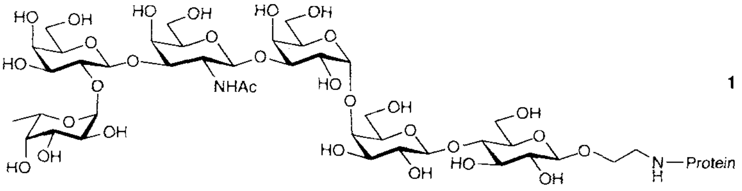


The cover picture shows a ribbon model of a hairpin pyrrole/imidazole polyamide–oligonucleotide simultaneously binding the major and minor grooves of DNA (red circles: *N*-methylimidazole; blue circles: *N*-methylpyrrole rings; diamond: β-alanine). The structural formulas on the right depict the molecular interactions responsible for sequence-specific recognition: T·AT and C+GC base triplets are formed by Hoogstein hydrogen bonding of T to a Watson–Crick AT base pair and protonated ^{Me}C to a Watson–Crick GC base pair. On the left is the complex of the polyamide ImPyPy-γ-ImPyPy-β with the site 5′-TGACA-3′ (circles with dots: lone pairs on N3 of purines and O2 of pyrimidines; circles containing an H: N2 hydrogen on guanine; dashed lines: putative hydrogen bonds). The energetics and specificity of the complex is reported by Szewczyk et. al. on pages 1487ff. The picture was generated with MacDraw Pro software.

REVIEWS

Contents

Open-minded carbohydrate chemists are well advised to consider glycals for oligosaccharide synthesis. Glycal-based methods, which obviate many of the onerous protecting group manipulations that have dominated this field, have led to syntheses of blood group determinants and antigen recognition domains. The artificial glycoprotein at the most advanced stage of preclinical development is the protein conjugate **1** of the human globo H breast tumor antigen.



1

S. J. Danishefsky,*
M. T. Bilodeau 1380–1419

Glycals in Organic Synthesis: The Evolution of Comprehensive Strategies for the Assembly of Oligosaccharides and Glycoconjugates of Biological Consequence

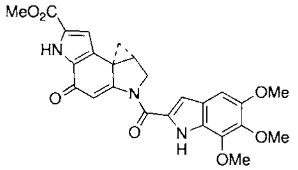
New precursors and different gelation processes are among the most important results to have emerged from the field of sol–gel chemistry in the last few years. In particular, the use of nonhydrolytic processes and the application of organic–inorganic precursors in the preparation of gels are very promising developments. These have brought the planned synthesis of solids with specific properties a step closer.

R. Corriu,* D. Leclercq 1420–1436

Recent Developments of Molecular Chemistry for Sol–Gel Processes

---

A class of potent antitumor antibiotics including CC-1065 and the duocarmycins (for example **1**) and their properties relevant for DNA alkylation are the topics of this review. The hypotheses on the mechanism of their function are defined with the evidence gleaned from synthetic derivatives and the *ent*-isomers of the natural products. The deduced fundamental relationships between structure, functional reactivity, and biological properties are described.



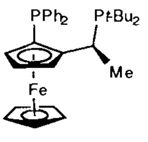
1, (+)-Duocarmycin SA

D. L. Boger,*
D. S. Johnson 1438–1474

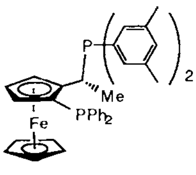
CC-1065 and the Duocarmycins: Understanding their Biological Function through Mechanistic Studies

HIGHLIGHTS

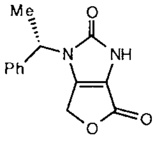
The first industrial applications of chiral ferrocenyl ligands of the Josiphos type have recently been disclosed. Compound **1a** is used in the Rh-catalyzed, asymmetric hydrogenation of **2**, a precursor in a new commercial synthesis of (+)-biotin. Ligand **1b** is part of the highly active Ir catalyst used for the reduction of imine **3**, from which the herbicide (*S*)-Metolachlor is made.



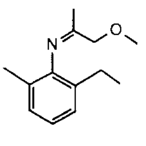
1a



1b



2



3

Å. Togni* 1475–1477

Planar-Chiral Ferrocenes: Synthetic Methods and Applications

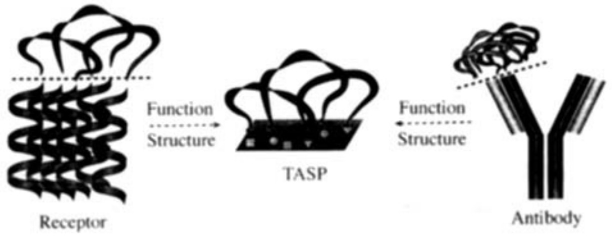
Why are diradicals used as hydrogen abstraction agents in the enediyne antitumor antibiotics, and what would happen if a "nonnatural" diradical were to be used? The very slow abstraction rates by arene diradicals suggest an answer to the question of the functional significance of diradicals versus monoradical abstraction agents in the natural products, and furthermore, suggest potential strategies for the rational modification of DNA-cleaving agents by alteration of the diradical "warhead".

P. Chen* 1478–1480

Design in Diradical-Based Hydrogen Abstraction Agents

COMMUNICATIONS

The bare essentials of a functional protein are all that are retained when the structural domain of a native protein is replaced by a synthetic template molecule (see picture below). New strategies for the synthesis of this novel type of template-assembled synthetic peptide (TASP) provide functional mimetics of receptors and antibodies.



M. Mutter,* P. Dumy, P. Garrouste,
C. Lehmann, M. Mathieu, C. Peggion,
S. Peluso, A. Razaname,
G. Tuchscherer 1482–1485

Template-Assembled Synthetic Proteins (TASP) as Functional Mimetics of Proteins

A Ni$_8$ cube, assembled with twelve bridging μ-violurato ligands, is present in **1** (H_3vi = violuric acid). The oximate groups of the ligands lie along the edges of the cube, connecting the metal ions in an unprecedented *trans* conformation (see picture, ● = Ni) and mediating a strong antiferromagnetic coupling between the paramagnetic centers about 5 Å apart. Counterions: Ni^{2+}, 4 K^+.

$[Ni_8(Hvi)_{10}(H_2vi)_2]^{6-}$ **1**

J. Faus,* F. Lloret, M. Julve,
J. M. Clemente-Juan, M. C. Muñoz,
X. Solans, M. Font-Bardia 1485–1487

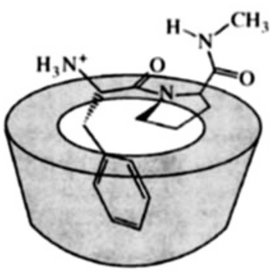
Synthesis, Crystal Structure, and Magnetic Properties of an Octanuclear Nickel(II) Complex with an Hexahedro-Ni$_8$ Core

A combination of the binding models for the simultaneous recognition of both grooves of DNA led to the design of a polyamide–oligonucleotide ligand that binds to a specific DNA sequence with an association constant of $K_a > 2 \times 10^{10}$ M^{-1}. The oligonucleotide portion forms a triple helix in the major groove of DNA, and the polyamide unit forms a hairpin in the minor groove (see ribbon model below).

J. W. Szewczyk, E. E. Baird,
P. B. Dervan* 1487–1489

Sequence-Specific Recognition of DNA by a Major and Minor Groove Binding Ligands

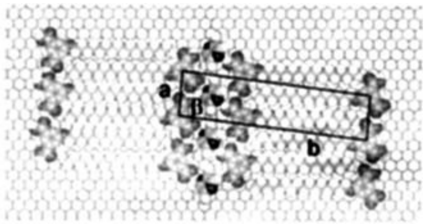
A combinatorial approach revealed the highly selective binding of the dipeptides L-Phe-D-Pro and D-Phe-L-Pro to β-cyclodextrin. NMR spectroscopy and molecular modeling provide a picture of the possible binding mode and an explanation of why those specific dipeptides were selected from the tripeptide library.



M. Maletic, H. Wennemers,
D. Q. McDonald, R. Breslow,*
W. C. Still* 1490–1492

Selective Binding of the Dipeptides L-Phe-D-Pro and D-Phe-L-Pro to β-Cyclodextrin

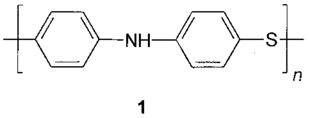
Molecular recognition in monolayers on graphite: Stoichiometric (2:1) donor–acceptor complexes of 5-alkoxyisophthalic acids with bifunctional aromatic bases have been detected with scanning tunneling microscopy (STM). The 2D crystal lattice of the donor–acceptor complex from the hexadecoxy-substituted isophthalic acid and 2,5-dimethylpyrazine is shown schematically below.



K. Eichhorst-Gerner, A. Stabel,
G. Moessner, D. Declerq, S. Valiyaveettil,
V. Enkelmann, K. Müllen,*
J. P. Rabe* 1492–1495

Self-Assembly of a Two-Component Hydrogen-Bonded Network: Comparison of the Two-Dimensional Structure Observed by Scanning Tunneling Microscopy and the Three-Dimensional Crystal Lattice

Two structures, one polymer. Two important materials, polyaniline and polyphenylenesulfide, have been combined to form a single compound, poly(phenylenesulfidephenylenamine) (PPSA, **1**). The new soluble polymer **1** can be obtained with well-defined structure and high molecular weight from a polysulfonium cation precursor.

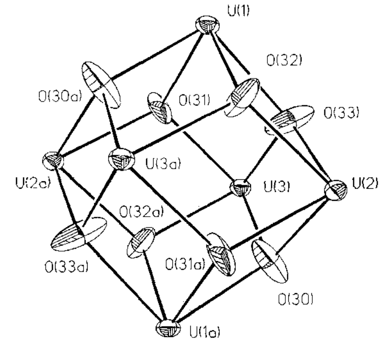


1

L. X. Wang, T. Soczka-Guth, E. Havinga,
K. Müllen* 1495–1497

Poly(phenylenesulfidephenylenamine) (PPSA)—the "Compound" of Polyphenylenesulfide with Polyaniline

The first high-nuclearity uranium complex contains an octahedral array of metal centers that is coordinated by twelve diphenylphosphate as well as eight oxo or hydroxo ligands. Although the degree of protonation of the capping centers could not be determined unambiguously, many of the findings point to OH ligands. The picture on the right shows the U_6O_8 framework of the complex.

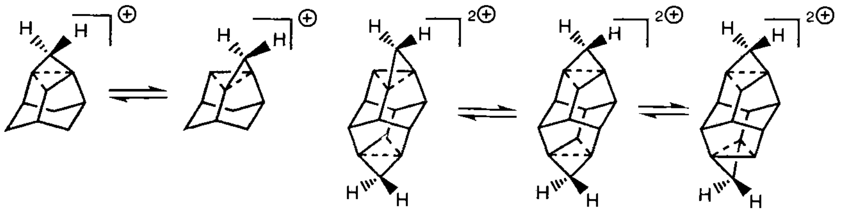


L. M. Mokry, N. S. Dean,
C. J. Carrano* 1497–1498

Synthesis and Structure of a Discrete Hexanuclear Uranium–Phosphate Complex

---

A description as sets of nonclassical, unsymmetric, bridged bicyclobutonium ions fits the title ions **1** and **2**. These are accessible by ionization of the corresponding methanol derivatives in superacidic media; the assignment of structure rests on ab initio calculations and on comparisons of experimental and calculated ^{13}C NMR chemical shifts.



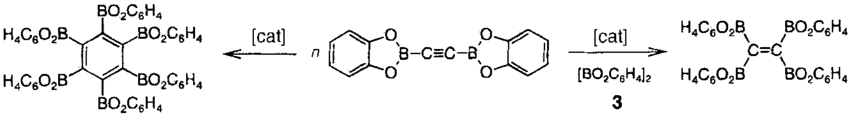
1a, 1b **2a** **2b** **2c**

G. A. Olah,* H. A. Buchholz,
G. K. S. Prakash,* G. Rasul,
J. J. Sosnowski, R. K. Murray Jr.,*
M. A. Kusnetsov, S. Liang,
A. de Meijere* 1499–1501

2-Triaxanemethyl Cation and 2,10-*para*-[$3^2.5^6$]Octahedranedimethyl Dication

---

Transition metal catalyzed reactions of the diborylacetylene 1 allow access to perborylated C–C multiply bonded systems. Cyclotrimerization of **1** results in the hexaborylbenzene **2**. Diboration of **1** with the diborane **3** provides the tetraborylethene derivative **4**. Compounds **2** and **4** react with LiMe and $AlMe_3$ under cleavage of the boron–oxygen bonds. The dodecamethyl derivative $C_6(BMe_2)_6$ forms the structurally characterized complex $[C_6(BMe_2)_6 \cdot 2Li_2O_2C_6H_4 \cdot 8NC_5H_5]$ with pyridine and $Li_2O_2C_6H_4$.

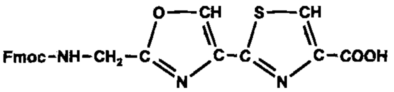


2 **1** **4**

A. Maderna, H. Pritzkow,
W. Siebert* 1501–1503

Hexaborylbenzene and Tetraborylethene Derivatives

An important step in the synthesis of heterocyclic amino acids such as 1, which can be used to modify and constrain peptide backbones, is the newly developed oxidation of dihydrooxazoles to give oxazoles with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)/CCl_4/acetonitrile/pyridine.



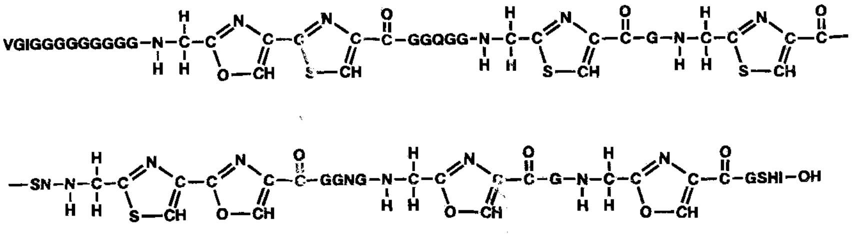
1

G. Videnov, D. Kaiser, C. Kempter,
G. Jung* 1503–1506

Synthesis of Naturally Occurring, Conformationally Restricted Oxazole- and Thiazole-Containing Di- and Tripeptide Mimetics

---

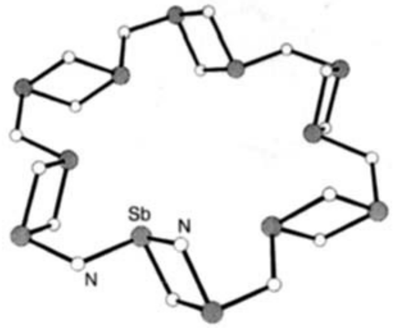
One of the most unusual ribosomally synthesized and posttranslationally modified polypeptides, microcin B17, is a polypeptide antibiotic (see structure below). The total synthesis of this large molecule with oxazole and thiazole rings now enables structure–activity studies in a very important field of drug targeting.



G. Videnov, D. Kaiser, M. Brooks,
G. Jung* 1506–1508

Synthesis of the DNA Gyrase Inhibitor Microcin B17, a 43-Peptide Antibiotic with Eight Aromatic Heterocycles in its Backbone

Six Sb_2N_2 rings linked by single imido- N bridges to give a 24-membered ring characterize the structure of the title compound (the core is shown on the right). This is the largest Group 15 metal-imido complex to be structurally characterized and the first p block metal-imido metallacycle.

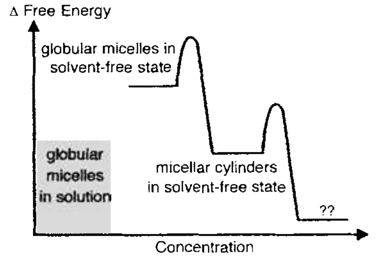


M. A. Beswick, M. K. Davies, M. A. Paver, P. R. Raithby, A. Steiner, D. S. Wright* 1508-1510

$[Sb_{12}\{(2\text{-MeO})C_6H_4N\}_{18}]\cdot 6THF$; a Twenty-Four Membered Imidoantimony(III) Metallacycle

---

Formation of reverse cylindrical micelles of a block copolymer with a long core block is kinetically controlled. The diagram shows the relative energy of the different structures.

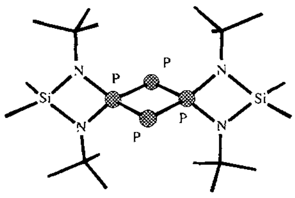


J. P. Spatz, S. Mössmer, M. Möller* 1510-1512

Metastable Reverse Globular Micelles and Giant Micellar Wires from Block Copolymers

---

The bonds are of equal length between the four P atoms, two with the coordination number 4 and two with the coordination number 2, that form the central four-membered ring of the dispirocyclic tetraphosphete **1**. This ring exhibits a large rhombic distortion that is manifested by an unusually acute λ^5P-λ^3P-λ^5P angle.



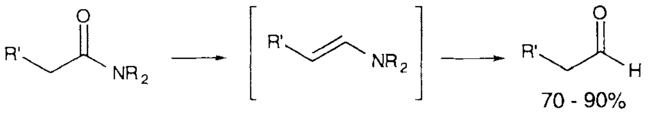
1

W. Frank,* V. Petry, E. Gerwalin, G. J. Reiss 1512-1514

Synthesis, Structure, and Bonding of a Mixed-Valent Tetraphosphete

---

A wide range of amides containing different functional groups were readily converted into their corresponding aldehydes by means of a simple protocol. The reaction with $[Ti(OiPr)_4]$ and Ph_2SiH_2 proceeds at room temperature via an enamine intermediate, which is then hydrolyzed to afford the aldehyde [Eq (a)].



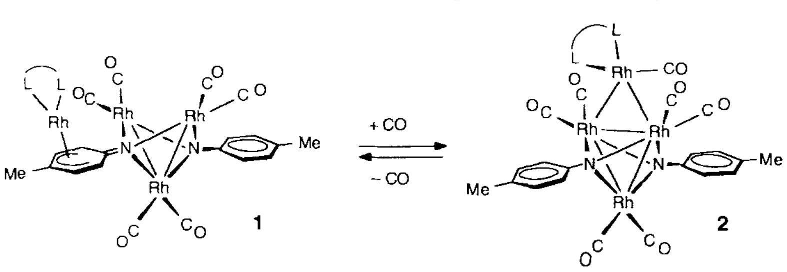
(a)

S. Bower, K. A. Kreutzer, S. L. Buchwald* 1515-1516

A Mild General Procedure for the One-Pot Conversion of Amides to Aldehydes

---

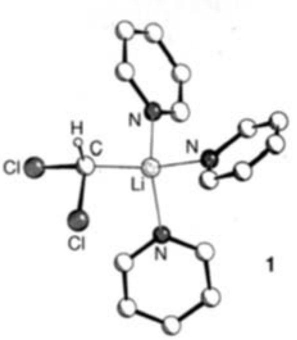
The formation of three new metal-metal bonds results from the addition of CO to the tetranuclear complex **1**. This process involves the migration of the Rh center coordinated to the arene ligand in **1** to the open edge of the Rh_3 core to give the complex **2**. The reaction is reversible, and thus the Rh center hops from one site to the other by addition or removal of a two-electron ligand. $\overset{\frown}{L\ L}$ = 1,5-cyclooctadiene.



C. Tejel, Y.-M. Shi, M. A. Ciriano,* A. J. Edwards, F. J. Lahoz, L. A. Oro* 1516-1518

Reversible Formation of Raftlike Organoimidotetrarhodium Clusters by the Migration of RhL_n^+ Fragments

C–Cl bonds approximately 10 pm longer than those in CH_2Cl_2 are present in $LiCHCl_2 \cdot 3C_5H_5N$ (**1**). This and the sum of the bond angles around C (308° excluding the C–Li bond) confirms the increased p character of the C–Cl bonds and thus the pronounced electrophilicity of carbenoids. Calculations on the solvated and nonsolvated carbenoid and the comparison with experimental data reveal the remarkable influence of solvation on structure, stability, and ^{13}C chemical shift, which is useful for predicting the structures of such molecules in solution.

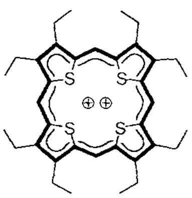


A. Müller, M. Marsch,
K. Harms, J. C. W. Lohrenz,
G. Boche* 1518–1520

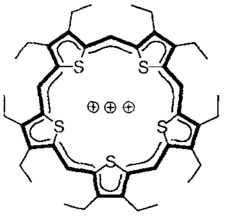
$LiCHCl_2 \cdot 3$ Pyridine, Structure of a Carbenoid with a Tetrahedral C Atom

---

As a model compound in the thiaporphyrin series, the perchlorate of the dication **1** is ideal because of its favorable solubility properties. The key step in its synthesis is the acid-induced condensation (not biomimetic!) of 3,4-diethyl-2-hydroxymethylthiophene that affords the tetra- as well as the pentacyclocondensation product. The latter product opens a route to the 22π pentathiapentaphyrin trication **2**, the sulfur analog of pentaphyrin.



1



2

E. Vogel,* M. Pohl, A. Herrmann, T. Wiss,
C. König, J. Lex, M. Gross,*
J. P. Gisselbrecht 1520–1524

Porphyrinoid Macrocycles Based on Thiophene—The Octaethyltetrathiaporphyrin Dication

---

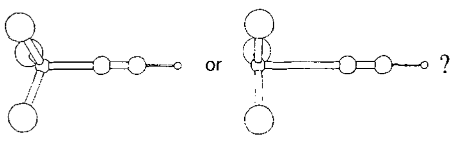
A comfortable fit is provided for the large tetrabutylammonium ion within the wide channels of the new host–guest compound $[(nBu_4N)_{0.5}(Me_3Sn)_{3.5}Fe(CN)_6]$. The lipophilic walls are formed by helical $\{$Fe-CN-Sn-NC$\}_x$ chains involving $\{Fe(CNSnMe_3)_6\}$ octahedra that are enantiomorphically derivatized due to cross-linking.

P. Schwarz, S. Eller, E. Siebel,
T. M. Soliman, R. D. Fischer,*
D. C. Apperley, N. A. Davies,
R. K. Harris* 1525–1527

Template-Driven Syntheses of Polymeric Metal Cyanides: A Chiral Nanoporous Host for the nBu_4N^+ Ion

---

The remarkable change in the B–N bond lengths of $CH_3CN \cdot BF_3$ and $HCN \cdot BF_3$ between the gas phase and the condensed phase has been attributed to effects of the surrounding medium. Results herein suggest that in BF_3-rich argon matrices, $CH_3CN \cdot BF_3$ and $HCN \cdot BF_3$ are present in the form with a short B–N bond, as is $CH_3CN \cdot BF_3$ in solution in benzene. The two structural alternatives for $HCN \cdot BF_3$ are shown schematically above.



I. R. Beattie,* P. J. Jones 1527–1529

The Effect of the Surrounding Medium on the Interaction of Nitriles with Boron Trifluoride

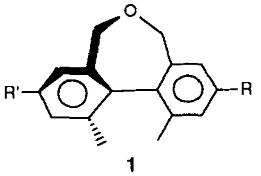
---

Rotations of the atoms around the center of gravity of the molecule characterize the cooperative intramolecular movement of the two lithium atoms in the solid amide $Li_2[(tBu{-}O{-}SiMe_2)_2N]_2$ just above room temperature. This movement can be stopped by cooling the sample, whereupon a phase transition occurs. A further phase transition occurs at temperatures above 100 °C leading to a "plastic phase" in which whole molecules tumble around their centers of gravity.

M. Veith,* M. Zimmer, K. Fries,
J. Böhnlein-Maus, V. Huch 1529–1533

Intramolecular Movements of Lithium in Crystals

Cholesteric mesophases are formed by compounds of type **1** with axial chirality. The key to this behavior is the rigid twisted biphenyl core; the planes of the two aryl rings form an angle of 56° ($R = R' = 4\text{-}C_8H_{17}OC_6H_4CO_2$).

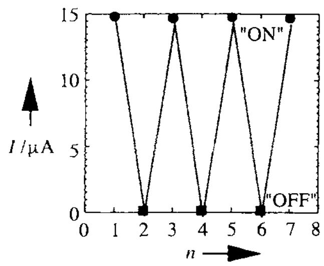


1

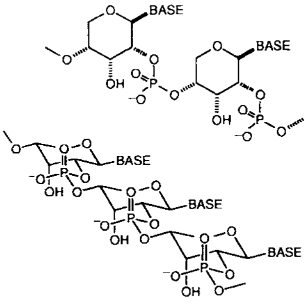
G. Solladié,* P. Hugelé, R. Bartsch,
A. Skoulios 1533–1535

New Family of Enantiomerically Pure Liquid Crystals Containing a Chiral Biphenyl Core

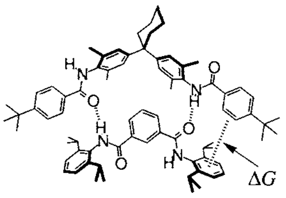
A phenoxynaphthacenequinone forms a densely packed monolayer together with 1-tetradecanethiol on a gold electrode. The assembly can be reversibly switched to enable amperometric transduction of an optical signal. In the diagram on the right the current is switched off by irradiation with UV light.



Pyranosyl-RNA, an isomer of natural RNA (constitution and pairing conformation shown on the right), displays remarkable properties. Homochiral pyranosyl-RNA strands with opposite senses of chirality are found to pair to give quasi-racemic duplexes. Correspondingly altered pairing rules result.

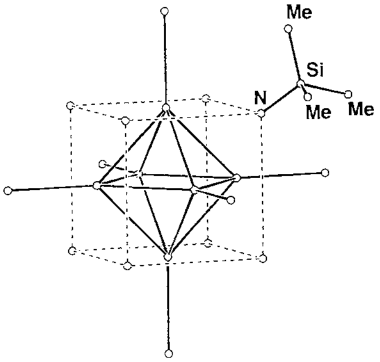


Quantitative descriptions of complex recognition processes rely on the measurement of the magnitude of weak intermolecular interactions such as the π–π interaction between arene units. In one approach thermodynamic cycles of compounds with structural variations (mutations) are constructed. The association energy ΔG for the edge-to-face π–π interaction in complex **1** was determined to be 1.4 ± 0.8 kJ mol^{-1}.

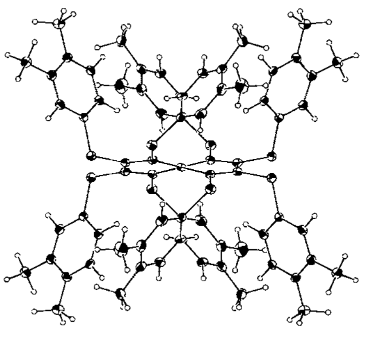


1

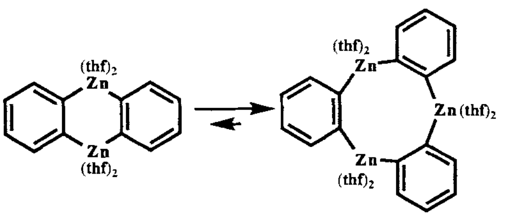
Under extremely mild conditions, $[Re_6Q_5Cl_9]^-$ ions (Q = S, Se) react with bis(trimethylsilyl)amine derivatives to give clusters of the type $[Re_6Q_5(\mu_3\text{-}NSiMe_3)Cl_8]^{2-}$ (shown on the right). These are isostructural and isoelectronic with the Chevrel–Sergent cluster cores $[Mo_6Q_8]^{4-}$. The μ_3-imido-functionalized clusters react with electrophiles and thus offer opportunities to extend the chemistry of genuine inorganic–organic hybrid compounds.



Nanoscale cavities with *T* symmetry capable of accommodating such diverse species as $S{=}CCl_2$, $PbEt_4$, and C_{60} are formed by the designed title compound. The adducts crystallize, uniquely for a purely organic system, in the cubic space group *Pn*$\bar{3}$. The crystal structure of the title compound in its $PbEt_4$ clathrate is shown on the right.



Dimeric in the crystal and trimeric in THF solution—this remarkable phenomenon is shown by *ortho*-phenylenezinc, which can be obtained from the analogous mercury compound and zinc. In solution the equilibrium shown below lies well to the right. The dimer probably crystallizes due to favorable packing effects.



M. Schreuder Goedheijt, T. Nijbacker,
O. S. Akkerman, F. Bickelhaupt,*
N. Veldman, A. L. Spek 1550–1552

Synthesis and Structure of *ortho*-Phenylenezinc

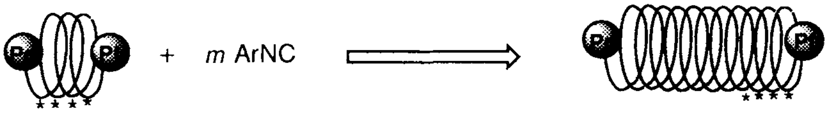
By employing boronato instead of carboxylato bridges in the dication $[\mathrm{Mn}_2^{IV}(\mu\text{-O})(\mu\text{-PhBO}_2)_2\mathrm{L}_2]^{2+}$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane), a Mn_2^{IV} unit has been stabilized for the first time. Together with the di-μ-carboxylato-μ-oxodimanganese complexes of analogous structure, there is now an "isostructural series" available containing Mn_2^{II}, $\mathrm{Mn}^{II}\mathrm{Mn}^{III}$, Mn_2^{III}, $\mathrm{Mn}^{III}\mathrm{Mn}^{IV}$, Mn_2^{IV} units. The Mn K-edge energy of the corresponding complexes increases linearly with increasing oxidation level. This is of importance for EXAFS investigations of metalloproteins containing manganese.

U. Bossek, H. Hummel, T. Weyhermüller,
K. Wieghardt,* S. Russell,
L. van der Wolf, U. Kolb 1552–1554

The $[\mathrm{Mn}_2^{IV}(\mu\text{-O})(\mu\text{-PhBO}_2)_2]^{2+}$ Unit: A New Structural Model for Manganese-Containing Metalloproteins

---

Single-handed helical polymers of the type **2** are the products of the screw-sense-selective polymerization of achiral isocyanides ArNC initiated by the helical oligomer complexes **1**. The latter are accessible from μ-ethynediyl-bridged dinuclear Pd,Pt complexes by reaction with $3\text{-CNC}_6\text{H}_4\text{CO}_2\text{R}^*$ (R* = (+)- and (−)-menthyl).



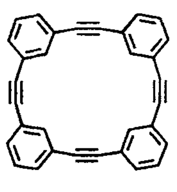
1 **2**

F. Takei, K. Yanai, K. Onitsuka,
S. Takahashi* 1554–1556

Screw-Sense-Selective Polymerization of Isocyanides by Dinuclear μ-Ethynediyl Complexes

---

The smallest [2$_n$]metacyclophan-*n*-yne known to date is the title compound **1**. It was synthesized from the precursor tetraenes by bromination/dehydrobromination and is stable at room temperature. According to an X-ray structure analysis, **1** is nearly planar and the alkyne units are slightly bent (167.7–169.9°).

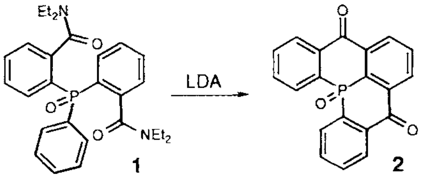


1

T. Kawase, N. Ueda, H. R. Darabi,
M. Oda* 1556–1558

[2.2.2.2]Metacyclophane-1,9,17,25-tetrayne

A new double anionic equivalent of the Friedel–Crafts reaction is observed upon treatment of the carbamoyltriarylphosphane oxide **1** with lithium diisopropylamide (LDA) to produce the phosphacycle **2**. The scope of this and related reactions is delineated.

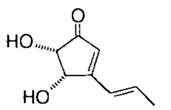


M. Gray, B. J. Chapell, N. J. Taylor,
V. Snieckus* 1558–1560

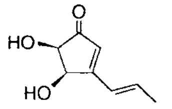
Carbanion-Mediated Heterocyclizations: Regiospecific, General Route to Dibenzo[*b,e*]phosphininones by Synthetic Anionic Equivalents of Friedel–Crafts Reactions and Remote Fries Rearrangement

---

The complete desymmetrization of optically inactive *meso*-tartaric acid with (+)-camphor in the presence of trimethyl orthoformate is the key to the synthesis of both enantiomers of the cyclopentenoid isoterrein in enantiomerically pure form.



(−) - (*S,S*) - isoterrein



(+) - (*R,R*) - isoterrein

M. Mikołajczyk,* M. Mikina,
M. W. Wieczorek,
J. Błaszczyk 1560–1562

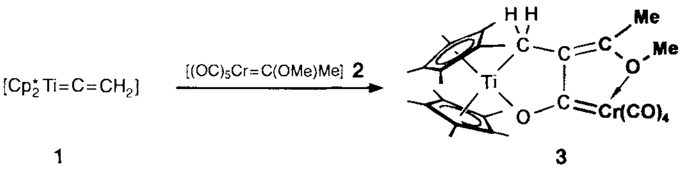
The First Synthesis of Enantiopure (−)- and (+)-Isoterrein from Optically Inactive *meso*-Tartaric Acid

High yields and selectivities are achieved for the alkylation of 1-naphthol with alcohols in the presence of an iron catalyst in a continuous gas-phase process. The resulting 2-alkyl-1-naphthols can be easily separated from the product mixture. This opens up new possibilities for the synthesis of important industrial intermediates.

H. Grabowska, W. Mišta, L. Syper,
J. Wrzyszcz,* M. Zawadzki 1562–1565

Alkylation of 1-Naphthol with Alcohols over an Iron Oxide Catalyst

The first example of an intermolecular carbene–carbene coupling reaction between a Fischer and a Schrock carbene ligand is achieved by coupling of the vinylidene fragment in **1** with the methoxyethylidene ligand in **2**. In the resulting red titanacyclic chromium carbene complex **3** the chromium is coordinated in such a way by the methoxy substituent that the bicyclic framework is virtually planar.

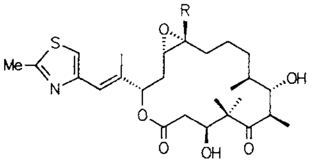


1 **3**

R. Beckhaus,* J. Oster, R. Kempe,
A. Spannenberg 1565–1567

Intermolecular Carbene–Carbene Coupling of a Nucleophilic Vinylidene and an Electrophilic 1-Methoxyethylidene Ligand

How similar must a compound be to taxol in order to displace it from its binding site on microtubules? The microbial secondary metabolites epothilones A (**1a**) and B (**1b**) provide an answer to this question. These comparatively small, simply constructed, and highly cytotoxic macrolides surprisingly show no similarity to taxol, according to X-ray and NMR spectroscopic results.

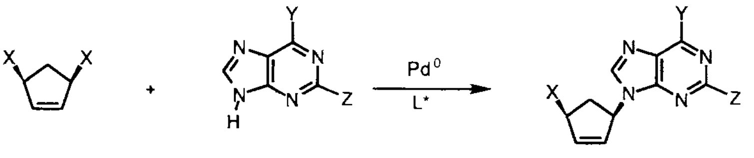


1a R = H
1b R = CH_3

G. Höfle,* N. Bedorf, H. Steinmetz,
D. Schomburg, K. Gerth,
H. Reichenbach 1567–1569

Epothilone A and B—Novel 16-Membered Macrolides with Cytotoxic Activity: Isolation, Crystal Structure, and Conformation in Solution

Surprisingly, purines, unlike other nucleophiles, affect the enantioselectivity of the Pd-catalyzed desymmetrization of *cis*-3,5-diacyloxycyclopent-1-enes **1**, even though they are formally not involved in the enantiodiscriminating step. Under suitable conditions this influence can be minimized. From **2**, the alkylated adenine and analogues **3** can be obtained, and the latter can be employed in the short asymmetric syntheses of antiviral agents (−)-carbovir and (−)-aristeromycin. X = $PhCO_2$; Y = $OCONPh_2$, NH_2, Cl; Z = H, NH_2, NHAc; L* = chiral ligand.

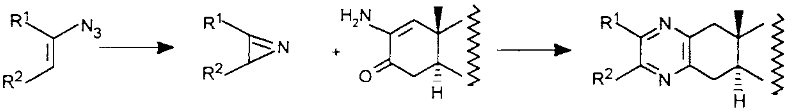


1 **2** **3**

B. M. Trost,* R. Madsen, S. G. Guile,
A. E. H. Elia 1569–1572

A Short Enantioselective Synthesis of Carbanucleosides

Thermolysis of vinylazides affords azirines that can be captured in situ with enamino ketones. This reaction sequence (see below) was developed into a new general method for the preparation of nonsymmetrical pyrazines and applied to the synthesis of cephalostatin analogues with high biological activity.



M. Drögemüller, R. Jautelat,
E. Winterfeldt* 1572–1574

Directed Synthesis of Nonsymmetrical Bis-Steroidal Pyrazines and the First Biologically Active Cephalostatin Analogues

---

* Author to whom correspondence should be addressed

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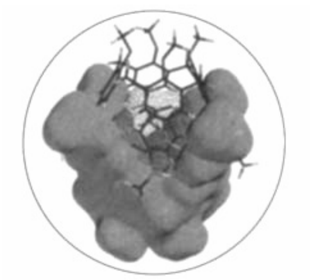
Pages 1249–1356

COVER PICTURE

The cover picture shows the van der Waals surface (represented by a grid) and the structure (stick model) of a benzene molecule included in the cavity of a molecular capsule. This host is composed of two calix[4]arenes that are held together by hydrogen bonds. The blue space-filling model at the bottom represents the van der Waals surface of the bottom calixarene, the gray stick model the structure of the upper calixarene. The host–guest complex is obtained within minutes by simply stirring a solution containing the calix[4]arene dimer and benzene. J. Rebek, Jr. et al. report more on p. 1326ff on the affinities of these calixarene capsules to other molecules.



REVIEWS

Contents

Chiral *ansa*-metallocene complexes are excellent catalysts for enantioselective carbomagnesations, hydrogenations, polymerizations, and Diels–Alder reactions. They can also be employed in stoichiometric amounts as chiral mediators in enantioselective reactions; however, recovery of the metallocene is not always possible. The future of chiral metallocene catalysts in preparative organic chemistry depends critically on their cost and ease of preparation.

A. H. Hoveyda,*
J. P. Morken 1262–1284

Enantioselective C–C and C–H Bond Formation Mediated or Catalyzed by Chiral ebthi Complexes of Titanium and Zirconium

---

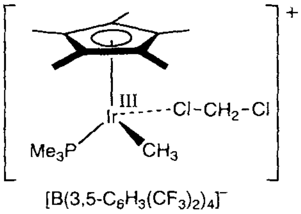
Predicting structures of solids capable of existence is the first step in planning the syntheses of solid-state compounds. The modular approach presented here determines such structure candidates by using global optimization methods to find metastable minima on the potential energy surface. So far the method has been applied to systems characterized by ionic or van der Waals bonding. The good agreement with experimental findings suggests that predictions for yet unknown compounds, for example alkali metal nitrides such as Na_3N and Ca_3SiBr_2, are also most likely to be correct.

J. C. Schön, M. Jansen* 1286–1304

First Step Towards Planning of Syntheses in Solid-State Chemistry: Determination of Promising Structure Candidates by Global Optimization

HIGHLIGHTS

Very selective and under mild conditions. These features characterize the cleavage of C–H bonds in alkenes and arenes by the cationic iridium(III) complex **1** developed recently by Arndtsen and Bergman. The extremely high reactivity of this compound is attributed to the presence of separated ion pairs, evident also in the crystal. The remarkable tolerance of **1** towards functional groups bodes well for possible applications in synthesis.



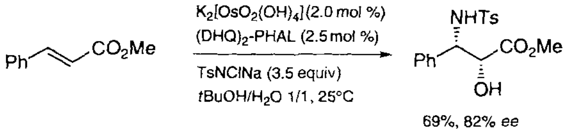
1

J. C. W. Lohrenz,*
H. Jacobsen* 1305–1307

Cationic Iridium(III) Complexes: A Step Towards Synthetic Applicability of C–H Activation

---

A dream became reality: Twenty years after the discovery of the basic process, Sharpless et al. have developed a catalytic asymmetric aminohydroxylation (AA) of alkenes. This reaction [Eq. (a)] provides an access to such important molecules as amino alcohols and α-hydroxy-β-amino acids in enantiomerically pure form.



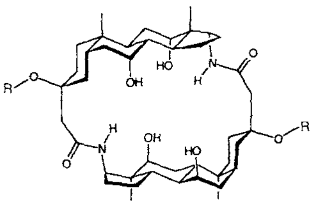
(a)

O. Reiser* 1308–1309

The Sharpless Asymmetric Aminohydroxylation of Olefins

COMMUNICATIONS

As a neutral, lipophilic, purely organic host, the macrocycle **1** may deservedly be labeled an "anion-binding counterpart" of a crown ether or cryptand. Macrocycle **1** was synthesized from the inexpensive steroid cholic acid. It forms 1:1 complexes with fluoride, chloride, and bromide and shows good discrimination in favor of the smaller anions. R = pentyl.



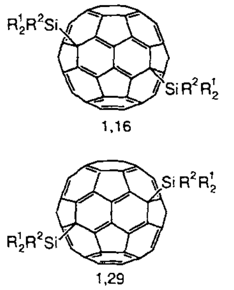
1

A. P. Davis,* J. F. Gilmer,
J. J. Perry 1312–1315

A Steroid-Based Cryptand for Halide Anions

Two silyl substituents without additional H substituents are the features of the bisadducts **1**, which are selectively obtained by the reactions of silyllithium compounds **2** with C_{60}. The single-crystal X-ray analysis of **1a** confirms 1,16 or 1,29 addition.

$R^1_2R^2SiLi$ **2**
a, $R^1 = R^2 = Me_3Si$; **b**, $R^1 = tBu$, $R^2 = Ph$



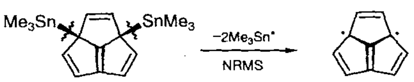
1

T. Kusukawa, W. Ando* 1315–1317

Reactions of Silyllithium with C_{60}: Isolation and X-ray Crystallographic Characterization of an Unusual Bissilylated-C_{60} Adduct

---

Neutralization–reionization mass spectrometry (NRMS) proved the existence of the highly strained acepentalene **2** generated from the precursor **1**. The experimental data agree well with the results of density functional theory computations, which predict that the C_s singlet **2** is about 3.9 kcal mol^{-1} more stable than the C_{3v} triplet **2**.



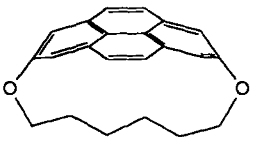
1 2

R. Haag, D. Schröder, T. Zywietz,
H. Jiao, H. Schwarz,*
P. von R. Schleyer,*
A. de Meijere* 1317–1319

The Long Elusive Acepentalene—Experimental and Theoretical Evidence for its Existence

---

Pyrene can be bent by almost 90°. This was confirmed by a crystal structure analysis of cyclophane **1**, which reveals an 87.8° bend over the length of the pyrene moiety and a stretched aliphatic chain (C-C-C bond angles up to 119.4°). The signals at highest field for the bridge protons are at $\delta = -1.47$. The arene's curved surface approximates part of the surface of D_{6h} C_{84}.



1

G. J. Bodwell,* J. N. Bridson,
T. J. Houghton, J. W. J. Kennedy,
M. R. Mannion 1320–1321

1,8-Dioxa[8](2,7)pyrenophane, a Severely Distorted Polycyclic Aromatic Hydrocarbon

0570-0833/96/3512-1252 $ 15.00+.25/0

Three different anions are contained in the novel lithium complex **1**, which has a "butterfly" structure. The preference of this structure over the common alternatives lies in the relative bridging abilities of the ligands present. The stability of the complex was impressively demonstrated by ab initio calculations.

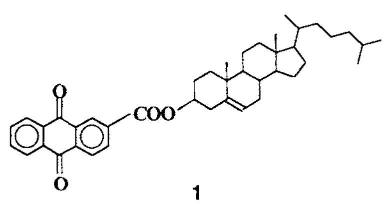
$[\mathrm{LiBr} \cdot \mathrm{LiN(SiMe_3)_2} \cdot \{\mathrm{LiOC}(t\mathrm{Bu}){=}\mathrm{CH_2}\}_2 \cdot (\mathrm{tmeda})_2]$ **1**

K. W. Henderson, A. E. Dorigo,
P. G. Williard,*
P. R. Bernstein 1322–1324

A Triple Anion Complex Containing Enolate, Amide and Halide—A New Structural Type in Lithium Chemistry

---

Well-structured physical gels, composed of an organic liquid and a small amount of a gelator molecule like the title compound **1**, are known to have microstructures of interlinked fibers. A method is described for the determination of the molecular packing arrangements of the gelator molecules in the fibers, based upon subtracting the X-ray powder diffraction pattern of the neat liquid component from that of the gel and relating the difference to the pattern of the morphs of the neat gelator solid.



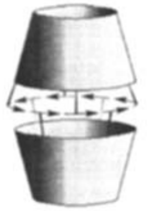
1

E. Ostuni, P. Kamaras,
R. G. Weiss* 1324–1326

Novel X-ray Method for In Situ Determination of Gelator Strand Structure: Polymorphism of Cholesteryl Anthraquinone-2-carboxylate

---

A capsule with a capacity of about 210 Å^3 (shown schematically on the right) is formed by the dimerization of two calix[4]arenes. Encapsulation of guest molecules such as benzene, fluorobenzene, and pyrazine within the capsule occurs on a time scale of minutes at room temperature.

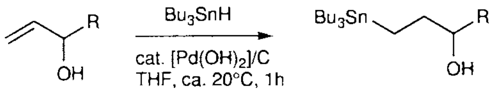


B. C. Hamann, K. D. Shimizu,
J. Rebek, Jr.* 1326–1329

Reversible Encapsulation of Guest Molecules in a Calixarene Dimer

---

A heterogeneous palladium catalyst enables the hydrostannation of alkenes with both great efficiency and generality. The method is illustrated for the allylic alcohols shown in Equation (a) (R = Ph (96%), 2-furyl (92%)).



(a)

M. Lautens,* S. Kumanovic,
C. Meyer 1329–1330

Heterogeneous Palladium-Catalyzed Regioselective Hydrostannation of Alkenes

---

A reduction of the CO partial pressure is sufficient to obtain single crystals of $[\mathrm{Pd_6Cl_{12}}]$ from the equilibrium (a) in thionyl chloride (solv.) at room temperature. The single-crystal and powder X-ray diffraction characterization of this Pd$^{\mathrm{II}}$ chloride is described.

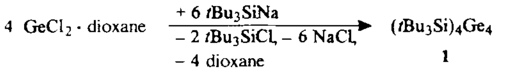
$$2\,\mathrm{PdCl_{2(s)}} + 2\,\mathrm{CO_{(solv)}} \rightleftarrows [\mathrm{Pd_2Cl_4(CO)_2}]_{\mathrm{(solv)}} \qquad \text{(a)}$$

D. Belli Dell'Amico,* F. Calderazzo,*
F. Marchetti, S. Ramello 1331–1333

Molecular Structure of $[\mathrm{Pd_6Cl_{12}}]$ in Single Crystals Chemically Grown at Room Temperature

---

Deep red, oxidation- and hydrolysis-sensitive crystals are formed by the title compound **1**, the first derivative of the *tetrahedro*-tetragermane $\mathrm{Ge_4H_4}$. It was prepared according to Equation (a), and isolated and characterized in crystalline form as $2(t\mathrm{Bu_3Si})_4\mathrm{Ge_4} \cdot (t\mathrm{Bu_3Si})_2$. In these crystals three of the four $t\mathrm{Bu_3Si}$ groups of **1**—possibly as a result of interactions with the $(t\mathrm{Bu_3Si})_2$ molecules—are not arranged in radial symmetric manner in the $\mathrm{Ge_4}$ tetrahedron, but are slightly bent.



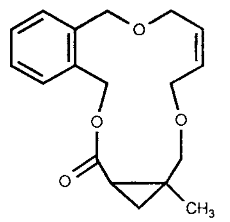
$$4\ \mathrm{GeCl_2 \cdot dioxane} \xrightarrow[-2\,t\mathrm{Bu_3SiCl},\,-6\,\mathrm{NaCl},\,-4\,\mathrm{dioxane}]{+6\,t\mathrm{Bu_3SiNa}} \underset{\mathbf{1}}{(t\mathrm{Bu_3Si})_4\mathrm{Ge_4}} \qquad \text{(a)}$$

N. Wiberg,* W. Hochmuth,
H. Nöth, A. Appel,
M. Schmidt-Amelunxen 1333–1334

Tetrakis(tri-*tert*-butylsilyl)-*tetrahedro*-tetragermane $(t\mathrm{Bu_3Si})_4\mathrm{Ge_4}$—The First Molecular Germanium Compound with a $\mathrm{Ge_4}$ Tetrahedron

---

A new method for the catalytic asymmetric synthesis of macrocycles is based on the intramolecular cyclopropanation of long-chain diazoacetates containing a double bond. Thus, for example, with $[\mathrm{Cu(MeCN)_4}](\mathrm{PF_6})$ in the presence of a chiral bis(dihydrooxazole) ligand, the 15-membered ring lactone **1** was formed not only with excellent regioselectivity (ratio of 15-membered to 10-membered ring is 25:1) but also with remarkably high enantioselectivity (90% *ee*).

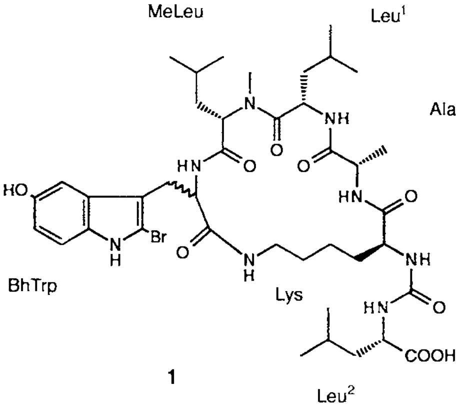


1

M. P. Doyle,* C. S. Peterson,
D. L. Parker, Jr. 1334–1336

Formation of Macrocyclic Lactones by Enantioselective Intramolecular Cyclopropanation of Diazoacetates Catalyzed by Chiral Cu$^{\mathrm{I}}$ and Rh$^{\mathrm{II}}$ Compounds

Revision is needed. The proposed structure of **1** for konbamide, a calmodulin antagonist isolated from the sea sponge *Theonella* sp., must be reconsidered. Both cyclic peptides of structure **1** containing L- and D-bromohydroxytryptophan were synthesized by bromination of the protected cyclic peptide. Their NMR spectra and HPLC traces were found to differ from those of the natural product, although the mass spectra are identical.



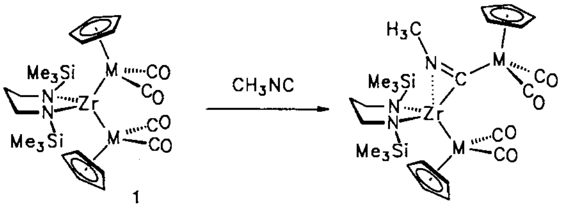
1

U. Schmidt,* S. Weinbrenner 1336–1338

What is the Structure of the Calmodulin Antagonist Konbamide from *Theonella* sp.? Synthesis of Two Isomers by Direct Biomimetic Introduction of Bromine in Hydroxytryptophan-Containing Cyclic Peptides

---

Exclusive mono-insertion into one of the polar metal–metal bonds is an apt description of the reaction of thermally stable ZrFe$_2$ and ZrRu$_2$ complexes **1** with methyl isocyanide [Eq. (a); M = Fe, Ru]. Thus surprisingly, the second of the two polar Zr–M bonds in **1** as well as the distorted tetrahedral coordination geometry of the Zr atom remain intact. The low degree of steric congestion in **1** is manifest in a rapid rotation about the Zr–M bonds that cannot be frozen out even on cooling to 180 K.

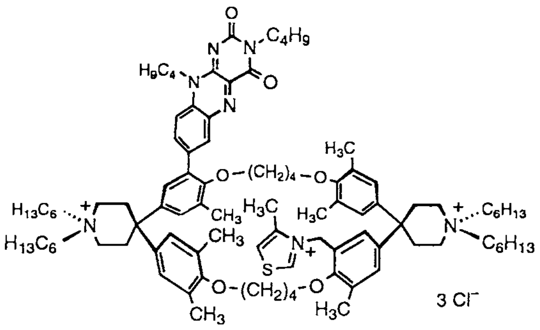


(a)

S. Friedrich, L. H. Gade,*
I. J. Scowen, M. McPartlin 1338–1341

A Chelate-Amidozirconium Fragment as Building Block for Unsupported Trinuclear ZrM$_2$ Heterobimetallic Complexes (M = Fe, Ru, Co)

The cyclophane 1 is the first functional model for the enzyme pyruvate oxidase in which flavin and thiazolium prosthetic groups are arranged close to a well-defined binding site. It catalyzes the oxidation of 2-naphthaldehyde to methyl 2-naphthoate in MeOH/Et$_3$N with high efficiency and complete reaction selectivity.



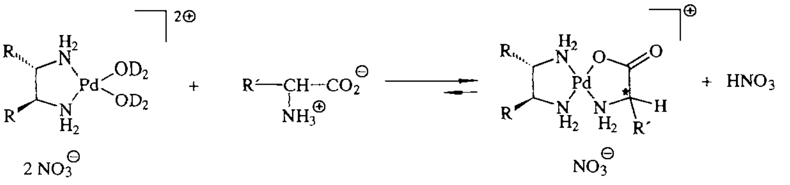
1

P. Mattei, F. Diederich* 1341–1344

A Flavo-Thiazolio-Cyclophane as a Functional Model for Pyruvate Oxidase

---

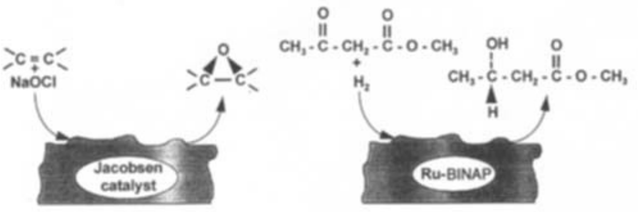
It could hardly be easier! The enantiomeric ratio of unprotected natural as well as artifical amino acids can be determined by ^{1}H NMR spectroscopy with an accuracy of ±1% in aqueous solution after coordination to a C_2-chiral palladium complex [Eq. (a); R = Me, Ph; R–R = –(CH$_2$)$_4$–].



(a)

B. Staubach, J. Buddrus* 1344–1346

Determination of the Enantiomeric Ratio of Unprotected Amino Acids by NMR Spectroscopy with C_2-Chiral Palladium Compounds



* Author to whom correspondence should be addressed

BOOKS

ANGEWANDTE CHEMIE

A Journal of the
Gesellschaft
Deutscher Chemiker

International Edition in English

1996
35/11
Pages 1141–1248

EDITORIAL

Science for the future—that is the slogan for the 75th anniversary of the founding of the VCH Verlagsgesellschaft. "Future grows from the past", and the latter is portrayed in this quick overview. The company was founded as "Verlag Chemie" by the Deutsche Chemische Gesellschaft (German Chemical Society), the Verein Deutscher Chemiker (Association of German Chemists) and the Verein zur Wahrung der Interessen der chemischen Industrie (Society for the Protection of the Interests of the Chemical Industry). From the beginning the traditional German chemical journals, *Angewandte Chemie*, *Chemische Berichte*, and *Liebigs Annalen*, have been the most important products of the company, and despite the drive for expansion in the last 15 years, little has changed in this respect.

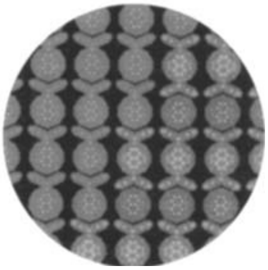
The Gesellschaft Deutscher Chemiker (GDCh) was the successor of two of the learned societies and for about 40 years, until the beginning of the nineties, the main owner of the publishing company. In this time Verlag Chemie, as it was known until the end of 1984, underwent continual expansion. Journals were published for other scientific organizations and societies (as they had been all along) and new ones were founded, an impressive book publishing program was established, and in recent years publishing interests beyond chemistry were nurtured, in particular by subsidiaries such as Ernst & Sohn, Akademie Verlag (both located in Berlin), and the Academy Group (London).

After more than a decade without the term "chemistry" in the company's name, the interests of chemistry are served better than ever: the traditional journals *Chemische Berichte* and *Liebigs Annalen* have been strengthened by a phase of reorientation; the former is now publishing inorganic and organometallic chemistry and the latter all fields of organic chemistry. In the material sciences *Advanced Materials* has secured its place as a top journal; *Angewandte Chemie* has continued its way as a leading international chemistry journal; the start of *Chemistry—A European Journal* could not have been more successful. VCH has become **the** textbook publishers in chemistry in Germany. Furthermore, there has been incredible success on the German-speaking market with books such as the "Chemische Kabinettstücke" by Roesky and Möckel; an English translation of the book ("Chemical Curiosities: Spectacular Experiments and Inspired Quotes") will appear in August, an Italian one is in preparation. Also in the international scene, recent new publications, for example, by Curran/Giese/Porter ("Stereochemistry of Radical Reactions"), Drauz/Waldmann ("Enzyme Catalysis in Organic Synthesis"), Fürstner ("Active Metals. Preparation—Characterization—Applications"), Lehn ("Supramolecular Chemistry. Concepts and Perspectives"), Nicolaou/Sorensen ("Classics in Total Synthesis"), Schmalzried ("Chemical Kinetics of Solids"), and Stang/Diederich ("Modern Acetylene Chemistry") have been extraordinarily well received. Our goal is to continue this path into the future.

With this background, the brand new alliance between VCH and Wiley—this renowned scientific publishing company founded in 1807 acquired a 90% interest in the VCH Publishing Group in early May—offers great opportunities: the GDCh journals (which continue to be owned by the GDCh and published by VCH) will certainly profit from Wiley's excellent worldwide distribution network; the same is true for the English book publishing program. The new partnership will be extremely beneficial also in terms of developments in electronic media. On the other hand, Wiley will profit from VCH's competence in all areas of science, and chemistry in particular, as well as its presence in the German-speaking and continental European market. Professor Dr. E. Winterfeldt, the President of the GDCh, said: "...we have been looking for a suitable partner to strengthen the Society's [international] publishing interests. Wiley has a high reputation in Germany and throughout Europe, and our publishing partnership will help us effect our ambitious plans for cooperation between all European chemical societies and chemists.... In fact, in accordance with an already published concept the GDCh—Wiley have already given their backing—will distribute ownership rights of the new top journal *Chemistry—A European Journal* to chemical societies in Europe. Real steps towards a European **chemistry for the future**".

COVER PICTURE

The cover picture shows schematically the progress of a thermally induced transformation to an ordered solid. This involves a kind of disproportionation of the monoadduct of [60]fullerene and anthracene into the parent [60]fullerene and the antipodal bisadduct as an ordered 1:1 mixture. More about this solid-state reaction, which opens a very efficient access to the bisadduct, is reported by B. Kräutler et al. on page 1204ff.



REVIEWS

Contents

The field of nanochemistry aspires to the synthesis of forms that exist and function at the nanometer scale. The question is, how can this goal be achieved? Self-assembly processes, ubiquitous in Nature, provide remarkably concise and efficient methods for arriving at such compounds and complexes. The burgeoning field of nanochemistry must, therefore, learn lessons from Nature and transfer concepts from biology to chemistry and apply these lessons to the synthesis of unnatural forms.

D. Philip, J. F. Stoddart 1154–1196

Self-Assembly in Natural and Unnatural Systems

HIGHLIGHTS

The potential of bioorganometallic chemistry as a new interdisciplinary research area is illustrated impressively by organoruthenium complexes with peptide ligands. Ruthenium–π-arene fragments are of interest both as markers for peptides that can be readily introduced and as promoters of complex synthetic transformations such as the preparation of cyclic peptide antibiotics and of linear oligopeptides in a one-pot procedure.

R. Krämer* 1197–1199

Application of π-Arene–Ruthenium Complexes in Peptide Labeling and Peptide Synthesis

---

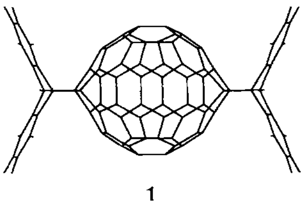
$[N_6CaBa_{14}]$ clusters separated by a matrix of sodium atoms that can alternatively be considered as stars of octahedra (shown on the right) comprising face-shared $[NCaBa_5]$ octahedra with common Ca vertices are present in $Na_{14}Ba_{14}CaN_6$ recently described by Simon and Steinbrenner (*Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 552). This compound, the first discrete subnitride cluster, is not only a link between Na/Ba subnitrides and the classic Rb/Cs suboxides, but also an important extension of the structural chemistry of this class of compounds—not least because a "real" cation (Ca^{2+}) is present in the saltlike interior of the cluster.

C. Röhr* 1199–1201

From Oxides to Nitrides:
Recent Developments in the Structural Chemistry of Alkali/Alkaline Earth Metal Sub-Compounds

COMMUNICATIONS

An unprecedented solid-state reaction of a fullerene monoadduct leads to the antipodal fullerene bisadduct **1**. This regiospecific transfer of anthracene appears to be driven by an increase in entropy.



1

B. Kräutler,* T. Müller, J. Maynollo,
K. Gruber, C. Kratky,
P. Ochsenbein, D. Schwarzenbach,
H.-B. Bürgi 1204–1206

A Topochemically Controlled, Regiospecific Fullerene Bisfunctionalization

---

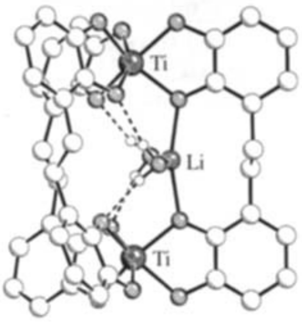
"This is a substance or group of substances about which there has been much discussion" is a statement we read in an older standard textbook of inorganic chemistry with reference to a (usually) amorphous blue material that was first mentioned by C. W. Scheele in 1778 and discussed by J. J. Berzelius in 1826, and that today is known as "molybdenum blue". Now based on the knowledge of compound **1** with an archetypal structure, the more than 200 year old mystery regarding the nature of this multifunctional material with its interesting properties has been partly unveiled.

$(NH_4)_{25\pm5}[Mo_{154}(NO)_{14}O_{420}(OH)_{28}(H_2O)_{70}]\cdot nH_2O$ **1**

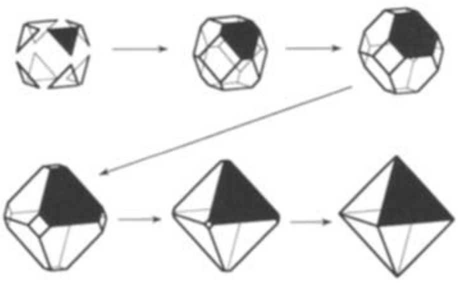
A. Müller,* J. Meyer, E. Krickemeyer,
E. Diemann 1206–1208

Molybdenum Blue: A 200 Year Old Mystery Unveiled

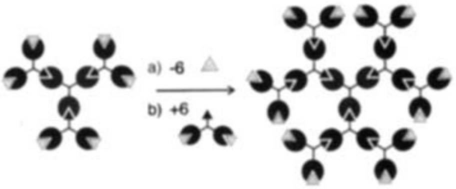
A distorted square-planar coordinated Li^+ ion is located in the pocket of the triple-stranded helicate (structure shown on the right) formed by self-assembly of three ethylene-bridged bis(catecholate) ligands, and two titanium(IV) ions. This unusual coordination geometry is the result of steric effects and stabilizing hydrogen bonds between the two water molecules bound to the Li^+ ion and oxygen atoms of the ligands.



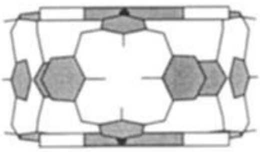
The growth of crystals of the structurally related zeolites FAU and EMT may be characterized by layer upon layer propagation. This previously proposed mechanism has been confirmed by results of an investigation into the crystal growth features in zeolite Y by atomic force microscopy. The intergrowing surfaces of the crystal (see schematic representation on the right) are constructed by the deposition of sodalite-like building units, leading to the formation of terraces.



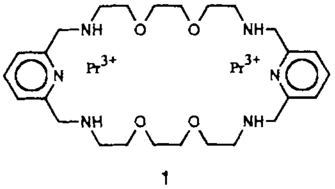
Up to third-generation metallodendrimers can be constructed by a repetitive sequence of reactions with building blocks that contain two coordinatively unsaturated Pd centers ("pie" shape) and one labile, coordinating cyano group (▲, see representation below). The key steps of assembly are the displacement of the chloro ligands (△) with $AgBF_4$ and the in situ reaction with the cyano groups of the dendrimer building blocks to give the next generation. The resulting dendrimers have molecular masses of up to 25 kDa.



The calix[4]arene skeleton serves both as a spacer and as a molecular platform for preorganization in molecular boxes such as **1** constructed from calixarene-based melamine and isocynanuric acid derivatives, which self-assemble in double-rosette structures (shown schematically on the right). These ensembles were characterized by 2D NOESY experiments, which provide information on intramolecular H–H distances and cross relaxation rates.



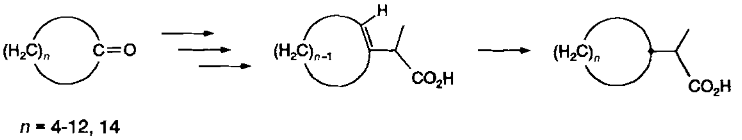
The hydrolysis half-life is reduced from 75 years to eight minutes for bis(*p*-nitrophenyl)phosphate (50 °C, pH 7) when binuclear complexes like **1** are added; related complexes lead to similar effects. The cleavage of plasmid DNA is also accelerated dramatically. In these catalyzed reactions the distance between the metal centers plays a critical role.



1

0570-0833/96/3511-1145 $ 15.00+.25/0

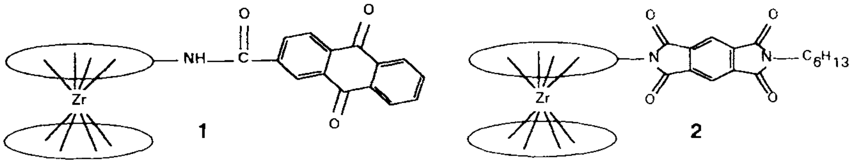
COX and LOX inhibitors analogous to 2-arylpropanoic acids have been synthesized (general route is shown below) and can be viewed as mimetics of arachidonic acid. Remarkably, even medium-sized cycloalkanones reacted almost quantitatively with zinc cuprates. Interesting differences in pharmacological activities related to ring size were observed.



B. Greve, P. Imming,*
S. Laufer 1221–1223

Efficient Synthesis of New 2-Cycloalk(en)ylpropanoic Acid Derivatives—Medium and Large Rings as Bioisosteres of Alkylphenyl Moieties?

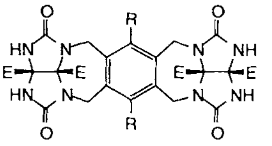
The first structural analogs of the photosynthetic reaction center (**1** and **2**) have been synthesized in which the electron acceptor is attached to an electron donor consisting of a pair of porphyrin subunits held within 3 Å of each other. Electrochemical studies of the anthraquinone derivative **1** suggest that the acceptor and the bis(porphyrinato) zirconium subunit are interacting electronically.



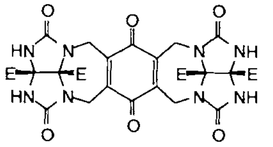
G. S. Girolami,* C. L. Hein,
K. S. Suslick* 1223–1225

A Zirconium Bis(porphyrinate) Sandwich Complex with an Appended Quinone

The π-electron density in the cavity affects the inclusion behavior of dimers, **1-1** and **2-2** as experiments with CH_4, C_2H_6, CH_3F, and CF_4 guests indicate.



1: R = OH ; E = $CO_2(n\text{-}C_4H_9)$

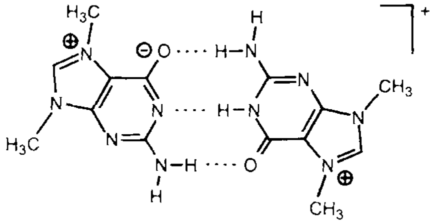


2: E = $CO_2(n\text{-}C_4H_9)$

X. Garcías, J. Rebek, Jr.* 1225–1228

Synthesis and Encapsulation Behavior of New Redox-Active Dimeric Assemblies

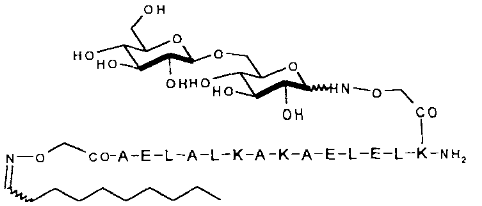
An unexpectedly high affinity for guanine is shown by the rare RNA nucleobase 7,9-dimethylguanine (7,9-DimeG). At pH 7 it forms a partially protonated homo base pair (see sketch) with its conjugated acid (7,9-DimeGH$^+$), the stability of which greatly exceeds that of the Watson–Crick base pair between guanine and cytosine.



S. Metzger, B. Lippert* 1228–1229

Self-Complementarity of 7,9-Dimethylguanine: A Base Pair Containing Three Hydrogen Bonds

Completely unprotected peptides carrying chemoselectively addressable groups react under very mild conditions with free reducing sugars or lipidic aldehydes to form glycopeptides or lipopeptides (for example the somatostatin analogue **1**) of any desired structural complexity.



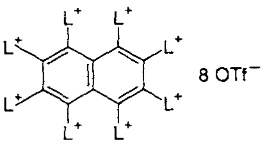
1

S. E. Cervigni, P. Dumy,
M. Mutter* 1230–1232

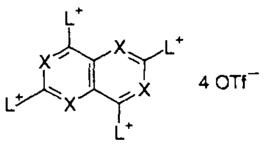
Synthesis of Glycopeptides and Lipopeptides by Chemoselective Ligation

0570-0833/96/3511-1146 $ 15.00+.25/0

An oxidative power comparable to quinonoid oxidants is a characteristic of the octakis- and tetrakis(onio)-substituted arenes **1** and **2a,b**, which are readily accessible by Me_3SiOTf-assisted poly(onio) substitution. **1**: L = 4-dimethylaminopyridine. **2a**: X = CF, **2b**: X = N; L in both cases PR_3.



1

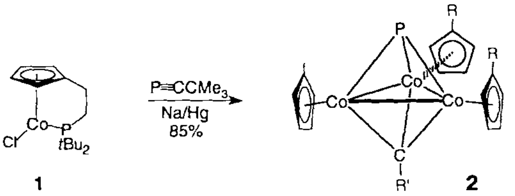


2 a,b

R. Weiss,* R. May,
B. Pomrehn 1232–1234

Charge and Potential: Arenes as Oxidants

Complete cleavage of the phosphorus–carbon triple bond is the characteristic step in the reaction of *tert*-butylphosphaethyne with **1** under mild conditions, which leads to the formation of the μ_3-carbyne-μ_3-phosphidotricobalt cluster **2**. The phosphido ligand in **2** can be oxidized with oxygen or sulfur to give PO and PS ligands, respectively. The phosphane arm in the starting material is evidently necessary for the formation of cluster **2**. R = $CH_2CH_2PtBu_2$, R' = *t*Bu

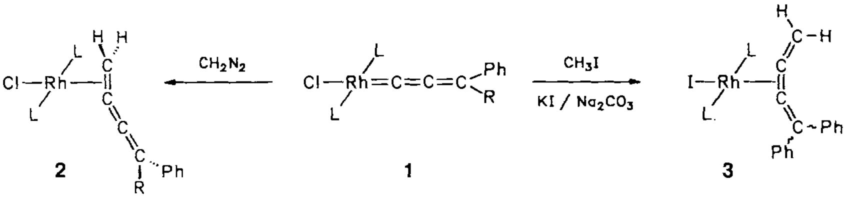


J. Foerstner, F. Olbrich,
H. Butenschön* 1234–1237

A New Mode of Reaction of *tert*-Butylphosphaethyne: Trinuclear Cyclopentadienylcobalt Clusters with P, PS, and PO as μ_3 Complex Ligands

---

The addition of a CH_2 group to the α-carbon atom of the metallacumulene unit Rh=C=C=C(R)Ph occurs with CH_2N_2 (**1** → **2**) and, surprisingly, also with CH_3I (**1** → **3**). The free butatriene $H_2C{=}C{=}C{=}C(tBu)Ph$ is generated from **2** (R = *t*Bu) and CO. Analogously, the allenes $H_2C{=}C{=}CRPh$ (R = Ph, CF_3) are accessible from the allene complexes *trans*-$[RhCl\{(1,2\text{-}\eta\text{-}H_2C^1{=}C^2{=}C^3(R)Ph\}(PiPr_3)_2]$, which are formed by hydrogenation of **1** (R = Ph, CF_3), and CO. L = *i*Pr_3.

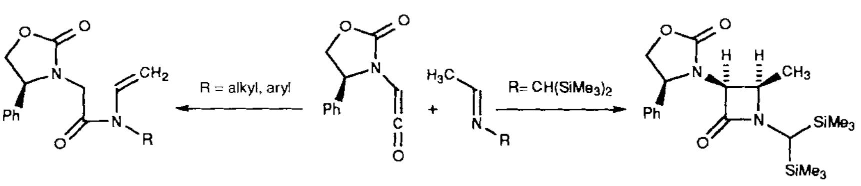


H. Werner,* M. Laubender,
R. Wiedemann,
B. Windmüller 1237–1239

Methyl Iodide as a Source of CH_2: Two Routes for Generating 1,1-Disubstituted Butatrienes in the Coordination Sphere of a Transition Metal

---

Silicon makes the difference! In contrast to known imines from alkyl- or arylamines, imines derived from *C,C*-bis(trimethylsilyl)methylamine and enolizable aldehydes react, as shown below, with ketenes to afford exclusively β-lactams. Furthermore, the reaction is highly diastereoselective when asymmetric ketenes are used.



C. Palomo,* J. M. Aizpurua,* M. Legido,
R. Galarza, P. M. Deya, J. Dunoguès,
J. P. Picard, A. Ricci,
G. Seconi 1239–1241

Imine Substituent Effects on [2+2]Cycloadditions with Ketenes

---

* Author to whom correspondence should be addressed

BOOKS

The following reviews will appear in future issues:

CC-1065 and the Duocarmycins: Mechanistic Studies
Dale L. Boger and Douglas S. Johnson

What Can We Learn from Molecular Recognition in Protein-Ligand Complexes for the Design of New Drugs?
Hans-Joachim Böhm and Gerhard Klebe

Recent Developments in Molecular Chemistry for Sol-Gel Processes
Robert Corriu and Dominique Leclercq

Glycals in Organic Synthesis: The Evolution of Comprehensive and Powerful Strategies for the Assembly of Oligosaccharides and Glycoconjugates of Biological Consequence
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Chemistry and Biology of the Zaragozic Acids (Squalestatins)
K. C. Nicolaou and Alan Nadin

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Recent Developments in Inorganic Polymer Science
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Chiral Recognition in π Complexes of Alkenes, Aldehydes, and Ketones with Transition Metal Lewis Acids; Development of a General Model for Enantioface Binding Selectivities
J. A. Gladysz, B. J. Boone

Structural Aspects of Nucleic Acid Analogs and Antisense Oligonucleotides
Martin Egli

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Deutscher Chemiker

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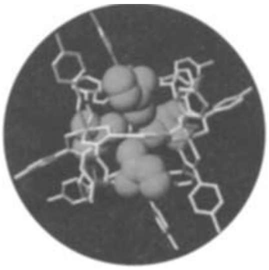
1996
35/10
Pages 1033–1140

COVER PICTURE

The cover picture shows the ball-and-stick model viewed down the crystallographic S_4 axis of a tetrahedral cluster formed by the self-assembly of four gallium(III) ions (green) and six ligands (gold). The cavity of the supramolecular assembly is penetrated by four dimethylformamide molecules (red; space-filling representation). The cluster formation is driven by symmetry number incommensurate lock-and-key interactions. More about this concept and its application is reported by Raymond et al. on pages 1084ff. The picture was generated from crystal coordinates with CAChe software.



REVIEWS

Contents

Rejuvenation of an almost forgotten reaction! The application of modern free-radical techniques has revealed the significant synthetic potential of free-radical carbonylation, which was long neglected after its discovery in the 1950s. A variety of carbonyl compounds including aldehydes, unsymmetrical ketones, macrolides, and δ-lactones can be prepared efficiently often in a single step.

I. Ryu,* N. Sonoda 1050–1066

Free-Radical Carbonylations: Then and Now

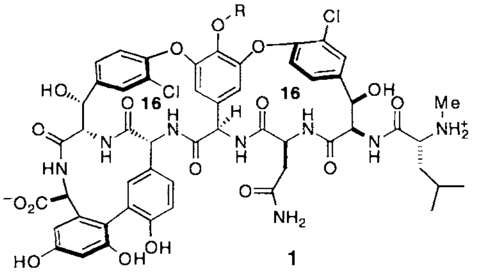
The activation of molecules containing σ bonds in homogeneous and heterogeneous phases is of fundamental importance in particular with regard to conversions of hydrocarbons such CH_4. However, structurally characterized model compounds with σ-coordinated alkanes are unknown to date. The development and the current level of understanding in the field of transition metal coordinated σ bonds is presented here using selected examples. Whether the recently synthesized organometallic silane complexes exhibit model character for isolable σ-alkane complexes is also discussed.

J. J. Schneider* 1068–1076

Si–H and C–H Activation by Transition Metal Complexes: A Step Towards Isolable Alkane Complexes?

HIGHLIGHTS

How one of the major obstacles to a total synthesis of vancomycin **1**, R = sugar, might be overcome has been demonstrated by Zhu et al. and others. They have used nucleophilic aromatic substitution reactions for biaryl ring formation and concomitant ring closure. Conditions for this transformation are sufficiently mild that it can be applied to form complex macrocycles like the 16-membered rings of vancomycin.

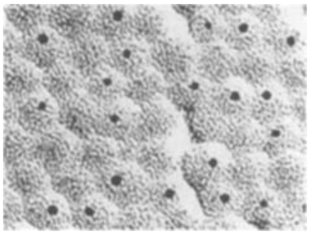


K. Burgess,* D. Lim,
C. I. Martinez 1077–1078

Nucleophilic Aromatic Substitution—A Possible Key Step in Total Syntheses of Vancomycin

---

Completely new materials arise when semiconductor nanoparticles are periodically ordered in superlattices. First pioneering preparations of such superlattices were achieved by self-organization of ligand-stabilized CdSe and CdS nanoparticles. The block polymerization to give micelles in the presence of gold salts and their reduction by the electron beam of a transmission electron microscope (TEM) led to ordered gold clusters. The picture on the right shows a TEM image of a material of this type.

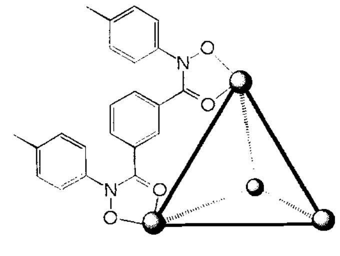


H. Weller* 1079–1081

Self-Organized Superlattices of Nanoparticles

COMMUNICATIONS

As deduced from Nature, the principle of symmetry-driven self-assembly, based on incommensurate coordination numbers, is employed to design clusters using metal coordination as the driving force. The ten-component cluster on the right demonstrates the predicted cooperativity in cluster formation.

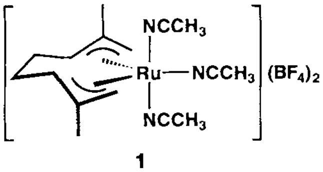


● = Fe^{III}, Ga^{III}

T. Beissel, R. E. Powers,
K. N. Raymond* 1084–1086

Symmetry-Based Metal Complex Cluster Formation

First activate, then polymerize. This is the way that ruthenium complexes such as **1** can be used to catalyze the ring-opening metathesis polymerization efficiently. Diazoalkanes serve as activating agents and depending on their substitution pattern subequivalent or excess amounts are required. When ethyl diazoacetate is used, turnover frequency values above $10^5\,h^{-1}$ have been achieved in the ring-opening metathesis polymerization of norbornene.



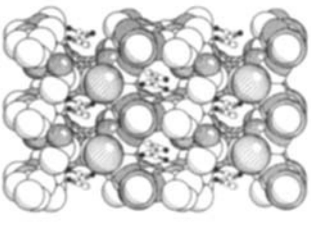
1

W. A. Herrmann,* W. C. Schattenmann,
O. Nuyken, S. C. Glander 1087–1088

Allylruthenium(IV) Complexes as Highly Efficient ROMP Catalysts

---

Unexpectedly, the reaction of tetracyanoethylene (TCNE) with acetone yields a tetracyanopentanonide that forms interesting coordination polymers with Ag^I and Cu^I ions. [Ag(AcTCNE)] is a layer structure consisting of twofold interpenetrated 2D nets of hexagonal meshes, while $[Cu(AcTCNE)]\cdot Me_2CO$ consists of a zeolite-like 3D network, whose large channels contain guest acetone molecules (shown on the right).

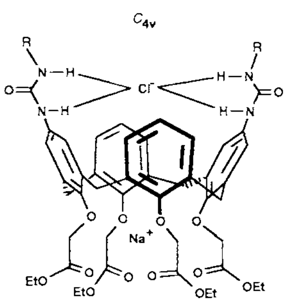


L. Carlucci, G. Ciani,* D. M. Proserpio,
A. Sironi 1088–1090

Polymeric Networks of Silver(I) and Copper(I) Ions Linked by an Anionic Acetonyl Derivative of Tetracyanoethylene

0570-0833/96/3510-1036 $ 15.00+.25/0

First the cation, then the anion. This describes the complexation of alkali metal halides with bifunctional receptors like that on the right (R = *n*-octyl) based on calix[4]arenes. The uncomplexed ligand has a strong intramolecular hydrogen bond between the urea moieties, which is disrupted by the conformational change induced by complexation of a Na^+ ion. Only then is an anion like Cl^- bound in the upper portion of the calixarene.

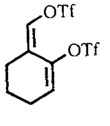


J. Scheerder, J. P. M. van Duynhoven, J. F. J. Engbersen, D. N. Reinhoudt* 1090–1093

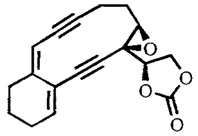
Solubilization of NaX Salts in Chloroform by Bifunctional Receptors

---

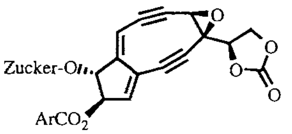
A seven-step synthesis starting from **1** furnished the dienediyne analog **2** of the pharmacophore **3** of the antitumor agent neocarzinostatin. The eleven-membered ring of **2** was formed by the McMurry cyclization of a ketoaldehyde precursor. The resulting C=C bond was epoxidized selectively by taking advantage of a combination of substrate and reagent control. Tf = CF_3SO_2, Ar = aryl.



1



2



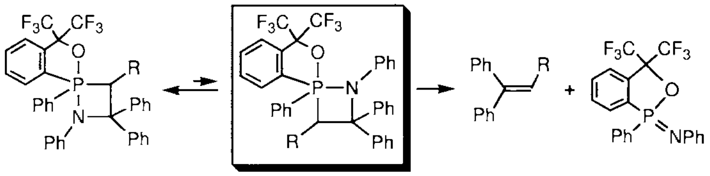
3

M. Eckhardt,* R. Brückner* 1093–1096

The First Model of the Neocarzinostatin Chromophore with an Epoxide Ring and a Carbonate Moiety

---

C-apical intermediates are implicated for the first time in the synthesis of olefins by the thermolysis of azaphosphetidines **1**. Compound **1** and its pseudorotamer **2** are the first reported azaphosphetidines containing pentacoordinate phosphorus. R = H, CO_2Me.

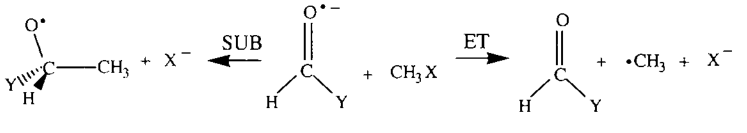


T. Kawashima,* T. Soda, R. Okazaki* 1096–1098

Synthesis, Structure, and Thermolysis of N-Apical 1,2λ^5-Azaphosphetidines with a Pentacoordinate P Center and the First Observation of Their N-Equatorial Pseudorotamers

---

A mechanistic continuum with a sharp changeover zone from electron transfer (ET) to substitution (SUB) reactions has been found in the analysis of the reactions of formyl radical anions with methyl halides (see below). The minimum C–C distance at which the transition state for ET collapses to that of SUB could be defined.



Y = H, Me, CN; X = Cl, Br, I

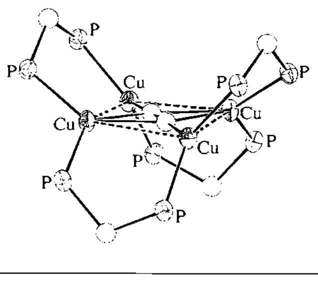
G. N. Sastry, D. Danovich, S. Shaik* 1098–1100

Towards the Definition of the Maximum Allowable Tightness of an Electron Transfer Transition State in the Reactions of Radical Anions and Alkyl Halides

---

A strong reducing power in the excited state is just one of the features of the tetranuclear copper(I) complex **1**. It contains an acetylide dianion bridging four copper atoms in both η^1 and η^2 bonding modes and exhibits long-lived luminescence. The central framework of the structure is shown on the right.

$[Cu_4(\mu\text{-}Ph_2P\text{-}CH_2\text{-}PPh_2)_4(\mu_4\text{-}\eta^1,\eta^2\text{-}C{\equiv}C)](BF_4)_2$ **1**



V. W.-W. Yam,* W. K.-M. Fung, K.-K. Cheung 1100–1102

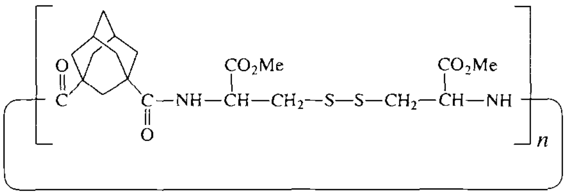
Synthesis, Structure, Photophysics, and Excited-State Redox Properties of the Novel Luminescent Tetranuclear Acetylidocopper(I) Complex $[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-}\eta^1,\eta^2\text{-}C{\equiv}C\text{-})](BF_4)_2$

The hydrolysis of tri-*sec*-butoxyaluminum in the presence of nonionic surfactants leads to mesoporous alumina molecular sieves with wormlike arrays of channels with uniform diameters in the range 2.4–4.7 nm, depending on the nature of the surfactant. Molecular sieves of this type are of interest as possible catalysts and catalyst supports. The transmission electron micrograph of an alumina of this type is shown on the right.

S. A. Bagshaw,
T. J. Pinnavaia* 1102–1105

Mesoporous Alumina Molecular Sieves

A one-step synthesis provided the cyclopeptides **1**–**4** (*n* = 2–5) composed of repeating adamantane and L-cystine units. These macrocycles assume a cavitand-like conformation, in which the interior is hydrophilic and the periphery hydrophobic. Consequently, they can transport Na^+ and K^+ ions selectively in model membranes.



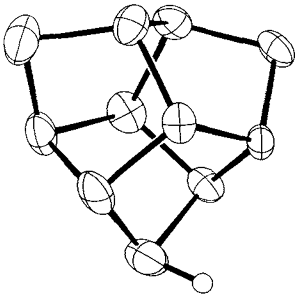
1–4

D. Ranganathan,* V. Haridas,
K. P. Madhusudanan, R. Roy,
R. Nagaraj, G. B. John,
M. B. Sukhaswami 1105–1107

Design, Synthesis, and Ion-Transport Properties of a Novel Family of Cyclic, Adamantane-Containing Cystine Peptides

---

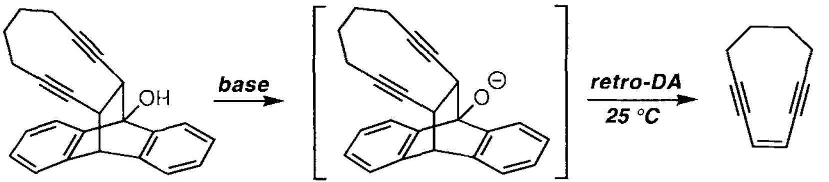
Rapid decomposition in solution is characteristic for hydrogen polyphosphides. Nevertheless, two simple new syntheses—each with a little trick—have made it possible to prepare two stable salts of the novel anion HP_{11}^{2-} (shown on the right) for the first time, starting from cesium undecaphosphide.



N. Korber,* J. Daniels,
H. G. von Schnering* 1107–1110

Directed Synthesis of Stable Hydrogen Polyphosphides: Preparation and Structural Characterization of HP_{11}^{2-} in $(NBnMe_3)_2HP_{11}$ and $(PBnPh_3)_2HP_{11}$ as Well as Its Comparison with the First "Naked" P_{11}^{3-} Ion in $(NEtMe_3)_3P_{11}$

Under remarkably mild conditions (25 °C) the oxide anion accelerated retro-Diels–Alder reaction of **1** leads to cyclodecenediyne (**3**) via intermediate **2**. This is a conceptually new strategy for the generation of reactive enediynes from stable 1,5-diyne progenitors, which should prove of wide applicability.

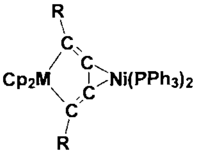


1 **2** **3**

M. E. Bunnage,
K. C. Nicolaou* 1110–1112

Enediyne Generation by a Retro-Diels–Alder Reaction

Ni(0) complexed metallacyclocumulenes such as **1** are intermediates in the heterobimetallic C–C cleavage reaction of disubstituted butadiynes. Furthermore, it was proven that the oxidative addition as well as the reductive elimination of butadiynes may proceed via metallacyclocumulenes.



1 (M = Ti, Zr)

S. Pulst, P. Arndt, B. Heller, W. Baumann,
R. Kempe, U. Rosenthal* 1112–1115

Nickel(0) Complexes of Five-Membered Titana- and Zirconacyclocumulenes as Intermediates in the Cleavage of C–C Bonds of Disubstituted Butadiynes

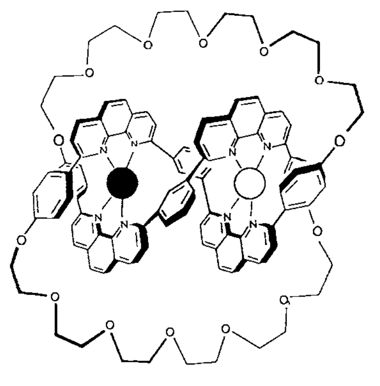
Six Ni^{IV} ions make up the coordination environment of each Fe^{IV} ion in the γ-NiOOH-like layer of the (electrochemically) oxidized form of the iron-substituted nickel(II) hydroxide **I**, as can be deduced from Mössbauer spectroscopic and electrochemical investigations. No Ni^{III} ions are present in the redox-active material. The direct two-electron step $Ni^{II} \rightarrow Ni^{IV} + 2e^-$ must be assumed.

$[Ni_{4.06}Fe_{0.94}(OH)_{10}]^{+0.94}[(CO_3^{2-})_{0.21}(HCO_3^-)_{0.59}(K^+)_{0.07}(H_2O)_{4.66}]^{-0.94}$ I

P. Axmann, C. Freire Erdbrügger, D. H. Buss, O. Glemser* 1115–1118

Formation of Fe^{IV} and Ni^{IV} by Electrochemical and Chemical Oxidation of an Iron-Substituted Nickel(II) Hydroxide: The Direct Two-Electron Step $Ni^{II} \rightarrow Ni^{IV} + 2e^-$

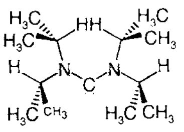
Surprisingly stable is the dinuclear complex cation $[1CuCu]^{2+}$ with entwined ligand **1** (shown on the right; ●, ○ = Cu^+) that can be demetalated in a stepwise manner. The singly demetalated complex $[1Cu]^+$ can be converted to give dissymmetrical heterodinuclear complexes $[1CuAg]^{2+}$ and $[1CuZn]^{3+}$ (○ = Ag^+ and Zn^{2+}, respectively). The electrochemical and spectroscopic properties of these molecular knots, in which the coordinating phenanthroline groups are linked through a "conducting" phenylene spacer, differ considerably from the corresponding compounds with "nonconducting" bridges.



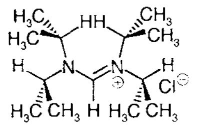
C. O. Dietrich-Buchecker, J.-P. Sauvage,* N. Armaroli, P. Ceroni, V. Balzani* 1119–1121

Knotted Heterodinuclear Complexes

The first acyclic diaminocarbene 1 can be isolated by deprotonation of the corresponding formamidinium ion **2**. In solution both compounds show dynamic behavior (interchange of *i*Pr groups) with activation barriers of 53 and 55 kJ mol^{-1}, respectively.



1



2

R. W. Alder,* P. R. Allen, M. Murray, A. G. Orpen 1121–1123

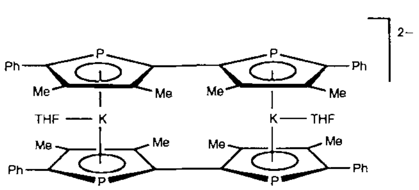
Bis(diisopropylamino)carbene

The lattice symmetry chiefly determines the structure of the XeF_7^- ion in $CsXeF_7$. The influence of the lone pair of electrons is here very weak, and the anion has a capped octahedral structure (C_{3v} symmetry). The dinuclear anion $Xe_2F_{13}^-$ in $NO_2Xe_2F_{13}$ can be structurally divided into an XeF_6 molecule and an XeF_7^- ion. In this case the anion XeF_7^- is a capped trigonal prism (C_{2v} symmetry).

A. Ellern, A.-R. Mahjoub, K. Seppelt* 1123–1125

Structures of XeF_7^- and $Xe_2F_{13}^-$

Phospholide anions can stabilize unusual structures, for example the first crystallographically characterized derivative of "kalocene" (structural formula on the right). Counterion: $[K([18]crown\text{-}6)(THF)_2]^+$.

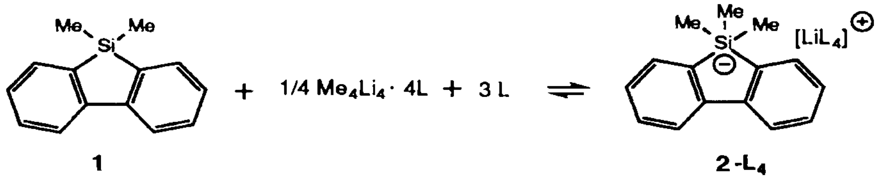


F. Paul, D. Carmichael, L. Ricard, F. Mathey* 1125–1127

Structural Diversity in Alkali Metal Phospholides: A Kalocene-Type Structure

---

Postulated previously only as intermediates, lithium pentaorganosilicates of type **2**-L_4 (L = THF, hexamethylphosphoric triamide), which are in equilibrium with silafluorene **1** and the corresponding organolithium, have now been detected at low temperatures by NMR spectroscopy.

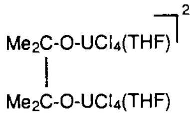


1 2-L_4

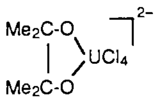
A. H. J. F. de Keijzer, F. J. J. de Kanter, M. Schakel, R. F. Schmitz, G. W. Klumpp* 1127–1128

Lithium 2,2′-Biphenyldiyltrimethylsilicate; First Observation of Pentaorganosilicates

New aspects of the mechanism of the McMurry reaction were revealed by studying the coupling of acetone with uranium tetrachloride and lithium or sodium amalgam. The two metallopinacolate intermediates **1** and **2** were isolated. Only the cyclic complex **2**, formed by reaction of **1** with the reducing agent, was transformed, under more forcing conditions, into tetramethylethylene. Counterion: Li^+.

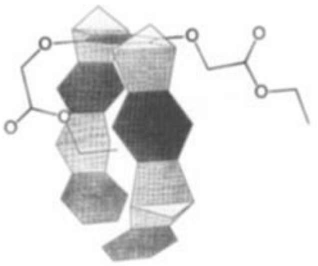


1



2

Highly stereoselective, repetitive Diels–Alder reactions provide a route to novel molecular tweezers, which are excellently preorganized for the formation of complexes and for the self-assembly of side chains. Bond angle deformations, which require little energy, allow the tweezer arms to be expanded or compressed; thus, as receptors they can, to a certain extent, provide a geometrical fit to the structure of a potential substrate. The structure of a tweezer of this kind is shown schematically on the right.



* Author to whom correspondence should be addressed

BOOKS

The following reviews will appear in future issues:

A First Step Towards Planning of Syntheses in Solid-State Chemistry: Determination of Promising Structure Candidates Using a Modular Approach
Martin Janssen and J. Christian Schön

CC-1065 and the Duocarmycins: Mechanistic Studies
Dale L. Boger and Douglas S. Johnson

What can We Learn from Molecular Recognition in Protein-Ligand Complexes of the Design of New Drugs?
Hans-Joachim Böhm and Gerhard Klebe

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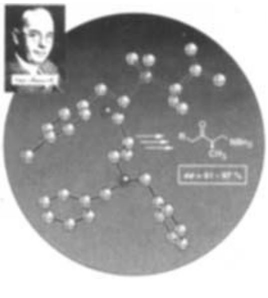
1996
35/9
Pages 921–1032

COVER PICTURE



The cover picture shows the ball-and-stick model of an α-silylated β-dibenzylamino ketone (color code: C = gray, O = red, N = blue, Si = green, and Br = claret), which is accessible in a straightforward manner from butanone and from which the corresponding amino ketone can be synthesized readily by racemization-free desilylation. This conversion can be achieved with a whole series of silylated precursors. Thus, roughly 80 years after the discovery of the aminomethylation of aldehydes and ketones by Carl Mannich, this procedure provides the first access to a practical enantioselective Mannich reaction. More about this novel synthetic route to β-amino ketones, which are of great preparative interest, is reported by D. Enders et al. on p. 981 ff.

REVIEWS

Contents

How can an enzyme accelerate a pericyclic reaction? The classical effects of solvents and catalysts, which were largely ignored by the chemical community, provide important information about the mechanism of the enzyme, and put the Claisen rearrangement in a new perspective. Nature, it seems, has been paying close attention to the chemical literature!

B. Ganem* 936–945

The Mechanism of the Claisen Rearrangement: Déjà Vu All Over Again

---

Counterintuitive product distribution results can be understood when the reaction mechanism is elucidated by kinetic analysis. Thus, the protonation of alkene complexes gives alkanes at low acid concentration and alkenes at high acid concentration, and this can be explained by pathways involving competitive protonation of the metal or the ligand. Mechanistic studies on the reactions of acids with complexes containing unsaturated hydrocarbon ligands show that the product selectivity need not be attributable to simple regioselective attack of the proton at the hydrocarbon. The ramifications of these mechanistic features on the control of the products of a reaction and their stereochemistry are discussed.

R. A. Henderson* 946–967

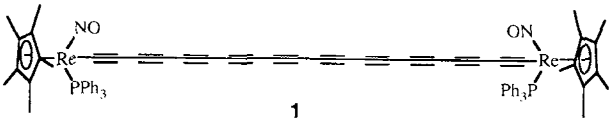
Protonation of Unsaturated Hydrocarbon Ligands: Regioselectivity, Stereoselectivity, and Product Specificity

HIGHLIGHTS

Predominantly air- and moisture-stable carbyne derivatives such as **1** have been synthesized by Gladysz et al. Compound **1** contains the longest C–C chain in compounds of this type to date. The rhenium centers in **1** are electronically independent from each other, which, however, is not true for the shorter homologues.

U. H. F. Bunz* 969–971

Organometallic "Carbon Chains": They Just Keep Getting Longer!

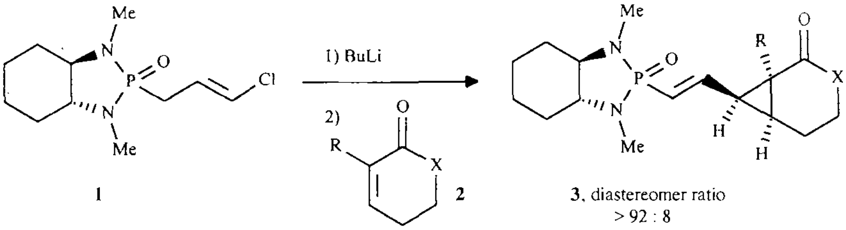


1

A new type of chiral vinylcarbene equivalent used by S. Hanessian et al. is the optically active chloroallylphosphonic acid amide **1**. After deprotonation it adds to α,β-unsaturated carbonyl compounds **2** (R = H, Me) to yield the highly functionalized cyclopropane derivatives **3** with a high degree of enantiomeric purity. The substitution pattern of the cyclopropane derivatives predestines them to be starting materials for many syntheses.

H.-U. Reissig* 971–973

Recent Developments in the Enantioselective Syntheses of Cyclopropanes

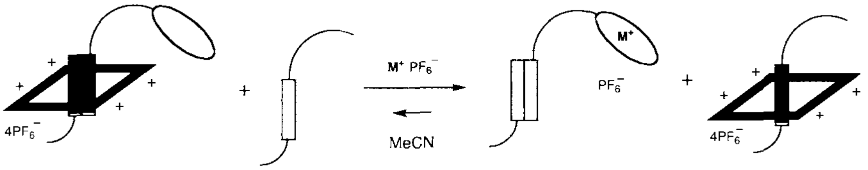


COMMUNICATIONS

A negative allosteric effect is observed in the [2]pseudorotaxane incorporating the 1,5-dioxynaphthalene derivative stoppered at one end by the [18]crown-6 macrocycle when it binds alkali metal cations. This effect can be exploited to elicit an optical response that can be monitored by UV spectroscopy. The principle is illustrated schematically below.

M. Asakawa, S. Iqbal, J. F. Stoddart*,
N. D. Tinker 976–978

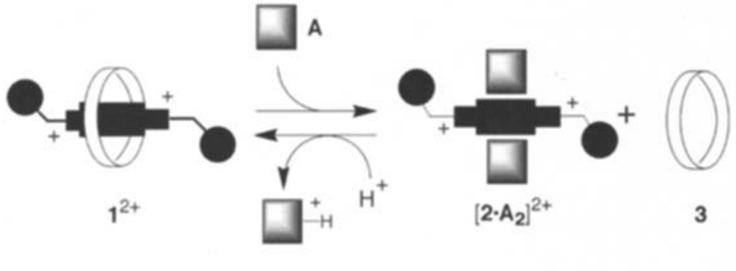
A Prototype of an Optically Responsive Molecular Switch Based on Pseudorotaxane



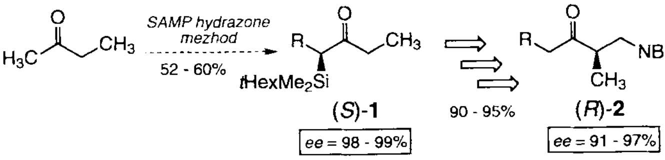
The 2,7-dibenzyldiazoniapyrene dication 2^{2+} is unthreaded from the pseudorotaxane 1^{2+} by addition of the aliphatic amine **A**. Protonation of the amine disrupts the interactions between **A** and 2^{2+} and thus rethreading of 2^{2+} by 1,5-dinaphtho[38]crown-10 (**3**) can occur, making the whole process reversible. The changes in the relative positions of the components can be monitored by absorption and luminescence spectroscopy.

R. Ballardini, V. Balzani, A. Credi,
M. T. Gandolfi, S. J. Langford, S. Menzer,
L. Prodi, J. F. Stoddart,* M. Venturi,
D. J. Williams 978–981

Simple Molecular Machines: Chemically Driven Unthreading and Rethreading of a [2]Pseudorotaxane



The readily accessible silyl ketone (*S*)-1 is an intermediate in the first practical, asymmetric Mannich reactions for the regio- and highly enantioselective α-aminomethylation of ketones. The synthetically and pharmaceutically valuable Mannich bases (*R*)-**2** are obtained in excellent yields and high enantiomeric excesses. *t*Hex = 1,1,2-trimethylpropyl.



D. Enders,* D. Ward, J. Adam, G. Raabe 981–984

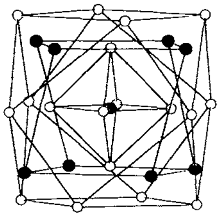
Efficient Regio- and Enantioselective Mannich Reactions

A new Zintl anion X_6^{10-} (X = Si, Ge) appears in the compounds $Ba_4Li_2Si_6$, $Ba_4Li_2Ge_6$, and $Ba_{10}Ge_7O_3$. Bonding within the anion and its interaction with the crystal field is described in terms of the electron localization function (ELF), which allows the visualization of covalent bonds, n electron pairs, and core shells. The existence of such cyclic anions indicates that in the solid-state structures of heavier Group 14 elements the formation of ten π electron Hückel arenes is preferred over the formation of discrete double bonds.

H. G. von Schnering,* U. Bolle, J. Curda, K. Peters, W. Carrillo-Cabrera, M. Somer, M. Schultheiss, U. Wedig 984–986

Hückel Arenes with Ten π Electrons: Cyclic Zintl Anions Si_6^{10-} and Ge_6^{10-}, Isosteric to P_6^{4-} and As_6^{4-}

Lithium-rich main group element clusters characterize the title compounds **1** and **2** (right: structure of **1** without silyl substituents; black = P,O, white = Li), which are obtained by lithiation of the appropriate primary silylphosphane and silylarsane, respectively, with two equivalents of *n*BuLi in the presence of Li_2O. The frameworks of **1** and **2** are topologically best described as two interpenetrating shells of silylated P or As dianions and Li cations, with a formal charge of −4, which encapsulate a $[Li_6O]^{4+}$ octahedron.



$[(RP)_8Li_{18}O]$ **1**, R = iPr$_2$(Mes)Si

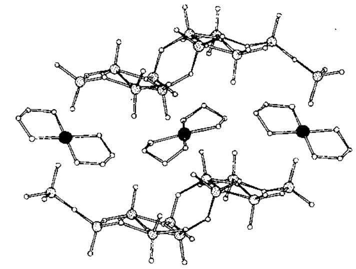
$[(RAs)_{12}Li_{26}O]$ **2**, R = Me$_2$(iPrMe$_2$C)Si

M. Driess,* H. Pritzkow, S. Martin, S. Rell, D. Fenske, G. Baum 986–988

Molecular, Shell-Like Dilithium (Silyl)phosphanediide and Dilithium (Silyl)arsanediide Aggregates with an $[Li_6O]^{4+}$ Core

---

A new class of solid-state materials are the hydrothermally synthesized compounds $(L_2M)_y[VO_x]$ (L = bidentate amine, M = Cu or Zn), which combine mixed-valence vanadium oxide layers with interlamellar coordination complexes. A section of the crystal structure of one example of these compounds with M = Cu and L = ethylenediamine is shown on the right.

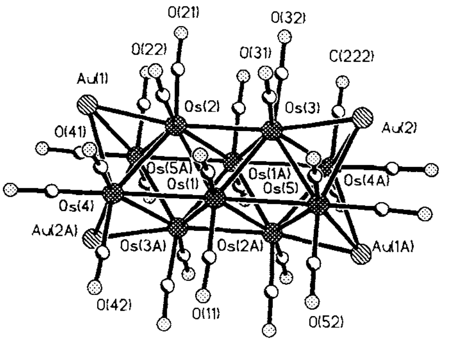


Y. Zhang, J. R. D. DeBord, C. J. O'Connor, R. C. Haushalter,* A. Clearfield,* J. Zubieta* 989–991

Solid-State Coordination Chemistry: Hydrothermal Synthesis of Layered Vanadium Oxides with Interlayer Metal Coordination Complexes

---

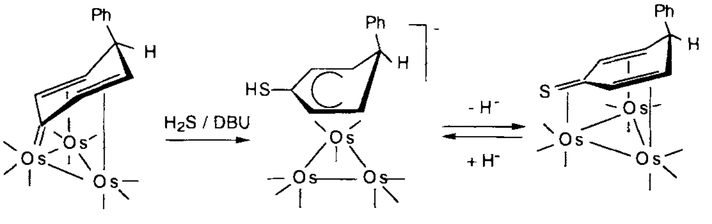
Weak Os–Os interactions are a feature of these open tubular clusters, which have not been previously observed in high nuclearity Os cluster compounds. The bond lengths have been determined by X-ray analysis for the case in which R = Me (see picture). These clusters were synthesized by reduction of the dianion $[Os_{10}(CO)_{26}]^{2-}$ and subsequent addition of the cation $[Au(PPh_2R)]^+$.



Z. Akhter, S. L. Ingham, J. Lewis,* P. R. Raithby 992–993

$[Os_{10}(CO)_{24}\{Au(PPh_2R)\}_4]$. A Tubular Heterobimetallic Carbonyl-Osmium Cluster

The thiol complex 2 is formed when the side-on-coordinated carbene ligand of cluster complex **1** reacts with H_2S/DBU. Abstraction of a hydride from complex **2** yields the thioketone complex **3** in a reversible reaction. A mechanism is proposed in which the hydride abstraction with $[Ph_3C][BF_4]$ proceeds by transfer of a proton from the thiol group to the cyclohexadienyl ring bearing an anionic charge. The hydrogen is finally removed as a hydride. DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.



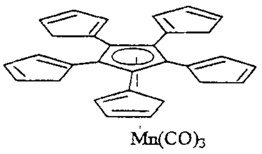
1 **2** **3**

J. U. Köhler, J. Lewis,*
P. R. Raithby 993–995

Reactions of a Triosmium Cluster Complex with a Side-On-Coordinated Carbene Ligand with Sulfur Compounds Resulting in the Formation of a Thioketone Complex

---

A one-step synthesis of the penta(cyclopentadienyl)cyclopentadienyl complex **1** can be achieved from $[Mn(\eta^5\text{-}C_5I_5)(CO)_3]$ and $CpSnMe_3$. Complex **1** can be converted to the corresponding novel pentaanion by reaction with BuLi. Because of their topography these compounds are interesting with regard to the construction of metalated semibuckminsterfullerenes and metallobuckminsterfullerenes.



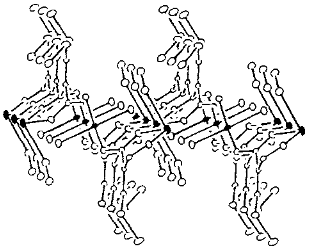
1

R. Boese, G. Bräunlich, J.-P. Gotteland,
J.-T. Hwang, C. Troll,
K. P. C. Vollhardt* 995–998

Metalated Tetra- and Penta(cyclopentadienyl)cyclopentadienyl Compounds: Syntheses by Multiple Pd-Catalyzed Cyclopentadienylations

---

Tethering manganese(II) and copper(II) ions with the dianion of (bis(methylthio)methylidene)malonic acid gives a two-dimensional ferrimagnetic layer compound. The layers are stacked with sulfur–sulfur interactions between the methylthio side arms; a section from the crystal structure is shown on the right.

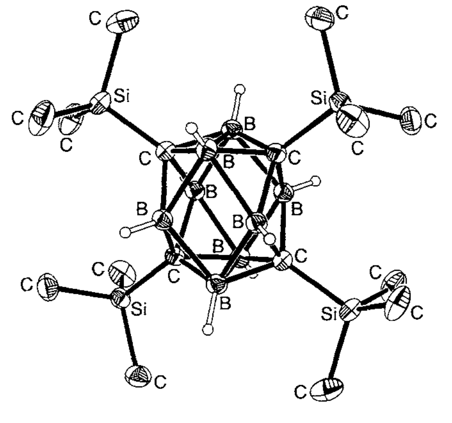


J. Kim,* J. M. Lim, Y.-K. Choi,
Y. Do* 998–1000

A Novel Heterobimetallic Layered Compound Showing Ferrimagnetism

---

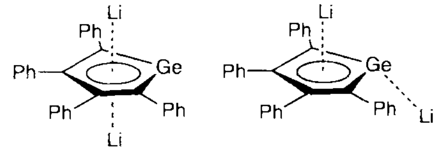
As intermediates in the rearrangement of icosahedral 1,2-carboranes to give the corresponding 1,7-carboranes, carboranes with cuboctahedral structure were postulated by Lipscomb in the 1960s. The first example of this type of carborane, $(CSiMe_3)_4B_8H_8$, has now been prepared and characterized (X-ray crystal structure on the right). The stability of this compound and the minor deviation of the C_4B_8 frame from cuboctahedral geometry can be explained by the steric demand of the silyl substituents.



N. S. Hosmane,* H. Zhang,
J. A. Maguire, Y. Wang, C. J. Thomas,
T. G. Gray 1000–1002

The First Carborane with a Distorted Cuboctahedral Structure

Not one, but two structurally distinct forms are obtained depending upon the crystallization temperature when $Li_2([PhC]_4Ge)$ crystallizes from dioxane. In one form (left) the two lithium ions are located on opposite sides of the germole rings each η^5 coordinated to all of the ring atoms. In the other form (right), one lithium ion is η^5 coordinated to the ring atoms and the other is η^1 coordinated to the germanium center. The C–C distances within the ring of the germole dianion are nearly equal, indicating that the bonding is highly delocalized.



R. West,* H. Sohn, D. R. Powell,
T. Müller, Y. Apeloig 1002–1004

The Dianion of Tetraphenylgermole is Aromatic

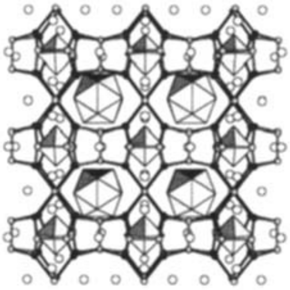
Only stable in the crystal, the title compound **1** contains the first example of a polynuclear organoantimony cation. Interionic Sb ··· Sb and Sb ··· Br contacts are observed in **1**, and reversible dissociation of **1** in solution gives the starting materials Me_2SbBr and Me_4Sb_2. These components exchange Me_2Sb groups in the formation of **1**.

$[Me_2Sb-Sb(Me_2)-SbMe_2][Me_2SbBr_2]$ **1**

H. J. Breunig,* M. Denker, E. Lork 1005–1006

A Trinuclear Organoantimony Cation: Structure of $[Me_2Sb-Sb(Me_2)-SbMe_2]$-$[Me_2SbBr_2]$

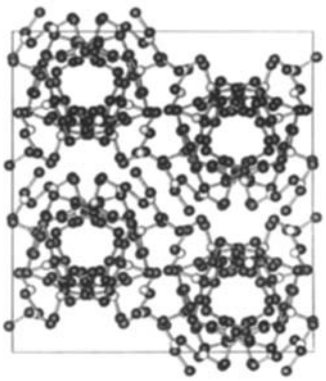
The cubic $Na_{14}K_6Tl_{18}M$ Zintl phases (M = Mg, Zn) are not only derivatives of the $Na_4K_6Tl_{13}$ structure, but also isopointal with the Mg_2Zn_{11}, $Mg_2Al_5Cu_6$, and $Na_2In_5Au_6$ intermetallic compounds. The section of the structure shown on the right depicts the two cation types and the isolated Tl octahedra and $Tl_{12}M$ icosahedra. A wide variety of bonding interactions and tuning prospects are evident.



Z.-C. Dong, J. D. Corbett* 1006–1009

$Na_{14}K_6Tl_{18}M$ (M = Mg, Zn, Cd, Hg) and $Na_{13.5}SM_{0.5}K_6Tl_{18}Na$: Novel Octahedral and Centered Icosahedral Cluster Phases Related to the Mg_2Zn_{11}-Type Structure

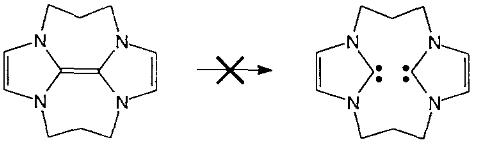
Tightly packed infinite zeolite-like tubes with an inner diameter of 4.1–4.5 Å are formed by the novel double calixarene in the solid state (see schematic representation of the crystal structure on the right). In solution, the calixarene binds Ag^I cations, both at the ends and inside the cylindrical cavity.



J.-A. Pérez-Adelmar, H. Abraham, C. Sánchez, K. Rissanen, P. Prados,* J. de Mendoza* 1009–1011

A Double Calix[4]arene in a 1,3-*alternate* Conformation

A genuine double bond joins the two imidazol-2-ylidene halves in compound **1**, which was characterized by both X-ray crystallography and NMR spectroscopy. The dissociation of **1** to **1'** was not observed, even though the strength of the C=C bond is estimated to be only a few kcal mol^{-1}. This is in accordance with theoretical predictions based on the very large singlet–triplet energy difference for the imidazol-2-ylidenes. Dissociation of the unbridged, singly bridged, or larger ring doubly bridged tetraazafulvalenes is therefore an entropy-driven process.

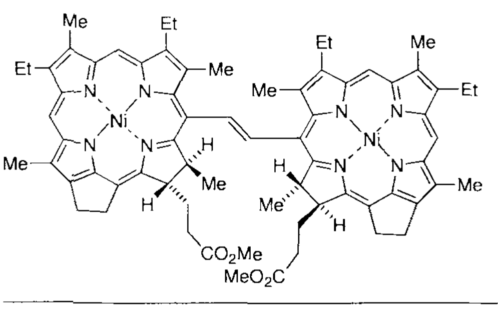


1 **1'**

T. A. Taton, P. Chen* 1011–1013

A Stable Tetraazafulvalene

The first ethylene-bridged bis(chlorins) (for example **1**) were obtained by coupling reactions of formylchlorins, either as the nickel(II) or zinc(II) complexes, with low-valent titanium. They can be partially oxidized at reflux in toluene/acetic acid to afford *trans*-chlorin/porphyrin compounds, or fully oxidized with isomerization to the *cis*-configured bis(porphyrin)s.

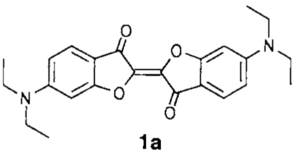


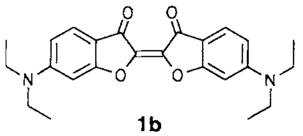
1

L. Jaquinod, D. J. Nurco, C. J. Medforth, R. K. Pandey, T. P. Forsyth, M. M. Olmstead, K. M. Smith* 1013–1016

Synthesis and Characterization of Bis(chlorin)s from the McMurry Reaction of Formylchlorins

Donor groups in positions 6 and 6′ transform *trans*-oxindigo into bathochromically absorbing fluorescent dyes, such as **1a**, with a large Stokes shift. The *cis* isomer **1b** exhibits an even larger bathochromic shift and an intense solid-state fluorescence that extends far into the NIR region.


1a

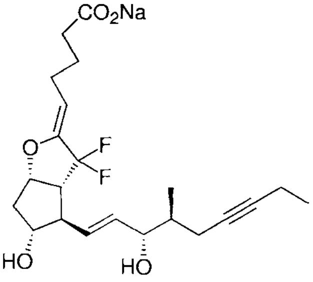

1b

H. Langhals,* B. Wagner 1016–1019

Oxindigo: Color Deepening, Strong Fluorescence, and Large Stokes Shift by Donor-Substitution

---

Markedly more stable than the natural product, difluoroprostacyclin **1** inhibits ADP-induced human platelet aggregation better than any other known prostacyclin derivative. Key steps in the synthesis of **1** are fluorination of the Corey lactone with $(PhSO_2)_2NF$ in the presence of $MgBr_2$ and subsequent Wittig reaction to attach the α side chain.


1

T. Nakano, M. Makino, Y. Morizawa, Y. Matsumura* 1019–1021

Synthesis of Novel Difluoroprostacyclin Derivatives: Unprecedented Stabilizing Effect of Fluorine Substituents

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A new facet of an old theme! Dyed crystals of aromatic carboxylic acids, a common topic in the scientific literature 100 years ago, are rarely discussed today. These mixed crystals are now reintroduced as superior model systems for studying the host–guest interactions that are so important in MALDI mass spectrometry. Orientations for included dyes are determined through polarization spectroscopy. The role of charge transfer is indicated by the X-ray structure of Malachite Green·hydrogen phthalate.

C. A. Mitchell, S. Lovell, K. Thomas, P. Savickas, B. Kahr* 1021–1023

Charge Transfer Interactions in Dyed Crystals of Aromatic Carboxylic Acids and Their Relevance to MALDI Mass Spectrometry

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* Author to whom correspondence should be addressed

BOOKS

ANGEWANDTE CHEMIE

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Deutscher Chemiker

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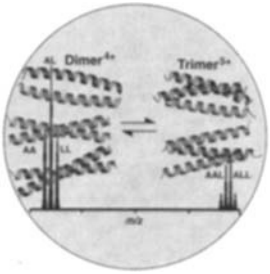
35/8
Pages 793–920

COVER PICTURE

The cover picture shows schematically the structures of dimeric and trimeric complexes of two leucine zipper peptides (designated A and L) and the assigned peaks of the molecular ions in the ESI mass spectrum. The equilibria between the three homo- and heteromeric dimers and the four homo- and heteromeric trimers are recognizable in the spectrum. The development of ESI mass spectrometry and its perspectives for analysis of supramolecular complexes are discussed by M. Przybylski and M. O. Glocker on page 806 ff.



REVIEWS

Contents

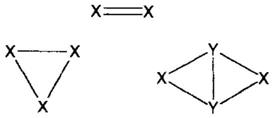
Soft ionization methods that yield singly and multiply charged ions of intact complexes containing noncovalent interactions enable the direct mass spectrometric analysis of biomacromolecular complexes such as protein dimers, double-stranded polynucleotides, enzyme–substrate and enzyme–cofactor complexes, and host–guest systems. The method of choice for analysis of supramolecular structures in solution is electrospray mass spectrometry, which is the focus of this review.

M. Przybylski,* M. O. Glocker .. 806–826

Electrospray Mass Spectrometry of Biomacromolecular Complexes with Noncovalent Interactions—New Analytical Perspectives for Supramolecular Chemistry and Molecular Recognition Processes

---

Carbon is an "exotic" element. This is the conclusion drawn following the comparison of the structures and electronic properties of olefins, cyclopropanes, and bicyclo[1.1.0]butanes with related compounds composed of the carbene-analogous elements or fragments X,Y of the heavier Group 13–15 elements (shown schematically on the right). The structures and properties of these inorganic compounds are determined by the intrinsic characteristics of the corresponding carbene analogues X:. The structural distortions in doubly bonded systems can be discussed on the basis of the Carter-Goddard-Malrieu-Trinquier (CGMT) model. Thus, rules with broad application concerning the prediction of structures and electronic character can be better derived by studying the compounds with heavy main group elements.



M. Driess,* H. Grützmacher * 828–856

Main Group Element Analogues of Carbenes, Olefins, and Small Rings

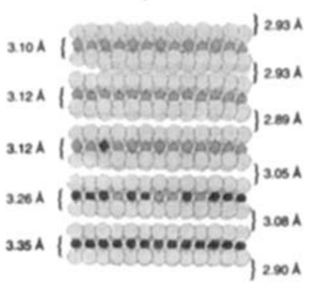
HIGHLIGHTS

The smaller the better! Capillary electrophoresis aims at ever smaller amounts of analyte, as demonstrated by the latest developments described here. Recent results fuel the ultimate dream of the chemist: to find the needle in the haystack and play with it, or to separate and identify by spectroscopy a single component in a complex mixture and subsequently manipulate it, even if it is a single molecule.

A. Paulus * 857–859

Separation, Characterization, and Fraction Collection in the Nanoliter Domain with Capillary Electrophoresis

Modulated thin layer precursor systems provide the basis for a novel rational synthesis strategy for the controlled preparation of complex metastable structures. By sequential deposition of the elements required and subsequent thermal treatment, specific superlattices with alternating composition can be synthesized. The picture shows, as an example, a niobium titanium selenide in which the niobium content increases from top to bottom (intra- and interlayer distances increase; one half of the unit cell of the superlattice is shown).

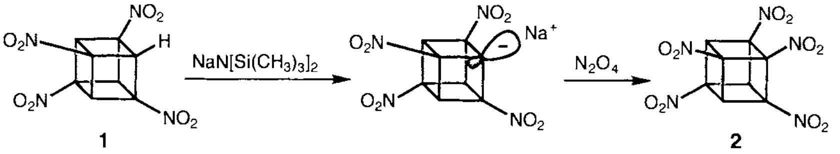


R. Schöllhorn * 859–861

Superlattices, Thin Films, and Materials Design—A Mechanistic Approach

COMMUNICATIONS

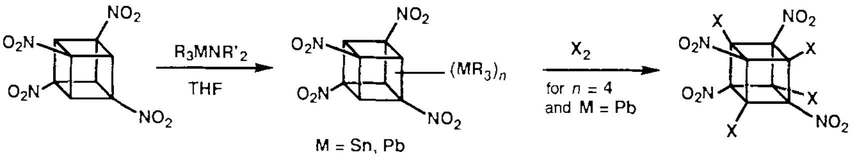
The first direct metalation of a β-C–H bond activated by nitro groups is seen in the reaction of 1,3,5,7-tetranitrocubane (**1**) with base (see below). Such β-nitro carbanions were used to synthesize penta- (**2**) and hexanitrocubanes, the first cubanes containing vicinal nitro groups.



K. Lukin, J. Li, R. Gilardi,
P. E. Eaton * 864–866

Anions Stabilized by β-Nitro Groups: The Acidity and *ortho*-Metalation of Nitrocubanes—Penta- and Hexanitrocubanes

A new synthetic method—β-metalation of nitrocubanes with amides of tin or lead—was used to make a series (n = 1–4) of stable stannyl and plumbyl derivatives. Appropriate cleavages of the cubyl–lead bonds provided tetrahalotetranitrocubanes and penta- and hexanitrocubanes (see below; R = Me, Et; R′ = Et, $SiMe_3$; X = Br, I).



K. Lukin, J. Li, R. Gilardi,
P. E. Eaton * 866–868

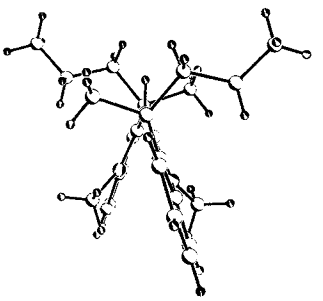
Stable Tin and Lead Derivatives of Nitrocubanes: Their Formation and Use in Multiple Functionalization

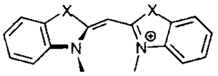
A one-dimensional polymeric anion chain, composed of octanuclear cyclic cluster fragments $[W_4Ag_4S_{16}]^{4-}$ linked through Ag^+ ions (see below), has been isolated from the ammonium tetrathiotungstate/silver nitrate system. Lanthanide(III) ions (Nd or La), which are coordinated by eight DMF ligands and play a crucial role in the formation of the cluster compound, are encapsulated between the chains.

Q. Huang, X.-T. Wu,* Q.-M. Wang,
T.-L. Sheng, J.-X. Lu 868–870

Heterometallic Polymeric Cluster Compounds Derived from Tetrathiotungstate and Silver(I): Syntheses and Crystal Structures of $\{[AgWS_4]\}_n[NH_4]_n$ and $\{[W_4Ag_5S_{16}]\}_n$ $[M(DMF)_8]_n$ (M = Nd and La)

The *P*-helically twisted chromophore of the chiral monomethine dye (*R,R*)-**1** (structure shown on the right) shows a negative Cotton effect for the long-wavelength cyanine band—in apparent violation of established helicity rules. Quantum mechanical calculations and a component analysis support the experimental findings, lending surprisingly additional support for those rules. X = $C(CH_3)C_3H_7$, counterion: ClO_4^-.





1

L. Eggers, V. Buss,*
G. Henkel 870–872

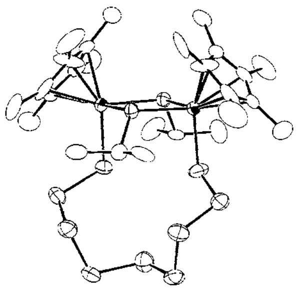
The First C_2-Symmetric Chiral Monomethine Dye—An Apparent Violation of the Helicity Rule for Optical Rotation

Surprisingly, nine sulfur atoms are present in the bridging polysulfido ligand in the diiridium complex **1** (shown on the right), which was prepared by the reaction of **2** with S_8. Upon treatment with $NaBPh_4$, the nonasulfido ligand in **1** is converted into a bridging disulfido ligand, and this reaction is accompanied by a one-electron oxidation of the diiridium core to give the paramagnetic diiridium cation **3**. Cp* = C_5Me_5.

$[Cp^*Ir(\mu\text{-}SiPr)_2(\mu\text{-}S_9)IrCp^*]$ **1**

$[Cp^*Ir(\mu\text{-}SiPr)_2IrCp^*]$ **2**

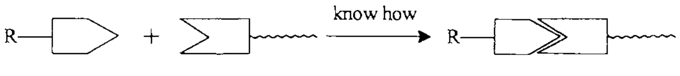
$[Cp^*Ir(\mu\text{-}SiPr)_2(\mu\text{-}S_2)IrCp^*]^+$ **3**



M. Nishio, H. Matsuzaka,
Y. Mizobe, M. Hidai * 872–874

Formation of a Novel μ-Nonasulfido Ligand and Its Degradation into a μ-Disulfido Ligand at a Diiridium Center

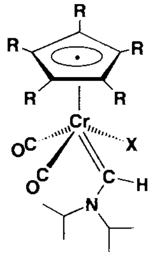
Derivatives of pyridine and benzoic acid having suitable structures can associate through single hydrogen bonds to form liquid crystalline systems. The "know-how" was established by systematically varying the substituents on the benzoic acid (see below): weakly electron-withdrawing substituents are the most efficient for inducing a liquid crystalline state when the substituent on the pyridine ring is an electron donor.



H. Bernhardt, W. Weissflog,
H. Kresse * 874–876

The Influence of Substituents on the Formation of Liquid Crystals Induced by Hydrogen Bonds

The first carbene complexes 1 (R = H, Me; X = Cl, Br) of divalent chromium were obtained selectively by addition of hydrogen halides to the metal–carbon triple bond in $[(\eta^5\text{-}C_5R_5)(CO)_2Cr{\equiv}CNiPr_2]$. These carbene complexes react with isocyanides, phosphanes, and phosphites to give cationic Cr^{II} carbene complexes.

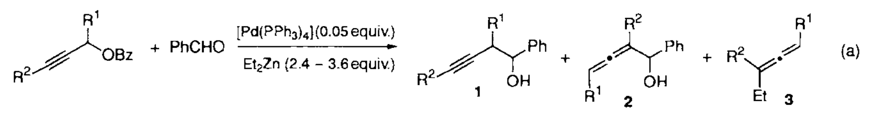


1

A. C. Filippou,* D. Wössner,
B. Lungwitz, G. Kociok-Köhn ... 876–878

Carbene Complexes of Divalent Chromium

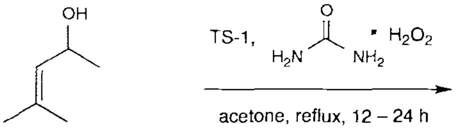
The first nucleophilic additions of propargylpalladium complexes have been achieved with the reactions (a), R^1 = H, Me, Ph, R^2 = H, Me, Ph, $SiMe_3$. In these reactions in addition to the homopropargyl alcohol **1**, the allenyl alcohol **2** was only formed for R^1 = H, R^2 = Me, Ph and the ethylallene **3** for R^1 = Ph, R^2 = H.



Y. Tamaru,* S. Goto, A. Tanaka,
M. Shimizu, M. Kimura 878–880

Propargylation of Carbonyl Compounds by Umpolung of Propargylpalladium Complexes with Diethylzinc

The *threo* epoxy alcohol 2 is the major stereoisomer formed in the epoxidation reaction of the chiral allylic alcohol 1 when the zeolite titanium silicate 1 (TS-1) is employed as heterogeneous catalyst and the urea hydrogen peroxide adduct (UHP) as oxygen source. The hydroxy-directing effect is rationalized in terms of hydrogen bond formation analogous to that for the mechanism of peracid epoxidation.

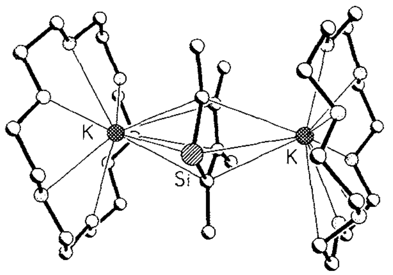


1 *threo*-**2**

W. Adam,* R. Kumar, T. I. Reddy, M. Renz 880–882

Chemo- and Diastereoselective Epoxidation of Chiral Allylic Alcohols with the Urea Hydrogen Peroxide Adduct, Catalyzed by Titanium Silicate 1

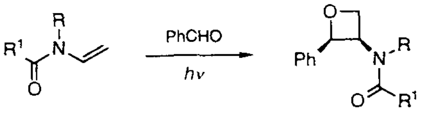
Nearly equivalent C–C distances in the five-membered ring of the dianion $C_4Me_4Si^{2-}$, which could be isolated in crystalline form as a potassium salt in the presence of [18]crown-6 (structure on the right), suggest a high degree of delocalization. In contrast, ^{29}Si and ^{13}C NMR spectroscopic investigations of the silolyl anions $C_4Me_4SiR^-$ (R = $SiMe_3$, $Si(SiMe_3)C_4Me_4$) show that delocalization in these systems is minimal.



W. P. Freeman, T. D. Tilley,* G. P. A. Yap, A. L. Rheingold * 882–884

Silolyl Anions and Silole Dianions: Structure of $[K([18]crown\text{-}6)^+]_2[C_4Me_4Si^{2-}]$

Photochemical reversal of polarity of a carbonyl compound facilitates the construction of N-substituted, α,β-difunctional amino oxetanes **2** by C–C bond formation. The reaction with suitable alkene substrates **1** provides the products in good yields and with excellent regio- and diastereoselectivity. R = H, alkyl; R^1 = alkyl, O*t*Bu.

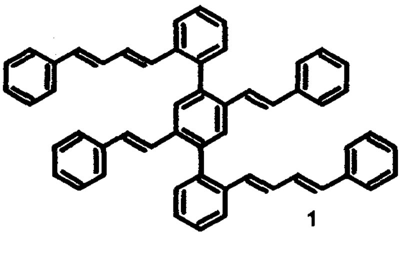


1 **2** (58-73 %)

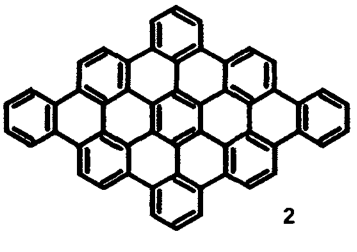
T. Bach * 884–886

N-Acyl Enamines in the Paternò–Büchi Reaction: Stereoselective Preparation of 1,2-Amino Alcohols by C–C Bond Formation

A simple route to the title compounds is accessible by the elegant and structure-specific cycloaddition–cyclodehydrogenation sequence (**1**→→→**2**). Owing to the high temperature stability of the large polybenzoid C_{54} hydrocarbons, they can be characterized in ordered vapor-deposited monolayers by means of scanning tunneling microscopy and electron diffraction.



1

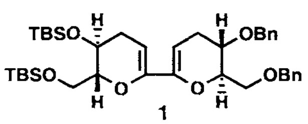


2

M. Müller, J. Petersen, R. Strohmaier, C. Günther, N. Karl, K. Müllen * 886–888

Polybenzoid C_{54} Hydrocarbons: Synthesis and Structural Characterization in Vapor-Deposited Ordered Monolayers

A simple and efficient route to bistetrahydropyranyl systems like **1** relies on the coupling of a stannyl enol ether with an enol triflate in the presence of a catalytic amount of $[Pd(PPh_3)_4]$ and excess amounts of CuCl and K_2CO_3. Complex polyether structures are also accessible in good yields, as the synthesis of a structural element of maitotoxin demonstrates.



1

K. C. Nicolaou,* M. Sato, N. D. Miller, J. L. Gunzner, J. Renaud, E. Untersteller 889–891

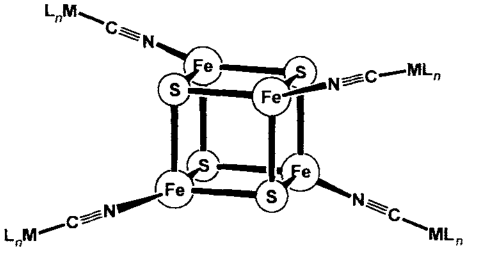
Copper(I)-Promoted Stille Cross-Coupling of Stannyl Enol Ethers with Enol Triflates: Construction of Complex Polyether Frameworks

Ion–molecule reactions between U^{2+} and oxygen donors or "charge-stripping" collisions between singly charged UO_2^+ ions and O_2 collision partners generate uranyl(2+) ions in the gas phase. These do not readily dissociate into singly charged fragments. The standard enthalpy of formation for UO_2^{2+} is estimated to be 371 ± 60 kcal mol^{-1}, in accord with the results of ab initio calculations.

H. H. Cornehl, C. Heinemann,
J. Marçalo, A. Pires de Matos,*
H. Schwarz* 891–894

The "Bare" Uranyl(2+) Ion, UO_2^{2+}

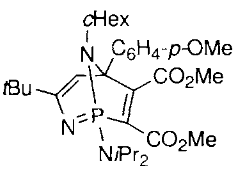
The unusually low magnetic moments of octanuclear complexes containing $[Fe_4S_4(NC-ML_n)_4]$ cluster ions (shown below) are unprecedented in the chemistry of Fe_4S_4 clusters and ferredoxins. The new compounds are redox-active mixed-valence complexes containing iron centers in the oxidation state +2.5 and show intense intervalence transfer absorptions.



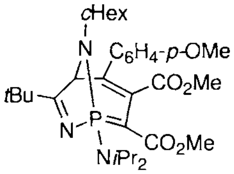
N. Zhu, J. Pebler,
H. Vahrenkamp* 894–895

Combination of the Fe_4S_4 and M-CN-Fe Redox Functions

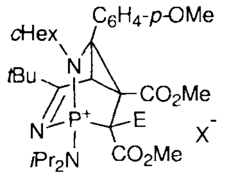
Unusual structure and reactivity characterize 1, an iminophosphorane, which is formed by a 1,5-dipolar cycloaddition from a diazaphosphinine and dimethyl acetylenedicarboxylate. Compound **1** rearranges into **2** in solution, and reacts with electrophiles to give **3a,b**.



1



2



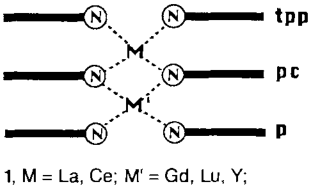
3a, E = H, $X^- = F_2ClCCO_2^-$
3b, E = Me, $X^- = I^-$

J. Barluenga,* M. Tomás, K. Bieger,
S. García-Granda,
R. Santiago-García 896–897

[5+2]Cycloaddition of Cyclic N-Phosphino-1-azadienes: Synthesis, Structure, and Reactivity of the First Seven-Membered Iminophosphorane

---

Either a metal atom or the phthalocyanine ligand is the site of the first oxidation of the heteronuclear triple-decker complexes of type **1**, depending on whether they contain an oxidizable Ce^{III} ion or not. Now the first X-ray structure of such a heteronuclear triple-decker complex (**1**, M = Ce, M′ = Gd, p = oep) has also been achieved.



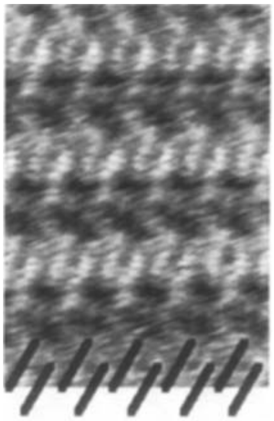
1, M = La, Ce; M′ = Gd, Lu, Y;
p = tpp, oep

D. Chabach, A. De Cian,
J. Fischer, R. Weiss,*
M. El Malouli Bibout 898–899

Mixed-Metal Triple-Decker Sandwich Complexes with the Porphyrin/Phthalocyanine/Porphyrin Ligand System

---

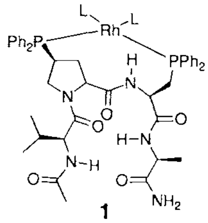
The formation of chiral structures from achiral or racemic components is of great interest because of its implications, for example, for the origin of biological chirality. Monolayers of racemic molecules can form chiral structures, but the precise origin of these structures has been unclear. Images of both enantiomers (that of the (S) enantiomer is shown on the right) and the racemate of a liquid crystal obtained by scanning tunneling microscopy present strong evidence that the racemate forms domains of enantiomerically pure molecules.



F. Stevens, D. J. Dyer,
D. M. Walba* 900–901

Direct Observation of Enantiomorphous Monolayer Crystals from Enantiomers by Scanning Tunneling Microscopy

Amino acids containing potential ligand sites offer interesting perspectives for peptide–metal complexes. FMOC and BOC forms of a proline derivative with phosphanyl groups have been synthesized, and this amino acid was incorporated into a short peptide possessing β-turn secondary structure. The structures of both the peptide and its rhodium complex **1** were analyzed by 2D NMR spectroscopy.



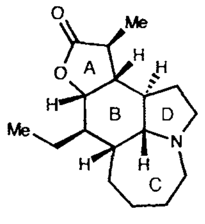
1

S. R. Gilbertson,*
R. V. Pawlick 902–904

Synthesis of Thiophosphoryl Derivatives of Proline: Building Blocks for Phosphanyl-Substituted Peptides with β-Turns

---

An asymmetric Diels–Alder reaction and an efficient construction of the A,B,D ring framework are the key steps of the highly stereoselective total synthesis of (−)-stenine (**1**). Alkaloids of this type of interest because of their possible applications in neuropharmacology.



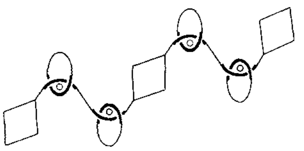
1

Y. Morimoto,* M. Iwahashi,
K. Nishida, Y. Hayashi,
H. Shirahama 904–906

Studies on the Asymmetric Synthesis of *Stemona* Alkaloids: Total Synthesis of (−)-Stenine

---

A copper(I)-templated synthesis furnishes rotaxanes, in which porphyrin subunits serve as bridges and bulky stoppers and the threaded rings contain chelating phenanthroline groups. A [5]rotaxane is shown schematically on the right. o = Cu^I, thick lines = phenanthroline units, ◇ = porphyrins.

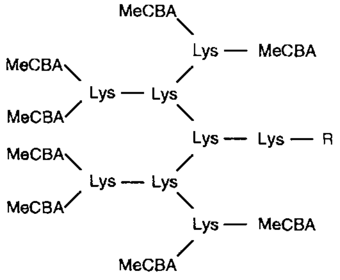


N. Solladié, J.-C. Chambron,
C. O. Dietrich-Buchecker,
J.-P. Sauvage* 906–909

Multicomponent Molecular Systems Incorporating Porphyrins and Copper(I) Complexes: Simultaneous Synthesis of [3]- and [5]Rotaxanes

---

A novel approach from dendrimer chemistry for the synthesis of marker molecules containing eight carboranyl amino acids (MeCBA) (see structure on the right) overcomes the known inconveniences in the syntheses of linear peptide constructs. Marker molecules of this type should be able to be used in electron microscopy. R = protected peptide terminus.



B. Qualmann,* M. M. Kessels,*
H.-J. Musiol, W. D. Sierralta,
P. W. Jungblut, L. Moroder 909–911

Synthesis of Boron-Rich Lysine Dendrimers as Protein Labels in Electron Microscopy

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* Author to whom correspondence should be addressed

BOOKS

ANGEWANDTE CHEMIE

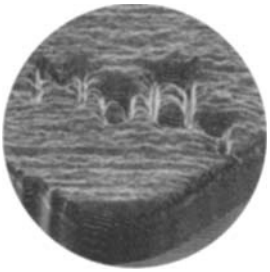
A Journal of the
Gesellschaft
Deutscher Chemiker

International Edition in English

1996
35/7
Pages 673–792

COVER PICTURE

The cover picture shows a force microscope image of a MoO_3 nanocrystal resting on the surface of a MoS_2 single crystal. The chemical formula of the nanocrystal was highlighted by writing "MoO_3" on its surface after its components, Mo and O, were identified by atomic resolution imaging. The desired pattern was engraved with a force microscope tip by scanning across the surface with an applied load that exceeded the critical force required to break bonds between atoms as the nanocrystal was plastically deformed. After this "nanomachining", the resulting changes to the MoO_3 nanocrystal were studied nondestructively using the same force microscope tip operating at a much lower load. The ability to manipulate and study the properties of materials on the atomic to nanometer scales is discussed by C. M. Lieber et al. on pp. 686

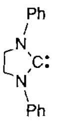


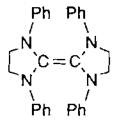
REVIEWS

Contents

HIGHLIGHTS

Over thirty years have passed since the pioneering work of H.-W. Wanzlick on nucleophilic carbenes. A much investigated model is the imidazolidinylidene **1**, which can be generated from dimer **2** and other substrates. The isolation of the stable carbene **3** by A. J. Arduengo III in 1991 sparked incredible developments: addition reactions with increases in the covalency and coordination of the carbene carbon atom dominate the chemistry of such molecules. Recently, Herrmann et al. reported on the use of carbenes as ligands for Pd catalysts.


1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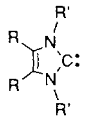
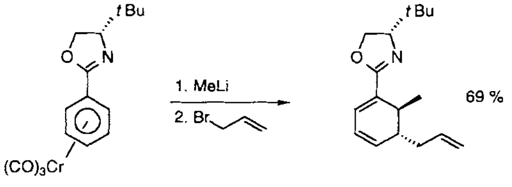

3

M. Regitz* 725–728

Nucleophilic Carbenes: An Incredible Renaissance

High economy and simple elegance distinguish the synthesis of functionalized cyclohexadienes by dearomatization of benzene derivatives. Modern processes of this type rely on the activation of arenes in transition metal complexes (Os, Cr, Mn), additions after Lewis acid complexation, and dihydroxylations catalyzed by enzymes. Stereoselective methods [see, for example, Eq. (a)] and C–C bond forming reactions deserve particular attention.



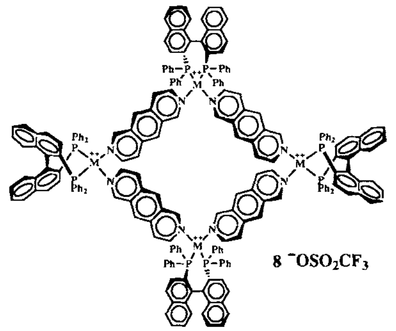
(a)

T. Bach* 729–730

Additions to Functionalized Arenes with Concurrent Dearomatization

COMMUNICATIONS

Exclusive formation of one of the six possible diastereomers (see formula on the right) is observed in the near-quantitative self-assembly of optically active tetranuclear molecular squares from a mixture of the corresponding triflate bisphosphane transition metal complexes and diaza ligands. Asymmetric induction through the chiral bisphosphane ligands and restricted rotation about the bonds between the metal centers and the nitrogen atoms of the heteroarene ligands play vital roles.



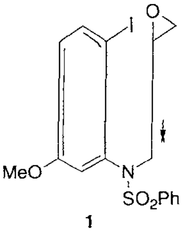
8 $^-OSO_2CF_3$

P. J. Stang,* B. Olenyuk 732–736

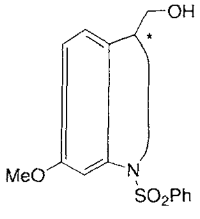
Directed Self-Assembly of Chiral, Optically Active, Macrocyclic Tetranuclear Molecular Squares

---

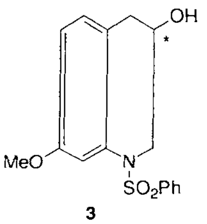
Regioselective reactions with almost no decrease in enantiomeric purity: the 5-*exo* (**2**) and 6-*endo* (**3**) cyclization products are formed from epoxide **1** on reaction with $[Li_3ZnMe_3(SCN)_2]$ and $[Li_3Cu(CN)Me_3]$, respectively. No further reagents are needed. Halogen–metal exchange of **1** with the appropriate ate complex and subsequent intramolecular epoxide opening by the arylcuprate moiety results in the asymmetric synthesis of **2** and **3**, potential precursors of the antibiotics CC-1065 and duocarmycin.



1



2



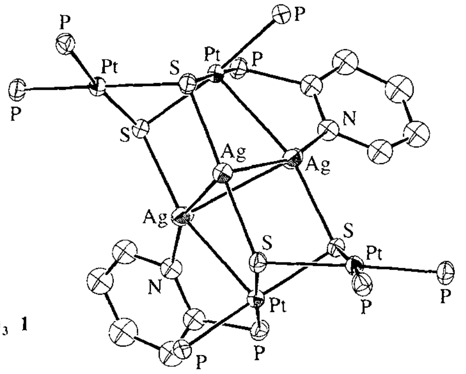
3

Y. Kondo, T. Matsudaira, J. Sato, N. Murata, T. Sakamoto* 736–738

Cuprates as Selective Metalating Reagents for Aromatic Halides

An isosceles triangle of silver atoms is present in the novel heptanuclear heterometallic complex **1** (the structure of the core of the cation is shown on the right). In the solid state, **1** luminesces at 560 nm, which can be attributed to a metal cluster core d-s/S →Ag ligand-to-metal charge transfer. dppy = diphenylpyridin-2-ylphosphane.

$[Pt_2(dppy)_4(\mu_3\text{-}S)_2Ag_3(\mu_3\text{-}S)_2Pt_2(dppy)_4](PF_6)_3$ **1**

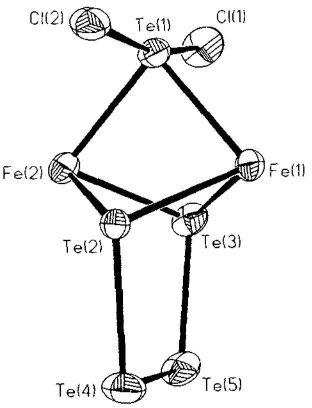


V. W.-W. Yam,* P. K.-Y. Yeung, K.-K. Cheung 739–740

An Unprecedented Example of Pt_4Ag_3 Cluster Formation: Synthesis and Crystal Structure of $[Pt_2(dppy)_4(\mu_3\text{-}S)_2Ag_3(\mu_3\text{-}S)_2Pt_2(dppy)_4]^{3+}$

A doubly bridging $(\eta^2,\mu_2,\mu_2\text{-}Te_4)^{2-}$ ion and a bridging $[TeCl_2]^{2-}$ ion with a nearly linear Cl-Te-Cl angle are the prominent structural features of complex **1** (shown on the right, CO ligands on Fe have been omitted), which contains both oxidized and reduced tellurium centers in the same molecule. This complex is stabilized through weak Te–Te interactions forming infinite sheets in the solid state, but is not stable in solution. Complex **1** is the ultimate product of a complex halogenation of $[Te_2Fe_3(CO)_9]$.

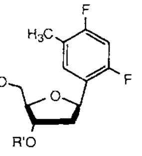
$[Fe_2(CO)_6(\eta^2,\mu_2,\mu_2\text{-}Te_4)(\mu\text{-}TeCl_2)]$ **1**



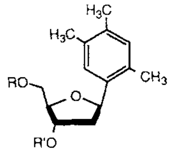
J. R. Eveland, K. H. Whitmire* 741–743

Synthesis and Characterization of the Novel Iron Carbonyl Tellurium Chloride Cluster $[Fe_2(CO)_6(\mu\text{-}Cl)(\mu\text{-}TeCl)_2]_2[\eta^2,\mu_2,\mu_2\text{-}Te_2Cl_{10}]$, and Its Decomposition to the Zintl Ion Complex $[Fe_2(CO)_6(\eta^2,\mu_2,\mu_2\text{-}Te_4)(\mu\text{-}TeCl_2)]$

The stability of hairpin structures formed from oligonucleotides depends on the units in the loop region. When the nonpolar nucleoside isosteres **1–3** replace the natural nucleosides thymidine and deoxyadenosine in the loop linking two octanucleotides, the corresponding duplex DNAs are considerably more stable than the natural analogues.



1



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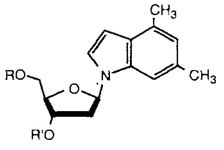
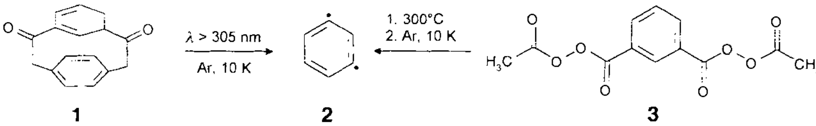


3

X.-F. Ren, B. A. Schweitzer, C. J. Sheils, E. T. Kool* 743–746

Formation of Stable DNA Loops by Incorporation of Nonpolar, Non-Hydrogen-Bonding Nucleoside Isosteres

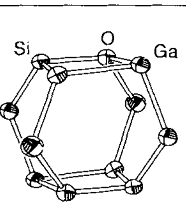
Photolysis of the cyclophane 1 and gas-phase thermolysis of the diacyl peroxide **3** both lead to *m*-didehydrobenzene (**2**). The IR spectrum obtained experimentally could be reproduced accurately by detailed calculations at the CCSD(T) level. The most intense band in the spectrum at 547 cm^{-1} was assigned to a ring deformation band characteristic for **2**.



R. Marquardt, W. Sander,* E. Kraka* 746–748

1,3-Didehydrobenzene (*m*-Benzyne)

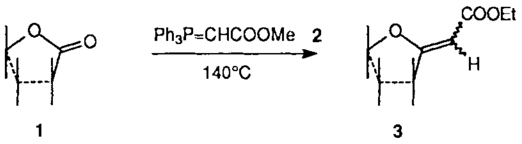
Molecular sieves from a building kit?! Gallium siloxanes of the type shown (substituents on the Si and Ga atoms have been omitted for clarity), which have been synthesized and structurally characterized for the first time, add to the number of molecules that can be considered for the directed synthesis of zeolite-like compounds. The understanding of catalytic processes can also be improved by a study of such model compounds.



A. Voigt, R. Murugavel, E. Parisini, H. W. Roesky* 748–750

Synthesis and Structure of Gallium Siloxane Cages: Model Substances for Gallium-Containing Silicates

With lactones like 1 derived from sugars, the stabilized phosphorane **2** reacts to give mixtures of (*E*)/(*Z*) olefins like **3** in good to excellent yields. In view of the sluggish reactivity of esters in Wittig reactions, this transformation opens promising perspectives.



M. Lakhrissi, Y. Chapleur* 750–752

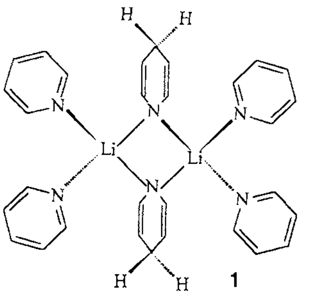
Wittig Olefination of Lactones

Layer compounds of the type $Y_2X_2C_2$ (X = Cl, Br, I) show superconductivity at temperatures between 2.3 and 11.2 K. The transition temperature is related to the tendency of conduction electrons toward pairwise localization in C_2-π* states at the Fermi level, and changes with the concentration of valence electrons, which is varied by intercalation of Na.

M. Bäcker, A. Simon,* R. K. Kremer, H.-J. Mattausch, R. Dronskowski, J. Rouxel 752–753

Superconductivity in Intercalated and Substituted $Y_2Br_2C_2$

By adding more than three molar equivalents of pyridine to *n*-butyllithium, a new reaction has been uncovered in which the novel bis(pyridine)dihydropyridyllithium dimer **1** is formed. The reduction process formally involves transfer of an in situ form of lithium hydride.



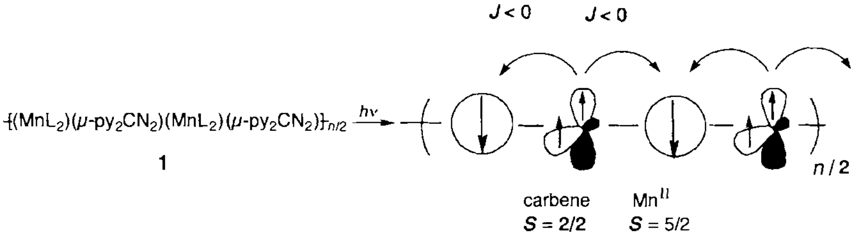
1

W. Clegg, L. Dunbar, L. Horsburgh, R. E. Mulvey* 753–755

Stoichiometric Dependence of the Long-Established Reaction of Butyllithium with Pyridine: A Hidden Secondary Reaction That Produces a Pyridine Adduct of a Lithiodihydropyridine

---

The *ferri*magnetic one-dimensional chain 1a was obtained by photolysis of the 1:1 complex **1** between $[Mn^{II}L_2]$ and diazodi(4-pyridyl)methane. The correlation length extended over 40 units at 3 K. L = hexafluoroacetylacetonate.



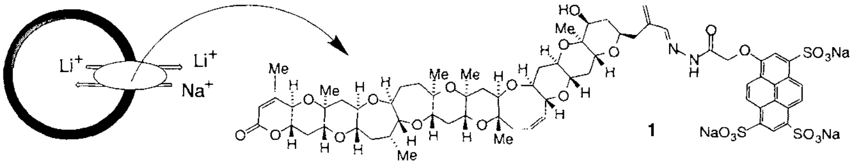
1a

N. Koga,* Y. Ishimaru, H. Iwamura* 755–757

Diazodi(4-pyridyl)methane and Diazophenyl(4-pyridyl)methane as Photoresponsive Ligands for Metal–Carbene Hetero-Spin Systems

---

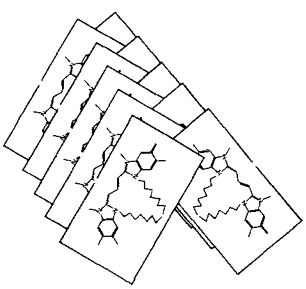
An assembly resembling an ion channel is formed by brevetoxin B in lipid bilayers—this was the conclusion drawn from studies with the fluorescence-labeled brevetoxin B derivative **1**. The finding that brevetoxin B promotes specific cation movements across membranes (see the schematic representation below) reveals a second possible facet of its bioactivity besides the previously observed activation of neuronal sodium channels.



S. Matile*, K. Nakanishi 757–759

Selective Cation Movement across Lipid Bilayers Containing Brevetoxin B

By combination of two types of interactions—self-association of organic dyes and hydrophobic interactions of long alkyl groups—chiral supramolecular systems are formed from achiral substances. Both the observed circular dichroism and the Davydov splitting in the absorption spectrum of the chiral J-aggregates suggest a twisted herringbone-type structure like that shown on the right.

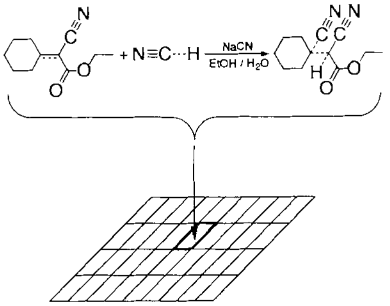


U. De Rossi,* S. Dähne, S. C. J. Meskers,
H. P. J. M. Dekkers 760–763

Spontaneous Formation of Chirality in J-Aggregates Showing Davydov Splitting

---

A two-dimensional projection of organic reactions into a self-organizing neural network (shown schematically on the right) makes it possible to perceive similarities between reactions, assign reaction types, and identify special reactions. Michael additions and related reactions are used here to illustrate this approach to analyzing chemical reactions.



L. Chen, J. Gasteiger* 763–765

Organic Reactions Classified by Neural Networks: Michael Additions, Friedel–Crafts Alkylations by Alkenes, and Related Reactions

---

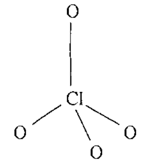
Secondary structural motifs found in peptides are also generated in model compounds containing α,β-didehydrophenylalanine residues (ΔPhe). A short peptide containing two ΔPhe units, Boc-Val-ΔPhe-Leu-Phe-Ala-ΔPhe-Leu-OMe, was found to assume a $3_{10}/\alpha$-helical conformation terminated by a Schellman motif.

K. R. Rajashankar, S. Ramakumar,
T. K. Mal, R. M. Jain,
V. S. Chauhan* 765–768

Schellman Motif in Dehydrooligopeptides: Crystal and Molecular Structure of Boc-Val-ΔPhe-Leu-Phe-Ala-ΔPhe-Leu-OMe

---

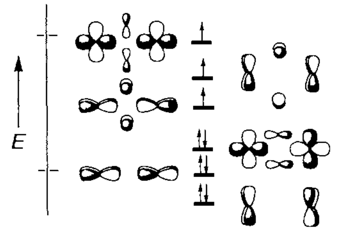
The last unknown mononuclear chlorine oxide has been found. Yellow ClO_4 was generated by vacuum thermolysis of Cl_2O_6 or Cl_2O_7 and isolated in a Ne matrix. The C_{3v}-symmetric structure shown on the right with one long (153 pm) and three short (142 pm) Cl–O bonds was deduced from the IR spectra of the radical.



H. Grothe, H. Willner* 768–769

Chlorine Tetraoxide

The electronic structure and the optimized geometry correlate! The results of local density functional calculations on $[(tpa)Fe(\mu\text{-}O)_2Fe(tpa)]^{3+}$ (tpa = tris(2-pyridylmethyl)amine) are consistent with experimental findings and provide a rationale for the quartet ground state (sketched out in the energy diagram on the right).

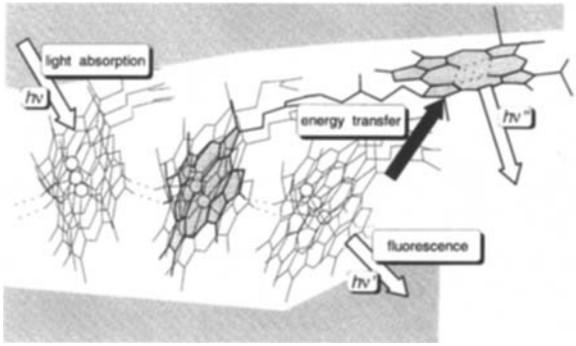


A. Ghosh, J. Almlöf,
L. Que, Jr.* 770–772

Electronic Structure of Non-Heme High-Valent Oxoiron Complexes with the Unprecedented $[Fe_2(\mu\text{-}O)_2]^{3+}$ Core

---

Fast and efficient—energy is transferred within a supramolecular system from the light-harvesting aggregate of zinc chlorins to the coaggregated metal-free bacteriochlorin chromophore (see schematic representation below). This is a first example of a self-assembled light-harvesting antenna that efficiently transfers light energy absorbed by a large number of donor molecules to a single acceptor molecule.

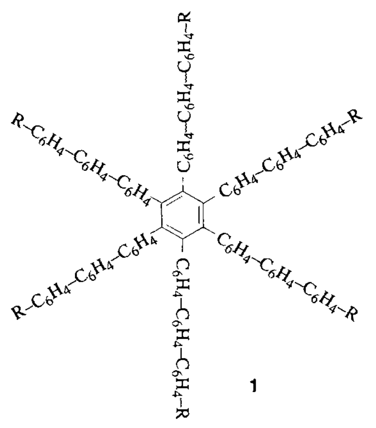


H. Tamiaki,* T. Miyatake, R. Tanikaga,
A. R. Holzwarth,*
K. Schaffner 772–774

Self-Assembly of an Artificial Light-Harvesting Antenna: Energy Transfer from a Zinc Chlorin to a Bacteriochlorin in a Supramolecular Aggregate

0570-0833/96/3507-0679 $ 15.00+.25/0

High fluorescence quantum yields are a feature of the oligo-*para*-phenylene **1** (R = $C(CH_3)_2C_{14}H_{29}$). This compound can be readily synthesized by the trimerization of a diterphenylylacetylene. If a further phenyl ring is to be introduced into each terphenylene chain, a different synthesis route must be chosen.

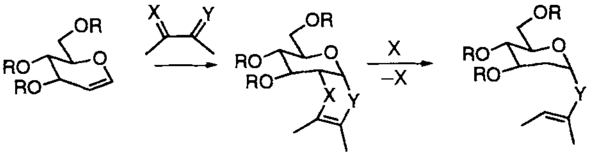


1

M. A. Keegstra, S. De Feyter, F. C. De Schryver, K. Müllen* .. 774–776

Hexaterphenylyl- and Hexaquaterphenylylbenzene: The Behavior of Chromophores and Electrophores in a Restricted Space

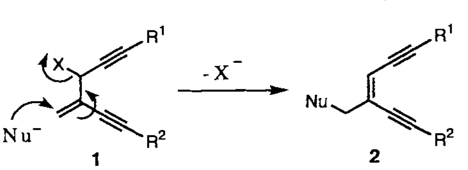
"...**invent truly new and different glycosylation strategies** that will not require a bimolecular reaction to occur between a developing oxocarbonium ion and a sterically hindered lowly nucleophilic alchol..." This challenge by F. Barresi and O. Hindsgaul to all carbohydrate chemists now has a novel reply, which can be described by the sequence in Equation (a).



G. Capozzi, A. Dios, R. W. Franck,* A. Geer, C. Marzabadi, S. Menichetti, C. Nativi, M. Tamarez 777–779

The Cycloaddition Way to Glycosyl Transfer

Simple rearrangement yields enediynes selectively! Rearrangement of the allylic double bond in compounds of type **1** yields the *cis*-enediynes **2** selectively. Cycloaromatization of **2** (R^1 = CH_2SO_2Ph) affords reactive diradicals analogous to those formed from the natural enediyne antitumor antibiotics. Nu = nucleophile.



1 **2**

W.-M. Dai,* K. C. Fong, H. Danjo, S.-i. Nishimoto 779–781

Synthesis of *cis*-Enediynes from 1,5-Diynes by Rearrangement of an Allylic Double Bond

* Author to whom correspondence should be addressed

BOOKS

ANGEWANDTE
CHEMIE

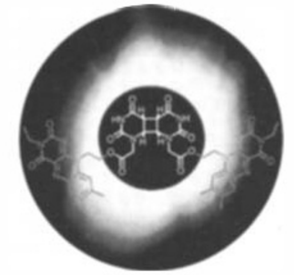
A Journal of the
Gesellschaft
Deutscher Chemiker

International Edition in English

1996
35/6
Pages 561–672

COVER PICTURE

The cover picture shows the structural formula of a uracil dimer (white) substituted with flavin units (yellow) and superimposed on a photograph of a solar eclipse (printed with permission from Eugene Aeppli, Zurich). This dimer was used to model the light-induced DNA repair reaction—the reversion of pyrimidine dimers, which are photoproducts formed on irradiation of DNA with UV light. For cleavage of the uracil dimer with light of longer wavelength (366 nm), the flavin substituents must be in reduced form; this is also a prerequisite for repair with DNA photolyase. T. Carell et al. report more on these model studies on p. 620ff.



REVIEWS

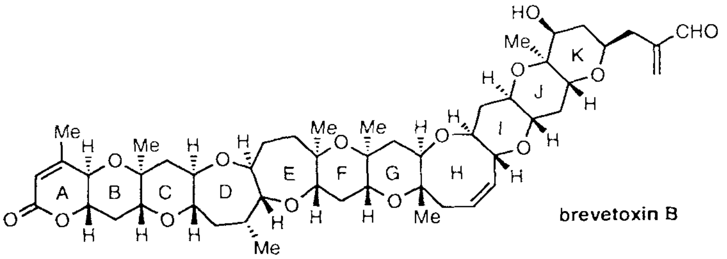
Contents

A rare anniversary gave the impetus for this review: the legendary physicist Friedrich Hund turned 100 years old on February 4, 1996. His significance for chemistry, which does not end with Hund's rules, is acknowledged and honored in this article. Hund and Mulliken cooperated on the development of MO theory, which initially stood in the shadow of VB theory, but eventually took over, becoming generally accepted. The scientific part of this article covers mainly recent insights into Hund's rules, his localization criteria, and coupling cases.

W. Kutzelnigg* 572–586

Friedrich Hund and Chemistry

What is the connection between the total synthesis of brevetoxin and the 1994 Soccer World Cup? Apparently irrelevant factors have extensive ramifications for natural product syntheses. The marine biotoxin brevetoxin B, which is responsible for mass poisoning of humans and marine life during "red tides", was the target of an intense research program in the Nicolaou group. Their perseverance paid off with a wealth of new reactions as dividends. In this "story behind the story" the author describes both the successes and failures along the way.

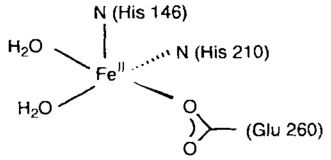


brevetoxin B

K. C. Nicolaou* 588–607

The Total Synthesis of Brevetoxin B: A Twelve-Year Odyssey in Organic Synthesis

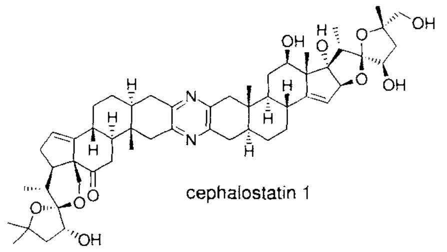
HIGHLIGHTS



Lipid dioxygenases, tyrosine hydroxylase, bleomycin, and isopenicillin N synthase are only a few of the O_2-activating mononuclear non-heme iron-containing biomolecules. In recent years a great deal of effort has been dedicated to the elucidation of the structures and the reaction mechanisms of these systems, as well as to the synthesis of model complexes. In many cases, an iron–peroxo species is proposed as a predominant intermediate. The picture on the right shows the structure of an extradiol catechol dioxygenase recently determined by X-ray structure analysis.

A. L. Nivorozhkin,
J.-J. Girerd* 609–611

Oxygen Activation by Mononuclear Non-Heme Iron Proteins



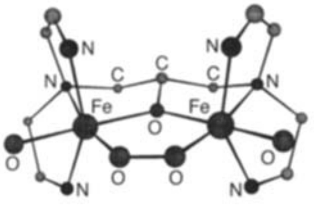
cephalostatin 1

Nearly a ton of marine tube worms was processed to obtain milligram quantities of cephalostatin 1. This compound belongs to a family of thirty highly cytotoxic dimeric steroids. Methods for their laboratory synthesis have now been developed.

A. Ganesan 611–615

The Dimeric Steroid–Pyrazine Marine Alkaloids: Challenges for Isolation, Synthesis, and Biological Studies

COMMUNICATIONS



The enhanced stability provided by two triphenylphosphane oxide ligands has enabled the first crystal structure analysis of a non-heme diiron–O_2 adduct (1) (structure of the core is shown on the right). Complexes of this type can be activated by introducing a more electron-donating carboxylate ligand. These observations rationalize the carboxylate-rich active sites of non-heme diiron oxygen-activating enzymes such as methane monooxygenase and ribonucleotide reductase.

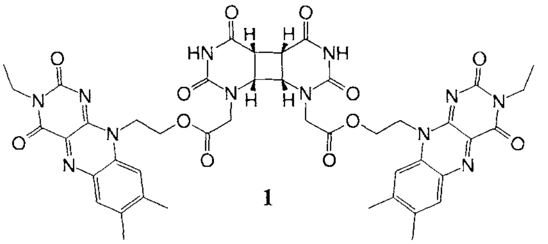
$[Fe_2(\mu\text{-}1,2\text{-}O_2)(N\text{-}Et\text{-}hptb)(Ph_3PO)_2](BF_4)_3$ **1**

Y. Dong, S. Yan, V. G. Young, Jr.,
L. Que, Jr.* 618–620

Crystal Structure Analysis of a Synthetic Non-Heme Diiron–O_2 Adduct: Insight into the Mechanism of Oxygen Activation

---

Irradiation with white light or monochromatic light at 366 nm causes the cleavage of the uracil dimer 1 at the cyclobutane moiety, providing that the flavin units are reduced prior to the reaction. This cleavage reaction of model compounds such as 1 forms the basis of DNA photolyase mediated DNA repair.



1

T. Carell,* R. Epple,
V. Gramlich 620–623

Synthesis of Flavin-Containing Model Compounds for DNA Photolyase Mediated DNA Repair

---

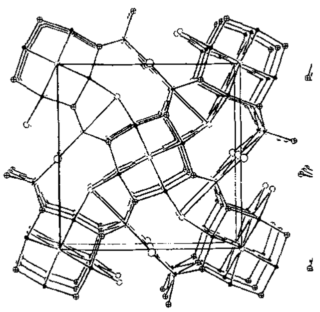
Well-defined poly(ethylene oxide)s with low polydispersities are formed in the anionic polymerization of ethylene oxide with an alkyllithium/phosphazene base initiator system. The base can be regarded as a cryptand for Li^+ ions. The equilibrium between complexed alkoxide ion pairs and reactive free anions is thus shifted.

B. Esswein, M. Möller* 623–625

Polymerization of Ethylene Oxide with Alkyllithium Compounds and the Phosphazene Base "*t*Bu-P_4"

© VCH Verlagsgesellschaft mbH, D-69451 Weinheim, 1996 0570-0833/96/3506-0564 $ 15.00+.25/0

Single crystals are not always necessary. The structure of $BaHg_2O_2Cl_2$ (section shown on the right), which was prepared by a solid-state reaction, was determined from laboratory powder X-ray diffraction data. Isolated Hg_4O_4 squares are the main building blocks.

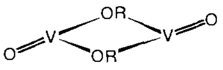


W. T. A. Harrison,* L. Liu,
A. J. Jacobson 625–627

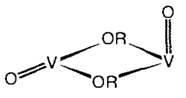
Synthesis and Structure Determination of $BaHg_2O_2Cl_2$ by Powder X-ray Diffraction: Isolated Hg_4O_4 Squares

---

The first edge-sharing octahedral oxovanadium(IV) dimers with an *anti*-coplanar and a twist configuration (shown on the right) exhibit ferromagnetic interactions between the metal centers and thus show that it is possible to enforce specific magnetic properties on such systems through choice of ligand. The magneto-structural correlation of this type of compound should aid the interpretation of magnetic interactions in larger vanadium(IV) clusters with similar structural features.



anti-coplanar



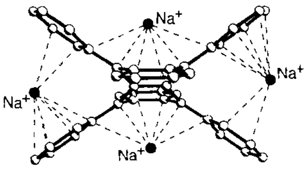
twist

W. Plass* 627–631

Magneto-Structural Correlations in Dinuclear d^1-d^1 Complexes: Structure and Magnetochemistry of Two Ferromagnetically Coupled Vanadium(IV) Dimers

---

Four negative charges in a π-hydrocarbon are generated by the reduction of rubrene, a tetraphenyl tetracene, at a sodium metal mirror. The black crystals of the contact-ion quintuple $[\{Na^+(thf)_2\}_4(rubrene^{4-})]$ (see structure; the thf molecules have been omitted) contain the first hydrocarbon tetraanion ever isolated. Its structure determination confirms the severe skeletal distortions: the tetracene plane, for instance, is bent up and down by 43°.

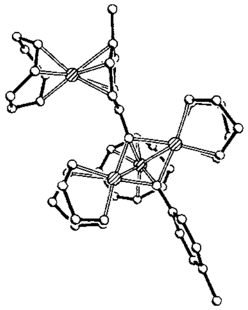


H. Bock,* K. Gharagozloo-Hubmann,
C. Näther, N. Nagel,
Z. Havlas 631–632

$[\{Na^+(thf)_2\}_4(rubrene^{4-})]$: Crystallization and Structure Determination of a Contact-Ion Quintuple for the First π-Hydrocarbon Tetraanion

---

A straightforward synthesis provides surprisingly stable, neutral and anionic μ_3-imidorhodium clusters. The unusual complex $[Rh_4(\mu\text{-}MeC_6H_4N)_2(cod)_4]$, whose structure is shown on the right, contains two bridging imido ligands that cap a triangle of metal atoms. One of these ligands, in addition, coordinates through the *p*-tolyl ring to a [Rh(cod)] moiety in a η^5-cyclohexadienyl-like fashion. cod = 1,5-cyclooctadiene.



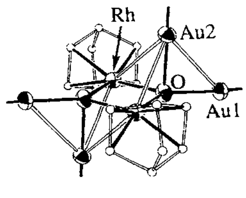
C. Tejel, Y.-M. Shi, M. A. Ciriano,*
A. J. Edwards, F. J. Lahoz,
L. A. Oro* 633–634

Novel Neutral and Anionic Rhodium Complexes Containing Imido Ligands

---

Not only Au–Au but also Rh–Au interactions are responsible for the unusual trigonal-pyramidal coordination of the oxygen atoms in the complex cation **1**. The picture on the right shows the $Au_4Rh_2O_2$ core of the cluster with norbornadiene (nbd) ligands at the Rh centers; the phosphane ligands have been omitted. The synthesis of this novel heteronuclear cluster is relatively simple.

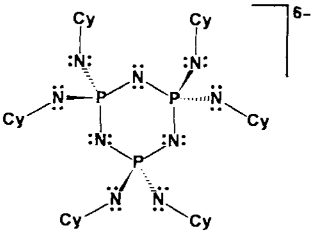
$[\{(nbd)Rh[\mu\text{-}O(AuPPh_3)_2]\}_2]^{2+}$ **1**



H. Shan, P. R. Sharp* 635–636

Double Oxygen Atom Centered Rhodium–Gold Clusters

All six NH functionalities in hexa(cyclohexylamino)cyclotriphosphazene $[NP(NHCy)_2]_3$ (Cy = cyclohexyl) can be deprotonated with *n*-butyllithium. The hexalithiated compound **1** has a dimeric structure in which two hexaanions are complexed to twelve lithium counterions. The high solubility in aprotic solvents makes **1** a potential new ligand system for a variety of metals.



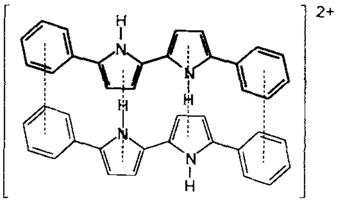
1

A. Steiner,* D. S. Wright 636–637

Hexalithiated Hexakis(cyclohexylamino)cyclotriphosphazene; a $(Li^+)_{12}$ Cage Containing Puckered $[NP(NCy)_2]_3^{6-}$ Ions

---

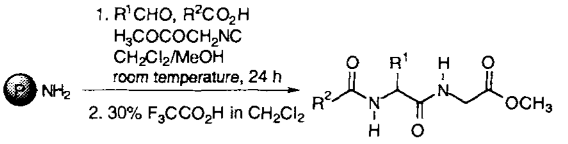
In two consecutive one-electron oxidations, oligopyrroles substituted with phenyl capping groups ($PhPy_nPh$, $n = 2-4$) can be oxidized reversibly to give stable cation radicals and dications. Spectroelectrochemical studies give direct evidence that diamagnetic π-dimers of cation radicals are formed in solution. Such dimers may be involved as charge carriers in conducting polypyrrole.



J. A. E. H. van Haare, L. Groenendaal, E. E. Havinga, R. A. J. Janssen,* E. W. Meijer 638–640

π-Dimers of End-Capped Oligopyrrole Cation Radicals

The number and availability of starting compounds determine the structure diversity possible in a multicomponent reaction. For example, in a set of parallel reactions an amino-functionalized resin (P) was treated with 8 aldehydes, 12 carboxylic acids, and 1 isocyanide to provide 88 of the desired α-acyl amino amides [Eq. (a)]. Additional isocyanides not available commercially can be prepared from α-lithiated benzylisonitrile and used without purification. R^1, R^2 = alkyl, aryl.



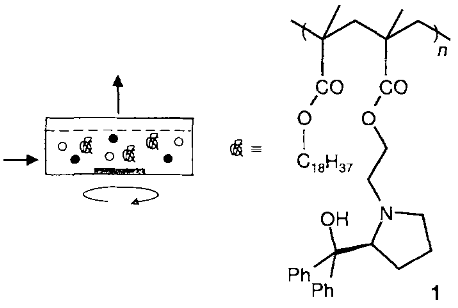
(a)

P. A. Tempest, S. D. Brown, R. W. Armstrong* 640–642

Solid-Phase, Parallel Syntheses by Ugi Multicomponent Condensation

---

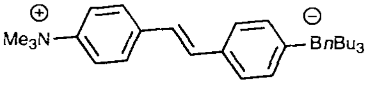
Adapted from biocatalytic reactions the principle of the membrane reactor (represented schematically on the right) is applicable to the continuous asymmetric addition of diethylzinc to benzaldehyde. α,α-Diphenyl-L-prolinol is coupled to a homogeneously soluble polymer (**1**), which enables it to be retained in the reaction vessel by an ultrafiltration membrane. By decoupling the residence time of reactants and the catalyst the total turnover number could be increased by a factor of 10.



U. Kragl,* C. Dreisbach 642–644

Continuous Asymmetric Synthesis in a Membrane Reactor

Ammonium and borate substituents polarize π-electron systems, which then exhibit internal CT bands in the UV/Vis spectrum. These systems (for example **1**) are distinctly more transparent than analogous push–pull-substituted compounds. Since their first-order hyperpolarizabilities are nevertheless similar to push–pull compounds, they are better suited to applications for second harmonic generation.

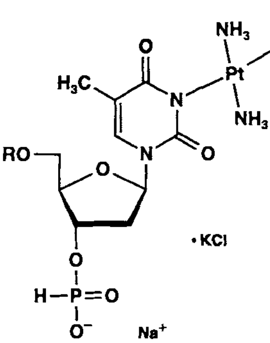


1

C. Lambert,* S. Stadler, G. Bourhill, C. Bräuchle 644–646

Polarized π-Electron Systems in a Chemically Generated Electric Field: Second-Order Nonlinear Optical Properties of Ammonium/Borate Zwitterions

The 3′-phosphonate building block 1 of a platinated nucleoside has been synthesized for the first time. A platinated nucleotide was then incorporated with specificity into an oligonucleotide by using standard procedures of automated DNA synthesis. This method should make it possible to prepare defined platinated oligonucleotides, and should facilitate studies of the mechanisms by which platinum complexes are biologically active.



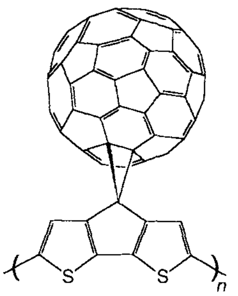
1

J. Schliepe, U. Berghoff, B. Lippert, D. Cech* 646–648

Automated Solid Phase Synthesis of Platinated Oligonucleotides via Nucleoside Phosphonates

---

A "charm bracelet" is a graphic description of the polymer prepared from cyclopentadithiophene with fullerene pendants. The interaction of the readily reducible fullerene moieties with the readily oxidizable polythiophene backbone makes **1** an interesting new material. Cyclic voltammetric studies have shown that the C_{60} substituents and the polythiophene chain retain their unique electrochemical properties in **1**.



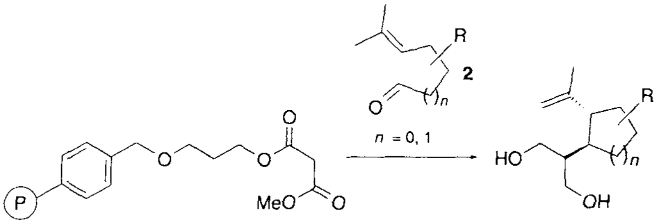
1

T. Benincori, E. Brenna, F. Sannicolò,* L. Trimarco, G. Zotti, P. Sozzani 648–651

The First "Charm Bracelet" Conjugated Polymer: An Electroconducting Polythiophene with Covalently Bound Fullerene Moieties

---

Diversomer libraries consisting of substituted cyclopentanes and cyclohexanes **3** were produced by Knoevenagel reaction of polymer-bound malonate **1** and aldehydes **2**, subsequent ene reaction, and cleavage from the support. In this domino solid-phase procedure the simple and induced diastereoselectivities of the ene reaction are generally very satisfactory (>99:1). R = H, Me, *n*Bu, Ph.



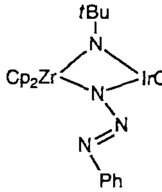
1 3

L. F. Tietze,* A. Steinmetz 651–652

Stereoselective Solid-Phase Synthesis of Cyclopentane and Cyclohexane Derivatives by Two-Component Domino Reactions: Generation of Combinatorial Libraries

---

An intact organonitrogen bridge is formed when ethyl diazoacetate or phenyl azide add across a Zr–Ir bond (for example, **1**; Cp = C_5H_5, Cp* = C_5Me_5). The ethyl diazoacetate complex is thermally stable, but heating the phenyl azide complex **1** leads to first-order loss of N_2 and formation of the bridging phenylimido complex.



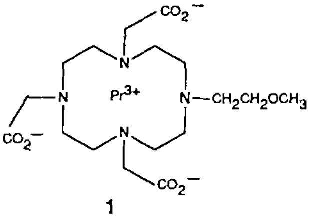
1

T. A. Hanna, A. M. Baranger, R. G. Bergman* 653–655

Addition of Organic 1,3-Dipolar Compounds across a Heterobinuclear Bond between Early and Late Transition Metals: Mechanism of Nitrogen Loss from an Organoazido Complex To Form a Bridging Imido Complex

---

The body temperature inside a living organism can be determined by measuring the ^{1}H NMR chemical shifts of the paramagnetic praseodymium chelate complex **1**. The complex is very stable and well-tolerated. In a first in vivo application the temperature inside the liver of a living rat was determined with an accuracy better than 0.5 K.

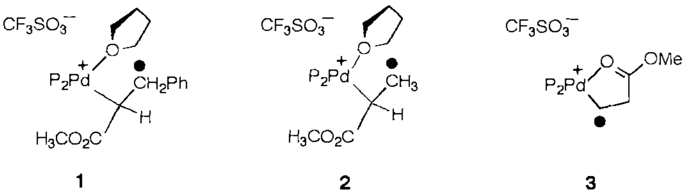


1

K. Roth,* G. Bartholomae, H. Bauer, T. Frenzel, S. Kossler, J. Platzek, B. Radüchel, H.-J. Weinmann ... 655–657

Pr[MOE-DO3A], a Praseodymium Complex of a Tetraazacyclododecane: An In Vivo NMR Thermometer

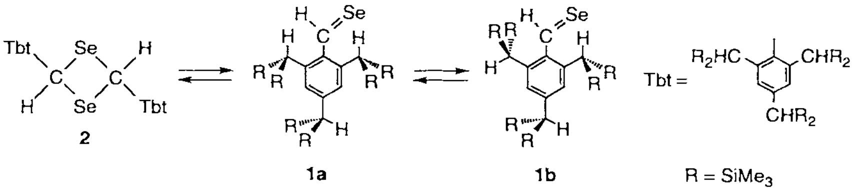
Strong competitive complex formation by H_2O is one of the significant results in this NMR spectroscopic study on the reactive intermediates in the Heck reaction of methyl acrylate. Compounds **1**–**3** were identified unambiguously as key intermediates with the aid of ^{13}C-labeled methyl acrylate (● indicates ^{13}C atom).



J. M. Brown,* K. K. Hii 657–659

Characterization of Reactive Intermediates in Palladium-Catalyzed Arylation of Methyl Acrylate (Heck Reaction)

Deselenation of the sterically congested cyclic polyselenide TbtCHSe$_n$ (n = 5.1) provided new access to selenobenzaldehyde **1a**, which is stable in solution but on concentration dimerizes to give the head-to-tail dimer **2**. Thermolysis of **2** (45 °C) resulted in formation of **1a** and its rotational isomer **1b**. Pentacarbonyltungsten complexes of both isomers were synthesized and characterized.

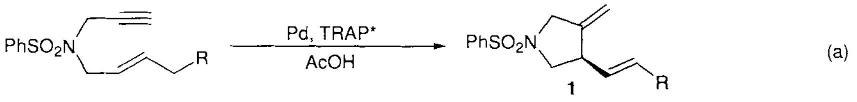


N. Takeda, N. Tokitoh, R. Okazaki* 660–662

The First Rotational Isomers of Stable Selenoaldehydes and Their η^1-Tungsten Complexes

---

Electronic and steric factors influence the enantioselectivity of the formation of pyrrolidines **1** in an asymmetric variant of the well-known Pd-catalyzed cycloisomerization of 1,6-enynes to give 1,4-dienes [Eq. (a)]. First hints to the importance of these factors were obtained by varying the R group in the enyne and the substituents on the P-aryl groups in the chiral ligand bis[(diarylphosphanyl)ethyl]biferrocene (TRAP*). R = Si(alkyl)$_3$, alkyl.



A. Goeke, M. Sawamura, R. Kuwano, Y. Ito* 662–663

Enantioselective Cycloisomerization of 1,6-Enynes Catalyzed by Chiral Diphosphane–Palladium Complexes

---

* Author to whom correspondence should be addressed

BOOKS

The following reviews will appear in future issues:

Understanding and Manipulating Inorganic Materials Using Scanning Probe Microscopes
Charles M. Lieber, Jie Liu, Paul E. Sheehan

Enzyme Mechanisms, Models, and Mimics
Anthony J. Kirby

Electrospray Mass Spectrometry of Supramolecular Complexes of Biomacromolecules--New Analytical Perspectives for Supramolecular Chemistry and Molecular Recognition Processes
M. Przybylski

Analogues of Carbenes, Olefins, and Small Rings from Main Group Chemistry
Matthias Driess and Hansjörg Grützmacher?

Protonation of Unsaturated Hydrocarbon Ligands: Regiospecificity, Stereospecificity, and Product Specificity
Richard A. Henderson

The Mechanisms of the Claisen Rearrangement: Déjà Vu All Over Again
Bruce Ganam

The Coordination of SiH_4 to Metals: A Step Towards the Complexation of Methane to Transition Metal Complexes
Jörg J. Schneider

Free-Radical Carbonylations: Then and Now
Ilhyong Ryu and Norboru Sonoda

A First Step Towards Planning of Syntheses in the Solid-State Chemistry: Determination of Promising Structure Candidate Using a Modular Approach
M. Janssen and J. C. Schön

CC-1065 and the Duocarmycins: Mechanistic Studies
Dale L. Boger and Douglas S. Johnson

What Can We Learn from Molecular Recognition in Protein-Ligand Complexes for the Design of New Drugs?
Hans-Joachim Böhm and Gerhard Klebe

Molecular Chemistry for Sol-Gel Processes
Robert Corriu and Dominique Leclercq

Glycals in Organic Synthesis: The Evolution of Comprehensive and Powerful Strategies for the Convergent Assembly of Oligosaccharides and other Glycoconjugates of Biological Consequence
Samuel J. Danishefsky and Mark Bilodeau

Self-Assembly in Natural and Unnatural Systems
J. Fraser Stoddart and Douglas Philip

Chemistry and Biology of the Zaragozic Acids (Squalestatins)
K. C. Nicolaou and Alan Nadin

Saccaride Sensing with Boronic Acid-based Molecular Receptors
K. R. A. Samankumara Sandanayake, Tony D. James, and Seiji Shinkai

Enantioselective Synthesis of C-C and C-H Bonds Mediated or Catalyzed by Chiral EBTHI Complexes of Titanium and Zirconium
James P. Morken and Amir H. Hoveyda

ANGEWANDTE
CHEMIE
A Journal of the
Gesellschaft
Deutscher Chemiker
International Edition in English
1996
35/5
Pages 465–560

EDITORIAL

Twelve monthly issues make up a volume, and with this first March issue of *Angewandte Chemie* you are receiving the twelfth issue of *Chemistry—A European Journal.* We are actually well into our second volume (nine issues must suffice for the first), but it seems appropriate to give an update on the current status of the two journals. Fraser Stoddart, a strong advocate of *Chemistry – A European Journal*, echoed the reaction of many readers to its inception when he claimed it was "the most significant positive development in the academic publishing business surrounding chemistry as a discipline in a long time." The overwhelmingly positive response is further documented in the following excerpt from a letter we received from K. Wieghardt. Looking ahead he maintains, "The future of this journal depends on how fast the number of printed, first-rate papers can be increased. The volume should quickly be doubled and tripled, but of course not at the expense of quality."

The editorial office has responded to this cry of "we want more" in the first three issues in 1996, and readers will not be disappointed with future contents. In this way we have been able to reduce the rather long publication times that had resulted from the enthusiatic response of authors to first call for papers for the "European Journal". Our goal is to publish manuscripts within three to four months of their final acceptance. Test us with your next top-notch full paper!

Now the interim report on *Angewandte Chemie*: In 1995 the editorial office received 47 reviews, 46 highlights, 1090 communications, and roughly 100 book reviews; 45 reviews, 43 highlights, 533 communications, and around 90 book reviews were published. Most of the reviews, highlights, and book reviews were submitted on invitation; however, we also welcome unsolicited manuscripts for these sections.

Of the 1090 communications received in 1995 (1005 in the previous year, +8 %), 715 (606, +18 %) came from outside of Germany. In mid-February the fate of only about 30 communications submitted in 1995 was still undecided; 566 (52 %) had been rejected. Over the past few years German authors have consistently submitted 300 to 400 communications annually; in 1995 they accounted for 375. The distribution of manuscripts from foreign contributors and its development over the past years are given in Table 1.

Table 1. Origin of manuscripts submitted from outside of Germany.

Country	1995	1994	1989
USA/Canada	225	185	66
Far East [a]	130	87	36
United Kingdom	76	63	28
France	54	57	28
Spain	41	38	19
Italy	37	30	15
Switzerland/Austria	36	43	21
Netherlands	22	22	9
Other	53	47	24

[a] Japan, Korea, China, Hong Kong, and Taiwan.

At the end of every year the Institute of Scientific Information discloses the Impact Factors and Immediacy Indices for the previous year. The trend here is also very positive (Table 2). The Impact Factors of *good* "review journals" are naturally high, and *Angewandte Chemie* profits from this trend. (Impact Factors of the life sciences journals are generally three times higher than those of chemistry journals because many more research groups exist in each specialty.) The Immediacy Index, which is

0570-0833/96/3505-0467 $ 15.00+.25/0

defined as the average number of times a publication is cited in the year in which it is published, is 1.58 for *Angewandte Chemie*, 1.80 for *Chem. Rev.*, 1.61 for *Acc. Chem. Res.*, 0.94 for *J. Am. Chem. Soc.*, 0.53 for *Chem. Commun.*, and 0.46 for *Chem. Soc. Rev.* Put simply, on average *each* publication in *Angewandte Chemie* is cited one to two times in the same year.

Table 2. Impact Factors of a number of important chemistry journals.

Journal	Impact Factors			
	1994	1993	1989	1984
Angew. Chem.	6.327	6.168	5.049	4.007
J. Am. Chem. Soc.	5.039	5.365	4.415	4.43
Chem. Rev.	14.24	15.748	9.656	8.024
Acc. Chem. Res.	9.126	10.879	7.419	7.653
Chem. Soc. Rev.	4.913	6.152	4.406	5.75
Chem. Commun.	2.575	2.54	2.223	2.437

The positive development reflected in all of these numbers led—in complete contrast to trends for most scientific journals—to an increase in the number of personal subscribers in 1995. This growth in individual subscriptions can be ascribed predominantly chemists outside of Germany. The excellent value of *Angewandte Chemie*, which is expressed in hard numbers in Table 3, may be one explanation.

Table 3. Costs of chemistry journals 1993 [a].

Journal	US \$ per 10^6 characters	Cost per unit Impact Factor
Angew. Chem. [b]	43.09	92.97
J. Am. Chem. Soc. [b]	9.51	196.64
Chem. Commun. [b]	66.98	329.13
Chem. Ber. [b]	57.25	549.69
Tetrahedron	145.29	3604.24
Inorg. Chem. Acta	174.08	2141.08

[a] From an article by J. Christman in *Chem. Ind. (London)* **1995**, 2236. [b] Journals published by a scientific society.

What lies ahead? In 1996 *Angewandte Chemie* and *Chemistry—A European Journal* will also make their debut on the World Wide Web. We plan to present our Tables of Contents and several other items, but more on this subject later. A number of journals are now available on CD-ROM. In a survey of readers/users of *Angewandte Chemie* in 1994 we found that interest in this format was not as high as some might have thought. But we continue to make preparations for developments in this direction. VCH is working in cooperation with the German Chemical Society (GDCh) on a project supported by the German Ministry of Education and Science ("The electronic publishing house"). The eventual goal is that every step, from submission of a manuscript (such an antiquated word!) to distribution and reading of the final product, proceeds electronically and without any abrupt change in media. We should not forget, however, that the quality of a journal in whatever format depends on people. A journal is the product of *authors* who write *good* manuscripts, *referees* who frequently contribute to further improving these manuscripts, and finally *editors* who strive for an optimal, reader-friendly presentation. The print medium is far from dead. Scientific journals such as *Angewandte Chemie* are read in the lab, in the office, at home, and during trips...

The editorial office now relies heavily on the most rapid means of communication. The majority of the referee reports are sent in by fax or e-mail. Of course, the rate-determining factors in the publication process remain the writing of the manuscript, the careful refereeing, and the frequently requested revision. The majority of communications last year were published four to five months after *initial submission.* In one extreme case we published a manuscript within four weeks—but that is pushing the referees, editors, and printers to their limits.

The main goal of *Angewandte Chemie* and *Chemistry—A European Journal* in 1996 continues to be rapid publication of excellent papers from all areas of chemistry. But we will not cut corners on our reader-friendly presentation. On the contrary, additional small improvements are planned. We introduced "keywords" this past year, which are intended to direct the reader to articles of interest quickly, and which also facilitate production of the yearly index. Frontispieces (large pictures at the beginning of each review and at the front of the communication section) will soon be in each issue. Chemists are visual people, and often a figure or a formula can convey much more than words can. We are eager to know how you receive this innovation. We encourage authors to give suggestions for these pictures as well as for the cover picture.

"The 20th century is the century of productivity. The 21st century will be the century of quality" was a recent prediction. At *Angewandte Chemie* and *Chemistry—A European Journal* we are prepared! We look forward to receiving your next manuscript!

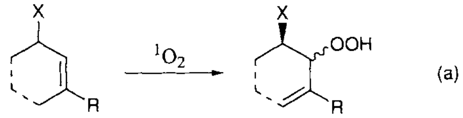
Peter Gölitz

COVER PICTURE

The cover picture shows the structure of the subnitride $Na_{14}Ba_{14}CaN_6$. Ion clusters (blue) of the composition Ba_8CaN_6 with a perowskitelike arrangement of atoms—Ca-centered Ba_8 cubes surrounded by N atoms above all faces—are dispersed in a metallic matrix (red) of sodium and barium. More about this compound, which can be considered a salt dissolved in a metal, is reported by U. Steinbrenner and A. Simon on p. 552 ff.

REVIEWS

The obstinate singlet oxygen can be tamed by a number of factors: steric, stereoelectronic, electronic, and conformational effects of the functional group X play an important role in controlling the direction of the attack of singlet oxygen on alkenes [Eq. (a)]. This unfortunately rarely employed reaction, the Schenck ene reaction, yields diastereoselectively oxyfunctionalized compounds—useful intermediates in organic synthesis. X = hydroxyl, amino, halogen, ether, ester, sulfoxide, sulfone.



M. Prein, W. Adam* 477–494

The Schenck Ene Reaction: Diastereoselective Oxyfunctionalization with Singlet Oxygen in Synthetic Applications

---

Simpler to apply than the original model and supported by the analysis of electron density distributions with the Laplacian operator, the reformulation of the VSEPR model of molecular geometry presented here is based on the concept of electron domains. In this form it is suitable as foundation for a qualitative understanding of the geometry of a large number of molecules, including those of metal compounds. Analyses of the valence and core electron densities with the Laplacian operator often also yield plausible explanations why some molecules do not have the structure predicted by the VSEPR model.

R. J. Gillespie,*
E. A. Robinson 495–514

Electron Domains and the VSEPR Model of Molecular Geometry

HIGHLIGHTS

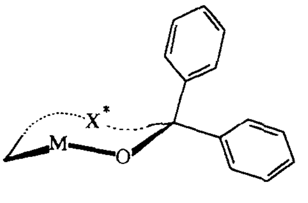
Structural design in the synthesis of solids is now a step closer, at least for mesoporous compounds. Surfactant assemblies are used as templates to structure metal oxides, which are formed from metal alkoxides. By adapting the headgroup of the surfactant to the inorganic component and exploiting the coordination chemistry of the metal atoms in the alkoxides, a wide range of mesoporous metal oxides, including alumina, titania, niobia, and zirconia, becomes available.

P. Behrens* 515–518

Voids in Variable Chemical Surroundings: Mesoporous Metal Oxides

---

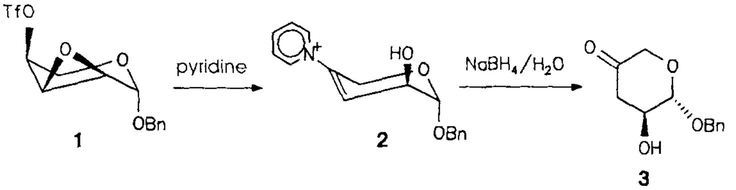
Increasing stereoselectivity in numerous recently developed methods of asymmetric synthesis is possible with the diarylhydroxymethyl group, which is typically employed in deprotonated form as a ligand in metal complexes. In the transition state of these reactions the geminal aryl groups are apparently fixed in a chiral conformation owing to the influence of a permanent stereogenic center X*. A schematic representation of this type of metal catalyst is shown on the right.



M. Braun* 519–522

The "Magic" Diarylhydroxymethyl Group

α,β-Epoxytriflates like epoxytriflate pyranoside **1** undergo rearrangement in a one-pot reaction after treatment with pyridine. The epoxy ring is opened giving N-vinylpyridinium derivatives such as **2**, which can be reduced with NaBH$_4$ and hydrolyzed under acidic conditions to give β-hydroxy ketones. This generally applicable procedure can be used to convert easily accessible epoxypyranoses into deoxyketo sugars like **3** in high yields.

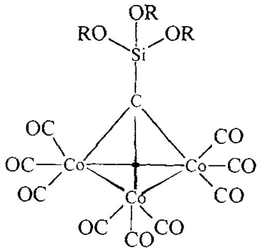


Y. Al-Abed, N. Naz, K. M. Khan, W. Voelter* 523–524

Pyridinium Ions Adjacent to Oxirane Rings: Useful Intermediates for the Stereospecific Synthesis of β-Hydroxy Ketones

---

Not water, but polyethyleneglycol serves as the solvent for the cobalt complex **1** (R = CH$_2$CH$_2$(OCH$_2$CH$_2$)$_n$OH, n = 9), an efficient catalyst for the hydroformylation of 1-hexene. Because complex **1** is not soluble in unpolar solvents, this highly chemoselective reaction can be conducted in the two-phase system polyethyleneglycol/hexene.



1

U. Ritter, N. Winkhofer, H.-G. Schmidt, H. W. Roesky* 524–526

New Cobalt Catalysts for Hydroformylations in Two-Phase Systems

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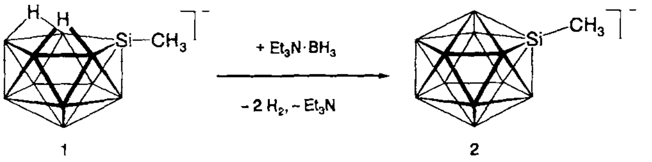
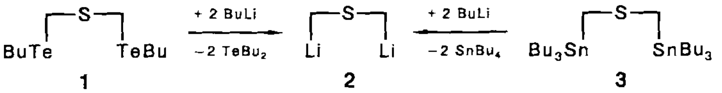
A cluster construction reaction starting with silaborane **1** and triethylamine–borane provides 1-methyl-1-sila-*closo*-dodecaborate(1–) **2** in 93% yield.



L. Wesemann,* U. Englert 527

The First *closo*-Monosilaborane

Although extremely useful, only a few 1,3-dilithiated organoelement compounds are known, because no suitable synthetic methods were available. Now bis(lithiomethyl) sulfide (**2**) has been prepared by double metal–lithium exchange (transmetalation) from **1** and **3**. At room temperature **2** is a colorless metastable powder.



C. Strohmann* 528–529

Bis(lithiomethyl) Sulfide, An Unexpectedly Stable 1,3-Dilithiated Synthetic Building Block

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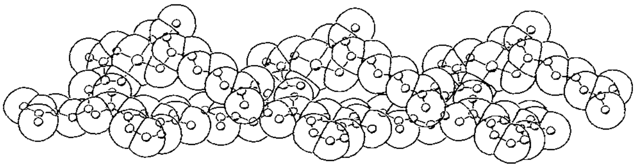
Transient detachments and even minor movements of chain segments of a single DNA molecule adsorbed on a substrate can be revealed by the method described in this communication. The scanning force microscopy image on the right shows a DNA molecule on mica with an open circular shape acquired after extensive detachments and movements.

B. Samorì,* C. Nigro, A. Gordano, I. Muzzalupo, C. Quagliariello .. 529–530

Trapping and Imaging Molecular Dynamics by Combining Scanning Force Microscopy with Topology

---

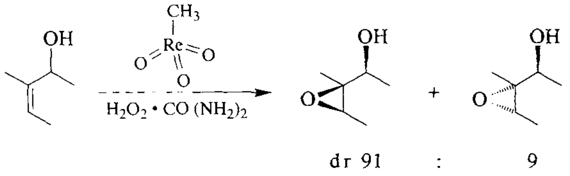
The dianion is the key! Complexes of the type [Cu(Arg)$_2$](L)·nH$_2$0 (L = aromatic dicarboxylate, n = 5,6) formed by self-assembly show double-helical structures in the solid state, which comprise infinite [Cu(Arg)$_2$]$^{2+}$-L^{2-} strands (shown schematically below). In these, the dianions function as bridging ligands, bound through guanidinium–carboxylate pairs, between the complex cations and read the information of handedness coded in the [Cu(Arg)$_2$]$^{2+}$ units.



N. Ohata, H. Masuda, O. Yamauchi* 531–532

Programmed Self-Assembly of Copper(II) -L- and -D-Arginine Complexes with Aromatic Dicarboxylates to Form Chiral Double-Helical Structures

High yields and only traces of side products are possible in the synthesis of epoxides by oxidation of alkenes when the urea/hydrogen peroxide adduct (UHP) is used as the oxygen donor in the methyltrioxorhenium(VII)-catalyzed reaction (see below). Chiral allylic alcohols with 1,3-strain were employed as stereochemical probes; the high *threo* diastereoselectivities obtained allow important mechanistic insights into the oxygen transfer process.

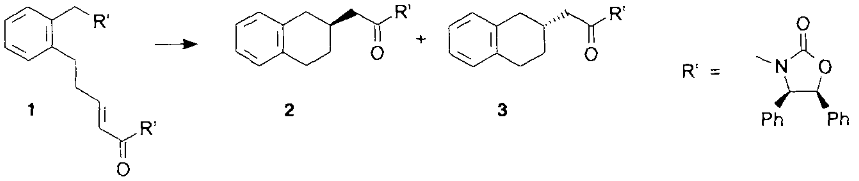


W. Adam,* C. M. Mitchell 533–535

Methyltrioxorhenium(VII)-Catalyzed Epoxidation of Alkenes with the Urea/Hydrogen Peroxide Adduct

---

A good yield, but only modest diastereoselectivity (**2**:**3** = 45:55) is achieved in the radical cyclization of **1** to give **2** and **3**. $MgBr_2 \cdot Et_2O$ was essential for good diastereoselectivity (**2**:**3** = 82:18). Transition state modeling with a specifically developed "radical force-field" suggested that the observed diastereoselectivities can be ascribed to van der Waals attractive interactions between arenes.

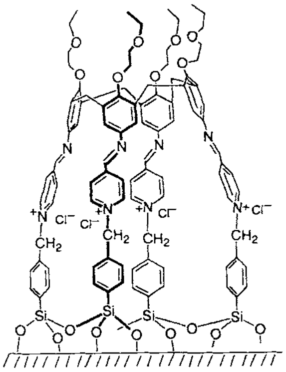


D. Badone,* J.-M. Bernassau, R. Cardamone, U. Guzzi 535–538

Diastereoselective Chelation-Controlled Radical Cyclization of Chiral Oxazolidinone-Derived 2-Alkenamides and Modeling of the Transition State

---

Ultrahigh second-order nonlinearities were observed in calix[4]arene-based, chromophoric supermolecules, which form densely packed, highly ordered monolayers on silica surfaces (shown on the right). The super chromophores consist of four stilbazole–imine units in a rigid cone conformation, in which all the dipoles are aligned in the same direction.

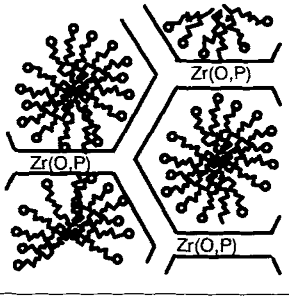


X. Yang, D. McBranch, B. Swanson, D. Li* 538–540

Synthesis and NLO Properties of Polar Self-Assemblies of Molecular Pyramids Covalently Bound on Oxide Surfaces

---

Analogous to the synthesis of MCM-41, a mesostructured product (shown schematically on the right) can be obtained from aqueous solutions of zirconium sulfate by addition of alkyltrimethylammonium salts. After a treatment with phosphoric acid, this material can be calcined without structural collapse. The resulting zirconium oxo phosphate shows BET surface areas of up to 400 $m^2 g^{-1}$.

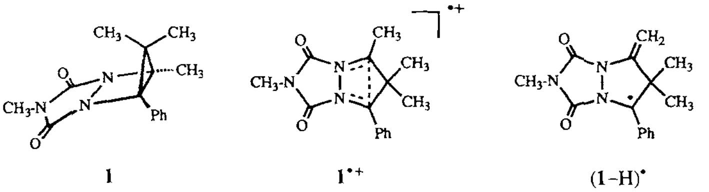


U. Ciesla, S. Schacht, G. D. Stucky, K. K. Unger, F. Schüth* 541–543

Formation of a Porous Zirconium Oxo Phosphate with a High Surface Area by a Surfactant-Assisted Synthesis

---

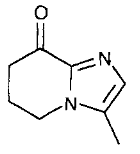
Instead of the 1,2-alkyl migration well-established for carbocyclic analogues, the 1,3-radical cation $1^{\bullet+}$, generated from the corresponding housane **1** by oxidation with $(4\text{-}BrC_6H_4)_3N^{\bullet+}SbCl_6^-$, undergoes an unexpected deprotonation to give the monoradical $(1-H)^{\bullet}$. In this process the proton is presumably transferred to one of the two carbonyl groups of the triazolidinedione ring.



W. Adam,* T. Kammel, S. Steenken* 543–545

Generation of a Heterocyclic 1,3-Cyclopentanediyl Radical Cation by Chemically Induced Electron Transfer Oxidation and Pulse Radiolysis

The first natural product of its structure type, azaindolizidine **1** was produced by fermentation of an isolate of thermophilic actinomyces obtained from a 60 °C hot spring at Lake Tanganyika (Africa). The structure of this compound was determined from NMR data and verified by synthesis from methylimidazole and 4-bromobutyronitrile.

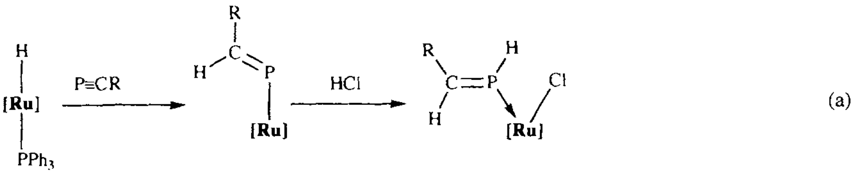


1

D. Hafenbradl, M. Keller,*
K. O. Stetter,
P. Hammann,* F. Hoyer,
H. Kogler 545–547

Sibyllimycine, 5,6,7,8-Tetrahydro-3-methyl-8-oxo-4-azaindolizidine, a Novel Metabolite from *Thermoactinomyces* sp.

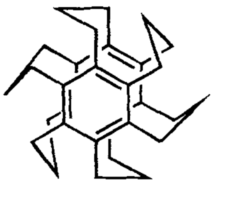
An unprecendently simple metallaphosphaalkene, which can be readily and reversibly protonated to provide a complex of the otherwise unstable phosphaalkene HP=CH*t*Bu, is the product of the first hydrometalation of phosphaalkynes [Eq. (a); [Ru] = RuCl(CO)(PPh$_3$)$_2$, R = *t*Bu].



R. B. Bedford, A. F. Hill,*
C. Jones* 547–549

Phosphaalkyne Hydrometalation: Synthesis of [RuCl(P=CH*t*Bu)(CO)(PPh$_3$)$_2$]

Six trimethylene bridges link the phenyl rings of the "pinwheel" compound **1**, which was synthesized from [3$_5$](1,2,3,4,5)cyclophane. An intramolecular aldol condensation serves as the key step for introducing the final trimethylene bridge. The NMR spectroscopic data suggest a highly symmetrical and dynamic structure for **1**.



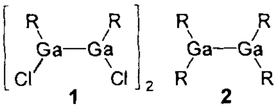
1

Y. Sakamoto, N. Miyoshi,
T. Shinmyozu* 549–550

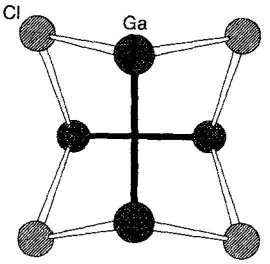
Synthesis of a "Molecular Pinwheel": [3.3.3.3.3.3](1,2,3,4,5,6)Cyclophane

---

A cage comprising four gallium and four chlorine atoms (shown on the right) is the characteristic feature of the first dimeric digallane **1** (R = Si(SiMe$_3$)$_3$) having two different substituents. It is synthesized together with the tetrasilyl-substituted digallane **2** from Ga[GaCl$_4$] and LiSi(SiMe$_3$)$_3$(THF)$_3$.



1 2

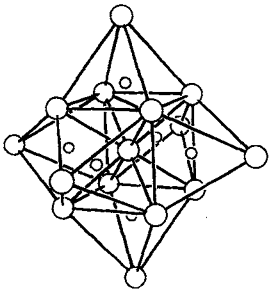


G. Linti,* W. Köstler 550–552

Synthesis and Structure of a Digallane with Tris(trimethylsilyl)silyl and Chloro Substituents

---

The new cluster Ba$_{14}$CaN$_6$, whose core Ba$_8$CaN$_6$ is a fragment of the perowskite structure type, is contained in the title subnitride. The structure of Na$_{14}$Ba$_{14}$CaN$_6$ (pictured on the right) represents a "nanodisperse" system of saltlike particles in a metallic matrix.



U. Steinbrenner, A. Simon* 552–554

Na$_{14}$Ba$_{14}$CaN$_6$—A Nanodispersion of a Salt in a Metal

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* Author to whom correspondence should be addressed

BOOKS

Stereochemistry of Organic Compounds · E. L. Eliel, S. H. Wilen — *U. Koert* 555

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ANGEWANDTE CHEMIE

A Journal of the
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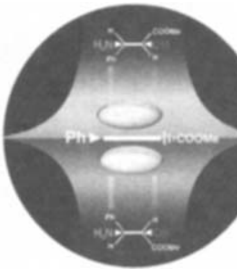
Deutscher Chemiker

International Edition in English

1996
35/4
Pages 353–464

COVER PICTURE



The cover picture shows the catalytic asymmetric aminohydroxylation (AA) of alkenes in action. Methyl cinnamate can be transformed directly into a derivative of the taxol side chain with the catalyst system $K_2OsO_2(OH)_4$ and a phthalazine ligand; Chloramine T serves as the nitrenoid source. Either enantiomer can be produced at will by selection of the appropriate ligand. The asymmetric aminohydroxylation (AA) follows the development of the asymmetric epoxidation (AE) and the asymmetric dihydroxylation (AD)—three reactions whose importance for organic synthesis cannot be overstated. Li, Chang, and Sharpless report more on the new catalytic AA on p. 451 ff. (The cover picture was created by Michael E. Pique, The Scripps Research Institute, La Jolla, CA, USA.)

REVIEWS

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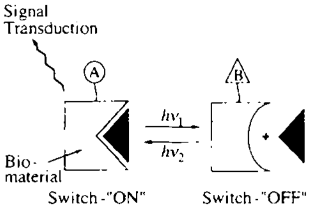
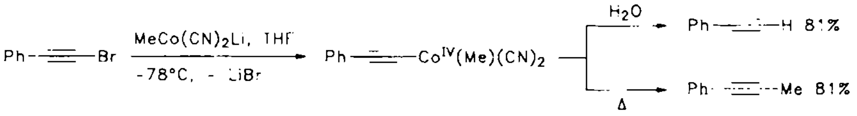


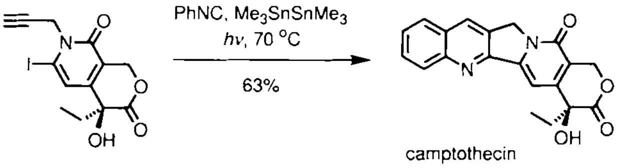
Two methods of making biomaterials photoswitchable are presented here: the covalent linkage of photoisomerizable components (A ⇌ B) to biomolecules and the interaction of the biomaterials with photoswitchable microenvironments. The diagram on the right illustrates the first principle with the formation and dissociation of, for instance, an enzyme–substrate or antibody–antigen assembly. In the isomer state A the bioactive structure of the biomaterial is retained, and formation of the complex with the substrate is activated. In the photoisomer state B the active site is distorted, and dissociation is induced. Such modified compounds form the basis of opto-bioelectronic devices.

The willingness to undergo oxidative addition of electrophiles, the high selectivity, and several unexpected reactions are responsible for making the title compounds, which had been disregarded or unknown for a long time, widely applicable, mild alkylating reagents. For example, (E,Z)-β-fluorostyrene can be converted with Me_4CoLi_2 into (E,Z)-1-phenylproprene in 92% yield. The reaction of bromophenylacetylene with $MeCo(CN)_2Li$ (see below) shows other possibilities.



HIGHLIGHTS

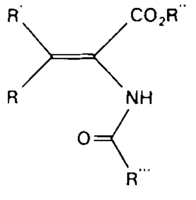
A prime example of applied radical chemistry is the last step of Curran's total synthesis of the antitumor agent camptothecin (below). This and other key sequences demonstrate the importance of radical reactions in natural products chemistry.



U. Koert* 405-407

Radical Reactions as Key Steps in Natural Product Synthesis

Very different ligands have been employed recently for enantioselective hydrogenation. With rhodium phospholane complexes, not only the usual, but also highly substituted enamides such as **1** and acylhydrazones can be hydrogenated. With ruthenium complexes containing chiral amino alcohols, ketones can be converted into the corresponding alcohols with high enantioselectivities.



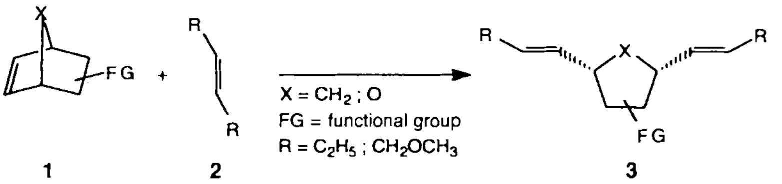
1

J. Albrecht, U. Nagel* 407-409

Enantioselective Catalytic Hydrogenation

COMMUNICATIONS

Crossed ring-opening metatheses (ROM) close the gap between ring-opening metathesis polymerization (ROMP) and ring-closing metathesis (RCM). According to this principle, easily accessible functionalized bicycles of type **1** and symmetric olefins **2** can be converted with ruthenium catalysts into highly substituted five-membered rings of type **3**.

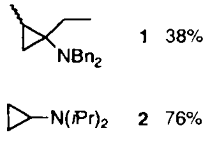


M. F. Schneider, S. Blechert* 411-412

Synthesis of Highly Substituted Cyclopentane and Tetrahydrofuran Derivatives by Crossed Olefin Metathesis

---

The reaction of acid *N*,*N*-dialkylamides with alkylmagnesium bromides in the presence of a stoichiometric amount of titanium tetra(2-propanolate) produces dialkylcyclopropylamines like **1** and **2** in moderate to good yields. Previously inaccessible aminocyclopropane derivatives are now readily available.

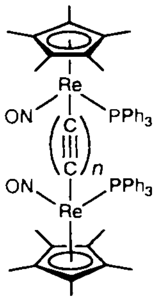


V. Chaplinski, A. de Meijere* 413-414

A Versatile New Preparation of Cyclopropylamines from Acid Dialkylamides

---

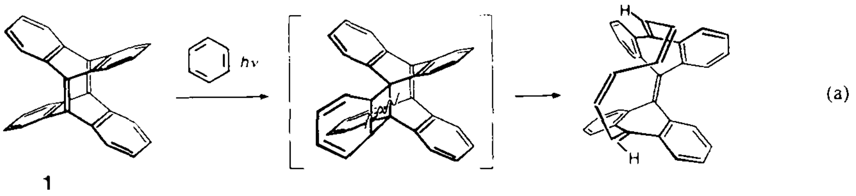
Novel chain extensions of [{Re*}−C≡C−C≡C−H] ({Re*} = (η^5-C_5Me_5)Re(NO)(PPh_3)) with alkyne or diyne building blocks lead to rhenium-capped oligomers of up to 20 sp carbon atoms (shown on the right, *n* = 6, 8, 10). This methodology allows, for the first time, access to such materials with a homogeneous chain length.



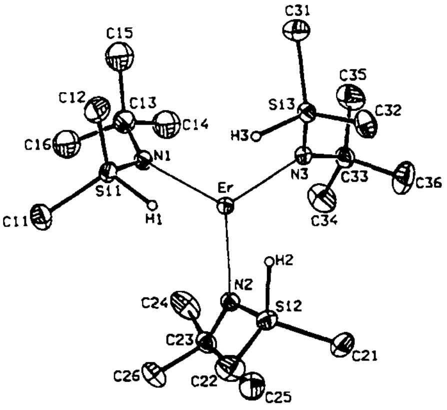
T. Bartik, B. Bartik,
M. Brady, R. Dembinski,
J. A. Gladysz* 414-417

A Step-Growth Approach to Metal-Capped One-Dimensional Carbon Allotropes: Syntheses of C_{12}, C_{16}, and C_{20} μ-Polyynediyl Complexes

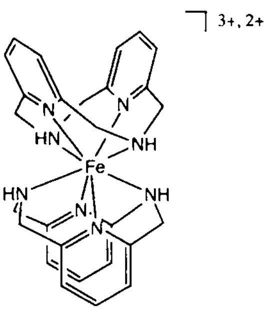
Relief of strain is the driving force for the [2 + 2] cycloaddition and subsequent [2 + 2] cycloreversion of **1** with both open-chain and cyclic alkenes. The metathesis can even be performed with benzene as the olefin component [Eq. (a)]. The product can be roughly described as a ribbon- or beltlike conjugated system.



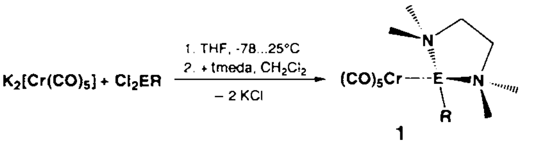
All the *tert*-butyl groups of $[Er\{N(tBu)[Si(CH_3)_2(H)]\}_3]$ (structure shown on the right) reside on the same face of the N_3 plane, whereas all $Si-CH_3$ groups are rotated toward the periphery of the molecule. This results in Er–H interatomic distances of 231.7–236.7 pm for the Si–H moieties folded in toward the metal center.



Eight-coordination and identical ligand environments have been unequivocally established in the pair of stable iron(II) and iron(III) complexes shown on the right. The synthesis, structures and electrochemical properties of these iron complexes are presented here, together with some Mössbauer spectroscopic data on the iron(II) complex.



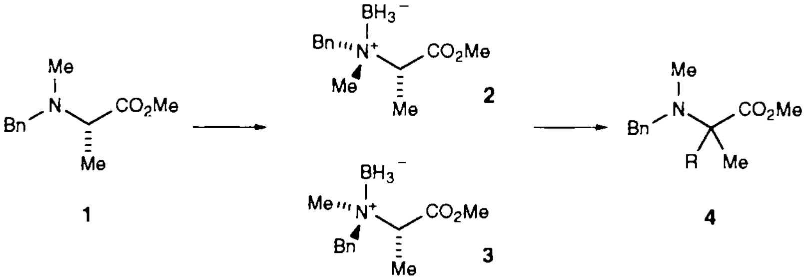
Redox reactions in the initial products formed from $K_2[Cr(CO)_5]$ and Cl_2ER (E = Al, Ga; R = Cl, alkyl) lead to the formation of aluminum(I) and gallium(I) transition metal complexes of type **1** (shown below) that are surprisingly stable. Stoichiometric CrGa films were prepared from **1** (E = Ga, R = CH_2CH_3) by MOCVD. tmeda = *N,N,N′,N′*-tetramethylethylenediamine.



Since the porous structure is completely retained upon surfactant removal, Nb-TMS1, a hexagonally packed mesoporous transition metal oxide, is an interesting molecular sieve. The synthesis of this material was accomplished by a novel route in which the inorganic precursor **1** and the surfactant **2** were attached by a covalent Nb–N bond; this bond is probably retained throughout the course of the synthesis.

$Nb(OEt)_5$ **1** $C_{14}H_{29}NH_2$ **2**

Enantiomeric excesses of up to 82% are obtained for the α,α-disubstituted products **4** arising from alkylation reactions of borane–amine adducts **2** and **3**, which have a chiral nitrogen atom. The structure of diastereomer **2**, which can be obtained selectively in the boration of **1**, has been established by single-crystal X-ray analysis.

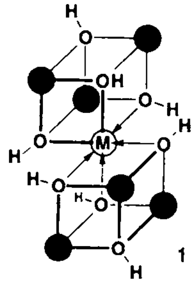


V. Ferey, L. Toupet, T. Le Gall,
C. Mioskowski* 430–432

Chiral Borane–Amine Adducts in Asymmetric Synthesis: Alkylation of Alanine Derivatives

---

A structure containing two cubes linked through a common metal atom (1) is formed on reaction of the novel tripodal ligand $[\{Re(CO)_3\}_3(OH)_4]^-$ with M^{II} salts (M = Mn, Cu). Crystals of **1** contain extended layers whose structures are determined by the type of coordination sphere of M^{II}. ● = $Re(CO)_3$; Counterion: NEt_4^+.

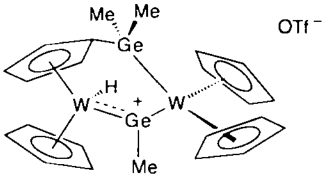


W. A. Herrmann,* A. Egli, E. Herdtweck,
R. Alberto, F. Baumgärtner 432–434

Heterobimetallic Hydroxy Complexes: $[Re_3(CO)_9(\mu_2\text{-}OH)_3(\mu_3\text{-}OH)]^-$ as a Novel Tripodal Ligand

---

A three-coordinate, cationic germanium center is the unusual feature of this dimeric tungsten complex **1** generated by the thermolysis of $[Cp_2W(SiMe_3)(GeMe_2OTf)]$. Delocalization of the charge onto only one of the tungsten centers is suggested by structural and orbital overlap considerations.



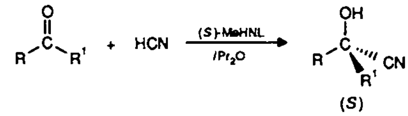
1

L. K. Figge, P. J. Carroll,
D. H. Berry* 435–437

Synthesis and Structure of a Bridging Germylidyne Complex: A Stable Germyl Cation

---

The cassava species *Manihot esculenta* provided the first recombinant hydroxynitrile lyase (MeHNL) that became accessible by overexpression in *E. coli*. This MeHNL catalyzes the enantioselective addition of HCN (depicted below) not only to aliphatic, aromatic, and heteroaromatic aldehydes, but also to ketones to give (*S*)-cyanohydrins in high optical yields. R = alkyl, aryl, heteroaryl; R^1 = H, CH_3.

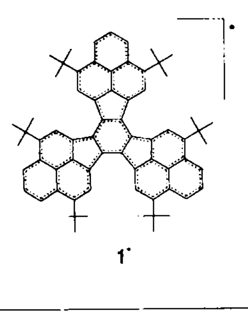


S. Förster, J. Roos, F. Effenberger,*
H. Wajant, A. Sprauer 437–439

The First Recombinant Hydroxynitrile Lyase and its Application in the Synthesis of (*S*)-Cyanohydrins

---

All seven redox states between the tricationic and the trianionic states of the decacyclenyl **1˙** are discernible by cyclic voltammetry. The electronic nature of the highly delocalized aromatic π-electron system of the neutral radical **1˙** and the charged species $\mathbf{1}^{3+}$ and $\mathbf{1}^{3-}$ has been investigated by ESR and NMR spectroscopy, respectively.

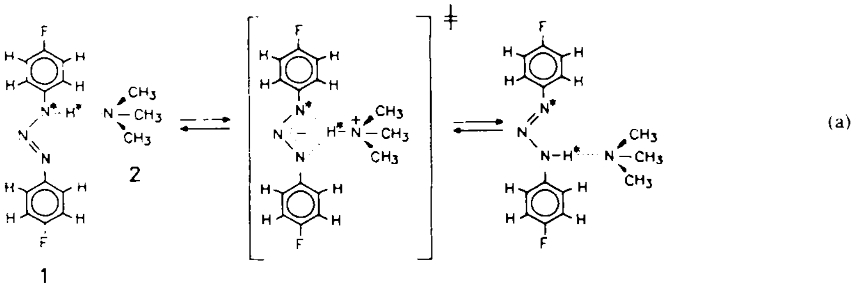


1˙

T. Kubo, K. Yamamoto, K. Nakasuji,*
T. Takui, I. Murata 439–441

Hexa-*tert*-butyltribenzodecacyclenyl: A Six-Stage Amphoteric Redox System

Through formation of a contact pair, bases are capable of transferring mobile protons from one molecular site to another. NMR experiments on a solution of diaryltriazene **1** in ethyl methyl ether in the presence of trimethylamine (**2**) [Eq. (a)] verify that the contact pair does not dissociate in the process.

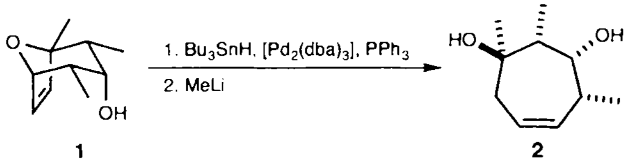


F. Männle, H.-H. Limbach* 441–442

An Intramolecular Base-Catalyzed Proton Transfer in 1,3-Bis(4-fluorophenyl)triazene

---

Tertiary alcohols like 2 can prepared from **1** in two steps by palladium-catalyzed hydrostannylation followed by an organolithium-induced ring opening. Compounds regioisomeric to those obtained with $[Ni(cod)_2]$/DIBAL-H are thus now available.

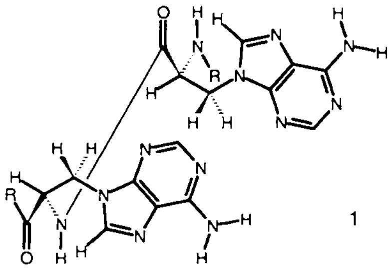


M. Lautens,* W. Klute 442–445

Regioselective Palladium-Catalyzed Hydrostannylation of Unsymmetrical Oxabicyclic Alkenes

---

Linear pairing complexes are presumably formed by peptide nucleic acids containing a backbone of alanyl amino acids with alternating configuration. The pairing of two strands is based on recognition of the nucleobases; however, unlike for DNA, stable self-pairing of a hexamer from adenine-substituted alanyl building blocks is possible for the PNA (**1**) described herein.

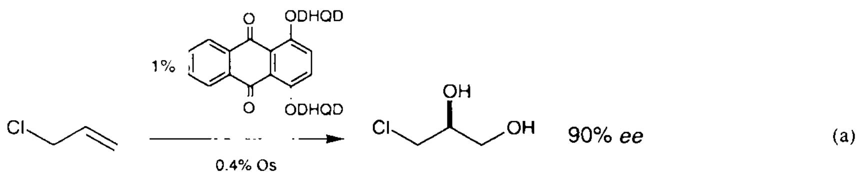


U. Diederichsen* 445–448

Pairing Properties of Alanyl Peptide Nucleic Acids Containing an Amino Acid Backbone with Alternating Configuration

---

Remarkably high *ee* values in the asymmetric dihydroxylation reaction (AD) can be achieved with the pseudo-enantiomeric ligand pair $(DHQD)_2AQN$ and $(DHQ)_2AQN$. These new ligands are superior for AD reactions of most olefins with aliphatic substituents and show exceptionally high enantioselectivity with olefins having heteroatoms in the allylic position [Eq. (a)]. DHQD = dihydroquinidinyl.

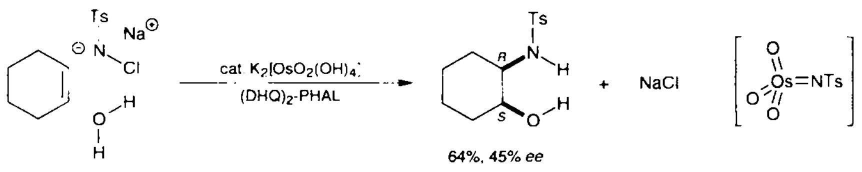


H. Becker, K. B. Sharpless* 448–451

A New Ligand Class for the Asymmetric Dihydroxylation of Olefins

---

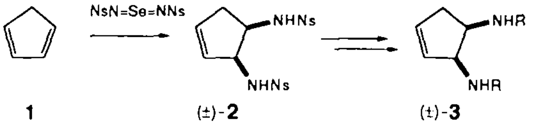
The stereospecific *cis* addition of "TsN" and H_2O yields α-hydroxy-*N*-tosylamines (see below). This osmium-catalyzed process, which depends on Chloramine-T as the nitrenoid source, is rendered asymmetric in the presence of cinchona alkaloid ligands. The selectivities for reactions of the six olefins studied range from 33% *ee* (*cis*-stilbene) to 81 % *ee* (*trans*-methylcinnamate). The active agent is presumably the compound $Os(O)_3NTs$ shown in square brackets. $(DHQ)_2$-PHAL = bis(dihydroquininyl)phthalazine (see preceding communication).



G. Li, H.-T. Chang,
K. B. Sharpless* 451–454

Catalytic Asymmetric Aminohydroxylation (AA) of Olefins

Replacing the tosyl with a nosyl (Ns) group—that is the key to an improved method for both allylic amination of olefins and 1,2-diamination of 1,3-dienes. The protecting group recently introduced by Fukuyama et al., the *o*-nitrobenzenesulfonyl (nosyl) group, can be employed with diimidoselenium reagents. The resulting nosylamides can be converted into primary and secondary amines in good to excellent yields. An example of this approach is sketched below in reaction (a) (R = Me, CH_2CHCH_2, CH_2Ph).



(a)

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* Author to whom correspondence should be addressed

BOOKS

The following reviews will appear in future issues:

The Total Synthesis of Brevetoxin B. A Twelve-Year Odyssey in Organic Synthesis
K. C. Nicolaou

Electrospray Mass Spectrometry of Supramolecular Complexes of Biomacromolecules—New Analytical Perspectives for Supramolecular Chemistry and Molecular Recognition Processes
M. Przybylski

Friedrich Hund and Chemistry
W. Kutzelnigg

A First Step towards Planning of Synthesis in Solid-State Chemistry: Determination of Promising Structure Candidates Using a Modular Approach
M. Jansen, J. C. Schön

Protonation of Unsaturated Hydrocarbon Ligands: Regiospecificity, Stereospecificity, and Product Specificity
R. A. Henderson

The Mechanism of the Claisen Rearrangement: Déja Vu All Over Again
B. Ganam

Analogues of Carbenes, Olefins, and Small Rings from Main Group Chemistry
M. Drieß, H. Grützmacher

What can we learn from Molecular Recognition in Protein-Ligand Complexes for the Design of New Drugs?
H.-Joachim Böhm, G. Klebe

Enzyme Mechanisms, Models and Mimics
A. J. Kirby

Understanding and Manipulating Inorganic Materials Using Scanning Probe Microscopes
C. M. Lieber, J. Liu, P. E. Sheehan

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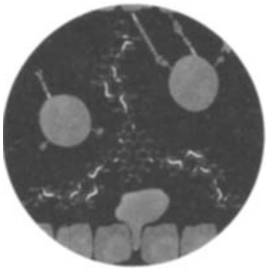
ANGEWANDTE CHEMIE

A Journal of the
Gesellschaft
Deutscher Chemiker

International Edition in English

1996
35/3
Pages 229–352

COVER PICTURE



The cover picture shows schematically how leukocytes from the blood stream bind to activated endothelium during inflammation processes and are finally extravasated into the surrounding tissue. The first step is the interaction of glycoproteins on leukocytes with adhesion molecules on the endothelium (P-, E-selectin). The tetrasaccharide sialyl Lewis^X has been identified as the binding epitope in complex glycoproteins, which are bound through carbohydrates to the selectins. Trivalent glycopeptides like that in the middle of the picture, which present three sialyl Lewis^X units, were synthesized by H. Kunz et al. with the goal of achieving improved receptor affinity. The authors describe the results of the adhesion tests and the synthesis of the glycopeptides on pages 321–324.

REVIEWS

Contents

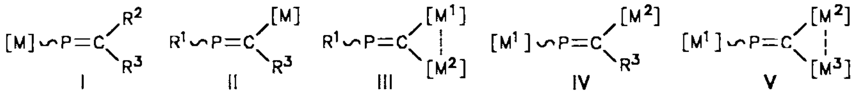
Still more can be expected from the Horner–Wittig reaction. Not only regioselective but also stereoselective Horner–Wittig additions and eliminations are possible with the bulky, anion-stabilizing Ph_2PO group. For example, alkenes having chiral centers on opposite ends of stereochemically defined double bonds can be constructed. Decisive advantages in these syntheses: Ph_2PO compounds are simple to purify, and diastereomeric β-hydroxy phosphane oxide adducts are easily separated.

J. Clayden,* S. Warren 241–270

Stereocontrol in Organic Synthesis Using the Diphenylphosphoryl Group

---

Cycloadditions and cyclooligomerizations are two of the reaction types that are possible with metallophosphaalkenes. The five modes of metalation in these compounds can be described by **I**–**V**. Syntheses, structures, and reactivity of these molecules, which are also versatile ligands, are presented herein.



$[M]{\sim}P{=}C\begin{smallmatrix}R^2\\R^3\end{smallmatrix}$ I, $R^1{\sim}P{=}C\begin{smallmatrix}[M]\\R^3\end{smallmatrix}$ II, $R^1{\sim}P{=}C\begin{smallmatrix}[M^1]\\[M^2]\end{smallmatrix}$ III, $[M^1]{\sim}P{=}C\begin{smallmatrix}[M^2]\\R^3\end{smallmatrix}$ IV, $[M^1]{\sim}P{=}C\begin{smallmatrix}[M^2]\\[M^3]\end{smallmatrix}$ V

L. Weber 271–288

Metallophosphaalkenes—from Exotics to Versatile Building Blocks in Preparative Chemistry

HIGHLIGHTS

Not only synthetic chemists, but also nature makes use of the spontaneous Diels–Alder reaction. Now there is also increasing evidence for a Diels–Alder-ase, for example in the biosynthesis of solanapyrones. The search for an enzyme-catalyzed [4+2]cycloaddition in nature will therefore certainly continue.

S. Laschat* 289–291

Pericyclic Reactions in Biological Systems—Does Nature Know About the Diels–Alder Reaction?

New impetus both for the organometallic chemistry of alkali metals as well as for organoboron chemistry should be stimulated by the synthesis of **1** by Fu et al. Though this compound is the second complex containing a hydrogen atom on the boron atom of boratabenzene, it is the first that has been characterized by X-ray structural analysis.

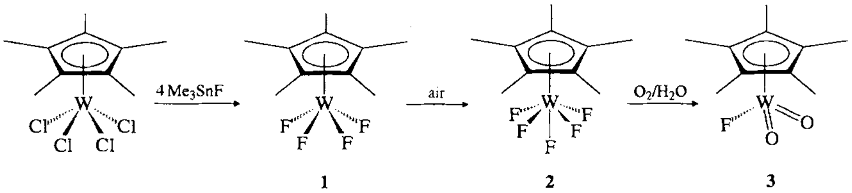
$Li(thf)_4[Li(H_5C_5BH)_2]$ **1**

H. Nöth,* M. Schmidt 292–293

Boron-Substituted Heterocycles as π-Donors in Organometallic Chemistry—A Sandwich Complex with 1-*H*-Boratabenzene and Lithium

COMMUNICATIONS

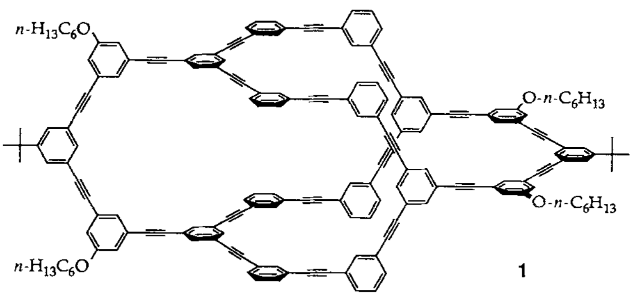
Tetrafluoride 1, pentafluoride 2, and fluoride dioxide 3 can be obtained from $[Cp^*WCl_4]$ and Me_3SnF according to the reaction scheme shown below. Complexes of type **2** were hitherto not obtainable with chromium, molybdenum, and tungsten. The structure analysis of **2** revealed that the W center is in a square-bipyramidal environment and that the compound exists as a monomer.



K. Köhler, A. Herzog, A. Steiner,
H. W. Roesky* 295–297

Synthesis and Structure of the First Cyclopentadienyl(halogeno)metal(VI) Complex of the Chromium Triad $[(\eta^5\text{-}C_5Me_5)WF_5)]$

The connectivity of a finite fragment of the prototypical silicon network of the intermetallic compound α-$ThSi_2$ is represented by the carbon-rich macrotricycle **1**. The compound has a cavity with dimensions of 36 × 12 × 12 Å^3. Calculations indicate that concerted torsional rotation around the parallel lateral bonds results in collapse to a nearly planar, folded structure. The flexibility of compounds like **1** single them out as promising building blocks for the preparation of auxetic materials.



1

Z. Wu, J. S. Moore* 297–299

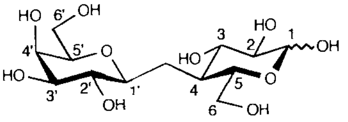
A Freely Hinged Macrotricycle with a Molecular Cavity

$[C(OR)_3]^+$ ions are stabilized differently than $[C(XR)_3]^+$ ions (X = S, Se, Te). While the stability of the RO-substituted carbenium ions can be attributed to the high polarity of the $C^{\delta+}-O^{\delta-}$ bond, the polarity of the C–X bond in the homologous S-, Se-, and Te-containing ions is reversed, and the stabilization is achieved by the σ- and π-dative effect of the chalcogen centers. These results were obtained by ab initio calculations on $[C(XH)_3]^+$ ions and by experimental studies on the new compounds $[C(XR)_3][PF_6]$ (X = S, Se, Te; R = 2,4,6-iPr$_3C_6H_2$).

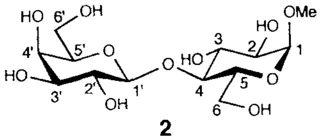
D. Ohlmann, C. M. Marchand,
H. Grützmacher,* G. S. Chen,
D. Farmer, R. Glaser,* A. Currao,
R. Nesper, H. Pritzkow 300–303

Tris(chalcogenato)carbenium Ions $[C(XR)_3]^+$ (X = O, S, Se, Te): An Experimental and Quantum-Chemical Comparison

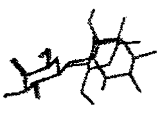
NMR experiments provide evidence that C- and O-glycosides such as **1** and **2**, respectively, are not necessarily bound in the same conformation by a protein. A projection of the conformations of **1** and **2** recognized by ricin B is shown on the lower right.



1



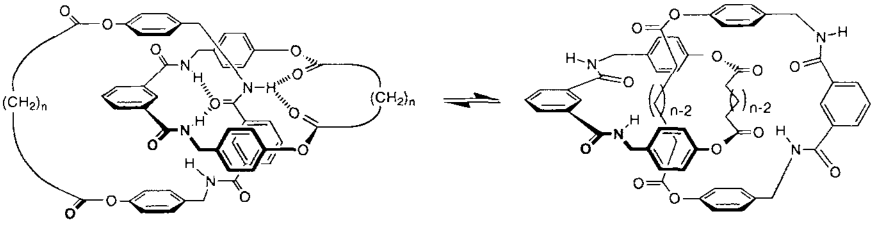
2



J.-F. Espinosa, F. J. Cañada, J. L. Asensio, H. Dietrich, M. Martín-Lomas, R. R. Schmidt, J. Jiménez-Barbero* 303–306

Conformational Differences of O- and C-Glycosides in the Protein-Bound State: Different Conformations of C-Lactose and Its O-Analogue are Recognized by Ricin B, a Galactose-Binding Protein

Intramolecular double bifurcated hydrogen bonding is responsible for the preferred conformation **I** of the catenane shown below in the solid state and in nonpolar solvents; in polar solvents competitive hydrogen bonding and polarphobic forces leads to conformation **II**.

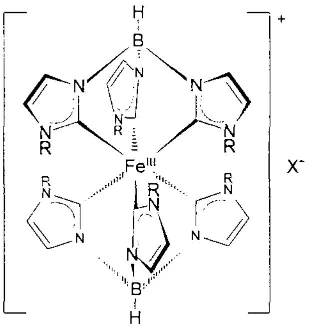


I II

D. A. Leigh,* K. Moody, J. P. Smart, K. J. Watson, A. M. Z. Slawin ... 306–310

Catenane Chameleons: Environment-Sensitive Translational Isomerism in Amphiphilic Benzylic Amide [2]Catenanes

A free tricarbene is most likely a long-lived intermediate in the formation of the first hexacarbene iron complex **1** (R = Me) from trimethylated tris(1-imidazolyl)borate, *n*-butyllithium, iron chloride, and tetraphenylborate. This tripodal *C,C′,C″*-chelating ligand, for which the authors predict a brilliant future, is an isomer of Trofimenko's tris(1-pyrazolyl)borate and represents a novel class of negatively charged six-electron donors with the greatest possible similarity to the cyclopentadienyl anion.

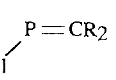


1 ($X^- = BPh_4^-$)

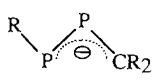
U. Kernbach, M. Ramm, P. Luger, W. P. Fehlhammer* 310–312

A Chelating Triscarbene Ligand and Its Hexacarbene Iron Complex

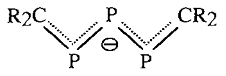
Three two-coordinate phosphorus atoms are present in the W-shaped 2,3,4-triphosphapentadienide **3**, which is obtained as a lithium salt from the reaction of the phosphaalkene **1** with **2** (R = $SiMe_3$). Heterocycles and heterobicycles containing three phosphorus atoms are accessible from **3**.



1



2

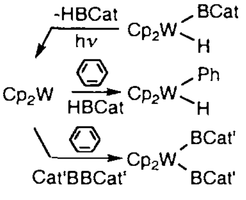


3

V. Thelen, D. Schmidt, M. Nieger, E. Niecke,* W. W. Schoeller 313–315

Synthesis, Structure, and Reactivity of a 2,3,4-Triphosphapentadienide

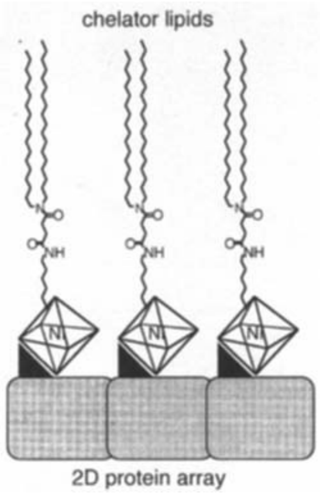
The selectivity for addition of the B–B bond of Cat′BBCat′ (Cat′ = 4-tBuC$_6$H$_3$O$_2$) to [Cp$_2$W] even in the presence of reactive C–H bonds in the solvent benzene is remarkable. In contrast to facile B–B cleavage, B–H bond formation occurred upon photolysis of [Cp$_2$W(H)(BCat)] (Cat = C$_6$H$_4$O$_2$). This facile cleavage of B–B bonds and the preferred formation of B–H bonds contrasts with the typical selectivities for C–C and C–H activation reactions. The formation and some reactions of tungstenocene are shown on the right.



J. F. Hartwig,* X. He 315–317

Reactivity of Tungstenocene with B–B and B–H Bonds versus C–H Bonds

A novel class of chelator lipids combines the fundamental properties of self-assembly with protein engineering techniques, leading to well-organized biofunctionalized interfaces and two-dimensional protein arrays. Reflection FT-IR spectroscopy at the air–water interface was used to monitor the formation of a metal-sensitive lipid film as well as the reversible and specific docking (represented on the right) of a fusion protein (B) to this chelator lipid layer through a histidine tag (A).

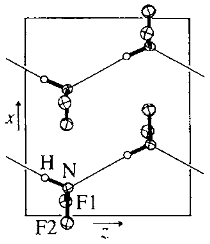


L. Schmitt, T. M. Bohanon, S. Denzinger, H. Ringsdorf, R. Tampé* 317–320

Specific Protein Docking to Chelator Lipid Monolayers Monitored by FT-IR Spectroscopy at the Air–Water Interface

---

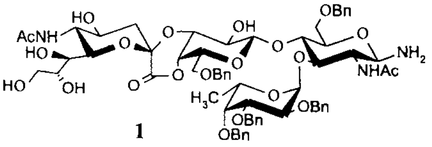
Potentially explosive difluoroamine, HNF_2, which is gaseous under normal conditions, is associated in the solid state through N–H···N hydrogen bonds—and not N–H···F bonds—to form infinite zigzag chains. The results of the X-ray structure analysis are consistent with those of earlier spectroscopic findings and theoretical calculations.



M. F. Klapdor, H. Willner,* W. Poll, D. Mootz* 320

The Crystal Structure of Difluoroamine

Threefold condensation of the sialyl Lewis^X amine derivative **1** with cyclopeptides leads to multivalent glycopeptides with repetitive saccharide units. A trivalent sialyl Lewis^X N-glycopeptide proved to be a potent antagonist of E-selectin.



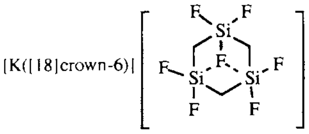
1

U. Sprengard, M. Schudok, W. Schmidt, G. Kretzschmar, H. Kunz* 321–324

Multiple Sialyl Lewis^X N-Glycopeptides: Effective Ligands for E-Selectin

---

Chair inversions and F–Si migrations can explain why in solution the trisilacyclohexane anion **1** provides only one ^{19}F and one ^{29}Si NMR signal. The ion shows fluxional behavior in the crystal as well, as is confirmed by the ^{29}Si CP/MAS NMR spectrum at 298 K, which contains only one signal.



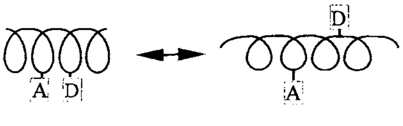
[K([18]crown-6)]-1

D. Brondani, F. H. Carré, R. J. P. Corriu,* J. J. E. Moreau,* M. Wong Chi Man 324–326

Synthesis and Dynamic Behavior of the Heptafluorotrisilacyclohexane Anion: A New Fluxional Silicate with Rapid Intramolecular Exchange of Fluoride Ligand

---

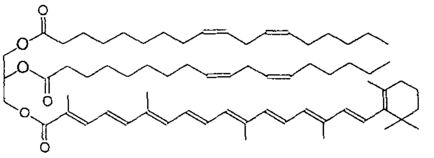
Two well-defined, interconvertible helical states are distinguishable by CD and fluorescence spectroscopy in a synthetic peptide containing both electron donor (D) and acceptor (A) units (shown schematically below). This provides a suitable model system for a molecular switch, regulated by conformational changes, with potential applications in molecular electronics.



G. Hungerford, M. Martinez-Insua, D. J. S. Birch, B. D. Moore* 326–329

A Reversible Transition between an α-Helix and a 3_{10}-Helix in a Fluorescence-Labeled Peptide

The first stable, highly unsaturated fat! Previous attempts at the synthesis of these compounds had led to rather unstable compounds without practical application; however, the use of a carotenoid as fatty acid has resulted in stable, conjugated polyene glycerides such as **1**.



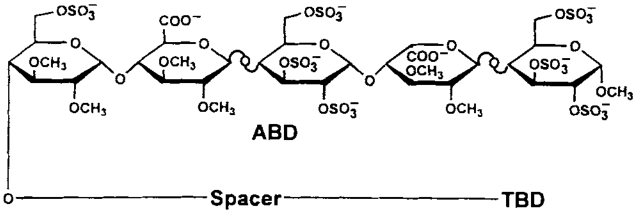
1

V. Partali, L. Kvittingen, H.-R. Sliwka,*
T. Anthonsen 329–330

Stable, Highly Unsaturated Glycerides—Enzymatic Synthesis with a Carotenoic Acid

---

A sufficiently long spacer between the antithrombin- and thrombin-binding domains (ABD and TBD, respectively) is necessary to impart antithrombin activity to a synthetic glycoconjugate (shown schematically below). The spacer need not consist of multiple sugar units as in heparin; a simple chain about 50 atoms in length suffices. In addition, varying the charge density of the TBD affects the inhibitor activity, and symmetric glycoconjugates (TBD = ABD) also display high antithrombin activities.

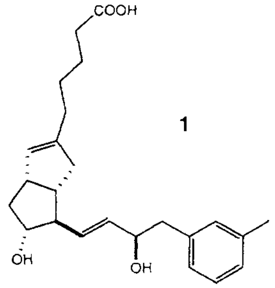


P. Westerduin, J. E. M. Basten,
M. A. Broekhoven, V. de Kimpe,
W. H. A. Kuijpers,
C. A. A. van Boeckel* 331–333

Synthesis of Tailor-Made Glycoconjugates Showing AT III-Mediated Inhibition of Blood Coagulation Factors Xa and Thrombin

---

Structural modification of the prostacyclin agonist isocarbacyclin resulted in the stable, highly selective ligand **1**, which displays high binding affinity for a prostacyclin receptor in the central nervous system. The binding profile of **1** thus contrasts markedly with those of cicaprost and iloprost.



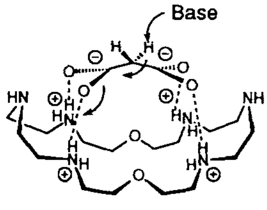
1

M. Suzuki,* K. Kato, R. Noyori,
Y. Watanabe, H. Takechi, K. Matsumura,
B. Långström, Y. Watanabe 334–336

(15*R*)-16-*m*-Tolyl-17,18,19,20-tetranorisocarbacyclin: A Stable Ligand with High Binding Affinity and Selectivity for a Prostacyclin Receptor in the Central Nervous System

---

In three ways at once the macrocyclic polyamine [24]aneN_6O_2 promotes the H/D exchange at the α position in malonate ions: The quadruply protonated species in neutral pH range forms a quite stable dicationic complex (**1**) with the malonate dianion, which facilitates the approach of a base and assists the enolization through the acidic NH^+ centers. The acceleration factor for the fourfold protonated polyamine [24]aneN_6O_2 is $k_{cat}/k_{uncat} \approx 1.4 \times 10^3$.



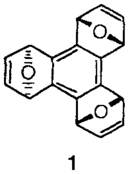
1

H. Fenniri, J.-M. Lehn,*
A. Marquis-Rigault 337–339

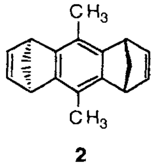
Supramolecular Catalysis of H/D Exchange in Malonate Ions by Macrocyclic Polyamines: A Model Enzyme with Enolase Activity

---

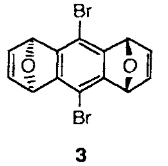
Pronounced bond length alternation in the central aromatic ring is the eye-catching structural feature of triepoxytriphenylene **1**. By contrast, no significant bond length alternation is observed in the linearly bisannelated compounds **2** and **3**. The key difference is ascribed to the position of annelations with the bicyclic units.



1



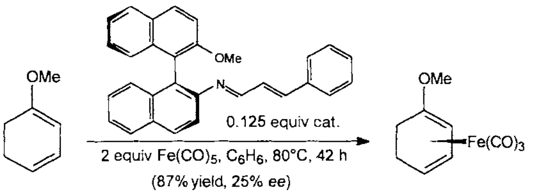
2



3

F. Cardullo, D. Giuffrida,
F. H. Kohnke,* F. M. Raymo,
J. F. Stoddart, D. J. Williams 339–341

Effects of Strained Bicyclic Annelation on the Benzene Nucleus: The X-Ray Crystal Structures of a Triphenylene and Two Anthracene Derivatives



(a)

* Author to whom correspondence should be addressed

BOOKS

ANGEWANDTE
CHEMIE

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Deutscher Chemiker

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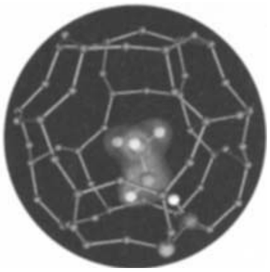
1996
35/2
Pages 117–228

COVER PICTURE

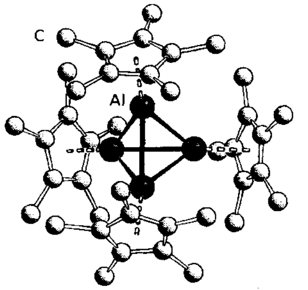
The cover picture shows a methanol molecule interacting with an acid site (AlOH) in the cage of a silicon-rich sodalite (Si = blue, O = red, Al = yellow, C = green, H = white). The spheres representing the alcohol and the acidic site have been enlarged by a factor of two for reasons of clarity, and the methanol molecule is surrounded by an isosurface of its electron density. The dynamic behavior of the alcohol at finite temperature is crucial for the understanding of many catalytic processes. These state-of-the-art computer simulations that provide new insights into the microscopic mechanism of the interaction of methanol with molecular sieves are discussed by E. Nusterer, P. E. Blöchl, and K. Schwarz on p. 175ff.



REVIEWS

Contents

A highlight in the rapidly developing field of Al^I and Ga^I compounds is the synthetic work with high-temperature molecules such as AlCl and GaCl at low temperature. Halides such as $[Al_4Br_4(NEt_3)_4]$ and $[Ga_5Cl_7(OEt_2)_5]$, and organometallic compounds such as [GaCp*] and $[Al_4Cp^*_4]$ (shown on the right) have been prepared, and their structures have been characterized unambiguously.



The atoms shape the properties of the molecules that are constructed from them. This assumption is the fundemantal idea behind the attempt to define electronegativities of atoms, and particularly of atomic (hybrid) orbitals, in a form that enables successful predictions of molecular properties without large theoretical effort. As examples, the comparisons between experimentally determined and theoretically predicted bond energies and force constants of bonds, amongst others, are described.

HIGHLIGHTS

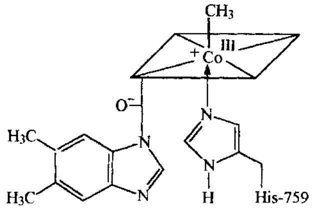
Contents

The search for simple and pharmacologically active enediynes should be considerably facilitated by a new sequence leading to acyclic and also cyclic enediynes, which proceeds via a carbenoid intermediate. The recently reported intramolecular variant yields functionalized enediynes on a multigram scale from readily accessible starting materials in yields of up to 95%.

B. König* 165–166

New, Efficient Routes to Cyclic Enediynes

The first X-ray analysis of a B_{12} protein, the B_{12}-binding domain of the methionine synthase of *Escherichia coli*, led to a surprising finding: there the B_{12} derivative, methylcobalamin, is not bound in the "base-on" form present in solution and in the crystal. Instead a histidine residue coordinates at the cobalt center of the protein-bound cofactor in place of the nucleotide function.



B. Kräutler,* C. Kratky* 167–170

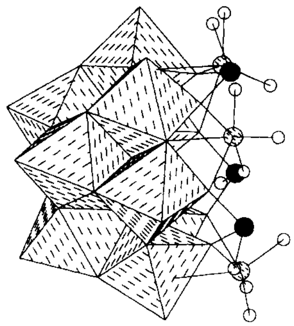
Vitamin B_{12}: The Haze Clears

COMMUNICATIONS

For the directed synthesis of polyoxometalates the linking of the heteropolyanion **1** (schematic representation shown on the right) to form the dimeric anion **2** is extremely significant. The formation of the corresponding potassium salts of **1** and **2** from K_2MoO_4 and As_2O_3 is controlled merely by the pH value of the solution.

$[(AsOH)_3(MoO_3)_3(AsMo_9O_{33})]^{7-}$ **1**

$[(AsOH)_6(MoO_3)_2(O_2Mo\text{-}O\text{-}MoO_2)_2(AsMo_9O_{33})_2]^{10-}$ **2**

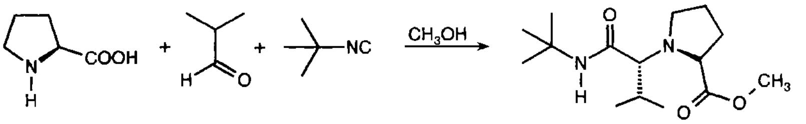


A. Müller,* E. Krickemeyer,
S. Dillinger, J. Meyer, H. Bögge,
A. Stammler 171–173

$[(AsOH)_3(MoO_3)_3(AsMo_9O_{33})]^{7-}$ and $[(AsOH)_6(MoO_3)_2(O_2Mo\text{-}O\text{-}MoO_2)_2\text{-}(AsMo_9O_{33})_2]^{10-}$: Coupling of Highly Negatively Charged Building Blocks

---

Not only yields of up to 98% but also diastereomeric excesses of up to 84% are the advantages of this effective and versatile multicomponent reaction for the synthesis of iminodicarboxylic acid derivatives in a one-pot reaction [Eq. (a)].



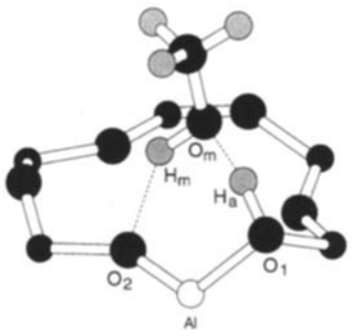
(a)

A. Demharter, W. Hörl,
E. Herdtweck, I. Ugi* 173–175

Synthesis of Chiral 1,1′-Iminodicarboxylic Acid Derivatives from α-Amino Acids, Aldehydes, Isocyanides, and Alcohols by the Diastereoselective Five-Center–Four-Component Reaction

---

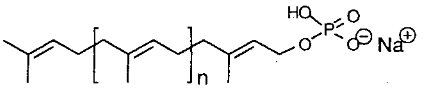
A direct view of a single methanol molecule as it interacts at finite temperatures with the acid site of a zeolite catalyst is obtained from molecular dynamics simulations. The results agree with experimental IR spectra, change the previously held notion of mechanisms of reactions in zeolites, and explain how the silicon-to-aluminum ratio of the framework influences the mode of adsorption for methanol in zeolites. One of the structures calculated is shown schematically on the right.



E. Nusterer, P. E. Blöchl,*
K. Schwarz* 175–177

Structure and Dynamics of Methanol in a Zeolite

Good candidates for model units from which the vesicles of the most primitive "protocells" may have been made are polyprenyl phosphates like **A**. These phosphates have carbon chains with fifteen or more C atoms. The vesicles can be observed by optical or electron microscopy.



A

G. Pozzi, V. Birault, B. Werner,
O. Dannenmuller, Y. Nakatani,
G. Ourisson,* S. Terakawa* 177–180

Single-Chain Polyprenyl Phosphates Form "Primitive" Membranes

Ti- and V-containing amorphous glasses with inner surfaces of several hundred m^2g^{-1} and pore diameters of 0.7 nm can be prepared by a sol–gel process. Like zeolites, these amorphous microporous mixed oxides AMM-M_xSi show catalytic shape-selectivites. The epoxidation of alkenes with *tert*-butylhydroperoxide on Ti-containing glasses is catalyzed size-selectively. In the hydrocracking test of decane, these materials show a product distribution that indicates the presence of Brønstedt centers in a shape-selective environment, as well as tubular pores, the lack of additional cavities, and an effective pore size comparable to those of 10- and 12-ring zeolites.

W. F. Maier,* J. A. Martens, S. Klein, J. Heilmann, R. Parton, K. Vercruysse, P. A. Jacobs 180–182

Shape-Selective Catalysis with Microporous Amorphous Mixed Oxides

---

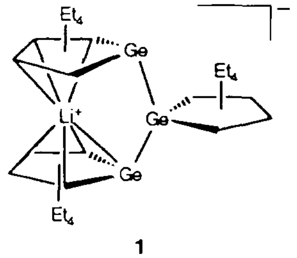
Ninety chiral centers and a molecular mass of 11354 Da are the outstanding features of the largest C_3-symmetric, chiral dendrimer to date. As general approach to these chiral polyether compounds 1) styrenes or stilbenes are converted into 1,2-diols by asymmetric dihydroxylation; 2) the resulting building blocks are then linked together to form dendrons by a uniquely effective ether-forming reaction, in which the vincinal hydroxyls are alkylated with benzylic bromides by using KOH pellets in refluxing toluene; 3) the dendrons are coupled to a core unit such as 1,3,5-benzenetricarbonyl trichloride.

H.-T. Chang, C.-T. Chen, T. Kondo, G. Siuzdak, K. B. Sharpless* 182–186

Asymmetric Dihydroxylation Enables Rapid Construction of Chiral Dendrimers Based on 1,2-Diols

---

A lithium-containing intermediate 1 can be isolated in the synthesis of a trigermole from 1,1-dichlorotetraethylgermole. NMR and X-ray diffraction studies reveal that one Li cation is part of a lithocene structure, while the second is in an environment similar to common organolithium compounds. In the solid state, the second lithium center is tetrahedrally coordinated to two nitrogen atoms of TMEDA, the oxygen atom of THF, and the Ge atom of one of the π-complexed germole rings.

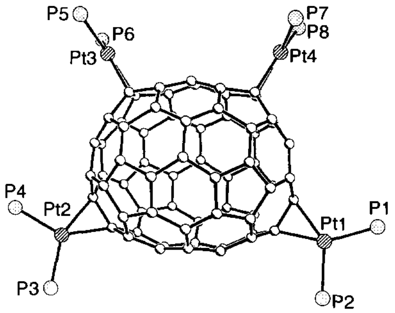


1

J.-H. Hong, Y. Pan, P. Boudjouk* 186–188

A Novel Lithocenophane Derivative of a Trisgermole Dianion: [Li(thf)(tmeda)]-[2,3,4,5-Et_4-*Ge,Ge*-{Li(2,3,4,5-$Et_4C_4Ge)_2$}C_4Ge]

Up to four platinum centers can be bound to C_{70}, as the synthesis of $[C_{70}\{Pt(PPh_3)_2\}_4]$ **1** with idealized C_{2v} symmetry has shown. The four $Pt(PPh_3)_2$ groups are bound at two types of 6–6 ring junctions. The stepwise addition of $Pt(PPh_3)_2$ groups occurs initially to the most pyramidalized C–C bonds at the poles of the fullerene with subsequent additions to the adjacent 6–6 ring junctions.

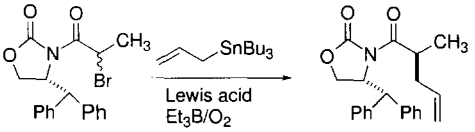


1

A. L. Balch,* L. Hao, M. M. Olmstead 188–190

Patterns of Multiple Additions to Fullerene C_{70}: Isolation and Structural Characterization of $[C_{70}\{Pt(PPh_3)_2\}_4]$

It's the addition of Lewis acids that does it! Reaction (a) proceeds with diastereoselectivities ≥100:1 if the radical transfer takes place in the presence of Lewis acids such as MgI_2, $MgBr_2$, or $Sc(OTf)_3$. The influence of the substituents at position 4 of the oxazolidinone ring on the allylation was also studied.



(a)

M. P. Sibi,* J. Ji 190–192

Acyclic Stereocontrol in Radical Reactions: ρ-Selectivity with Oxazolidinone Auxiliaries

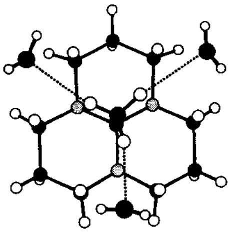
---

High activity and negligible coke formation in the course of the catalytic partial oxidation of CH_4 to syngas are characteristics of the $Ni/Ca_{1-x}Sr_xTiO_3$ catalyst, which is readily accessible by the citrate method from nickel nitrate, alkaline earth metal carbonates, and tetraisopropoxidotitanium. The properties and efficiency of the catalyst are normally only associated with catalysts that contain considerably more expensive metals such as Rh, Ir, and Ru.

T. Hayakawa,* H. Harihara, A. G. Andersen, A. P. E. York, K. Suzuki, H. Yasuda, K. Takehira* 192–195

A Sustainable Catalyst for the Partial Oxidation of Methane to Syngas: $Ni/Ca_{1-x}Sr_xTiO_3$, Prepared In Situ from Perovskite Precursors

The electrostatic molecular potential and a molecular orbital analysis give evidence why the unusual eclipsed conformation is preferred for the $C_{sp^3}-CH_3$ bond in the crystal of $1 \cdot 3\,H_2O$. The studies conclude that three C–H ··· O interactions can indeed overcome the low rotational barrier of **1**.

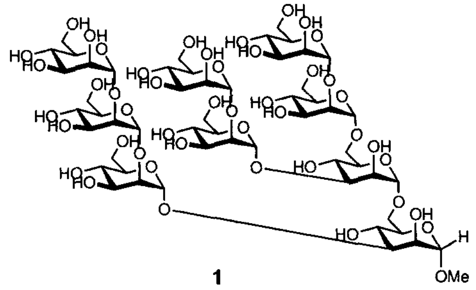


$1 \cdot 3H_2O$

I. Chao,* J.-C. Chen 195–197

Resolving the Puzzling Eclipsed Conformation of the Methyl Group in a Tricyclic Orthoamide Trihydrate

Deliberate tuning of the reactivity of the appropriate glycosyl donors enables nonamannan **1** to be prepared efficiently in a concise manner. Bound through a disaccharide linker, **1** is a major constituent of the envelope glycoprotein gp120 of the human-immunodeficiency virus (HIV). Gp120 plays an important role in the attachment to and penetration of target cells by HIV and in the antiviral response.

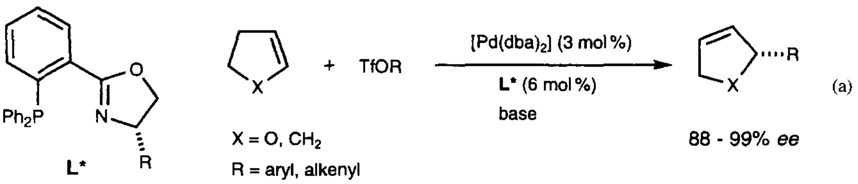


1

P. Grice, S. V. Ley,* J. Pietruszka, H. W. M. Priepke 197–200

Synthesis of the Nonamannan Residue of a Glycoprotein with High Mannose Content

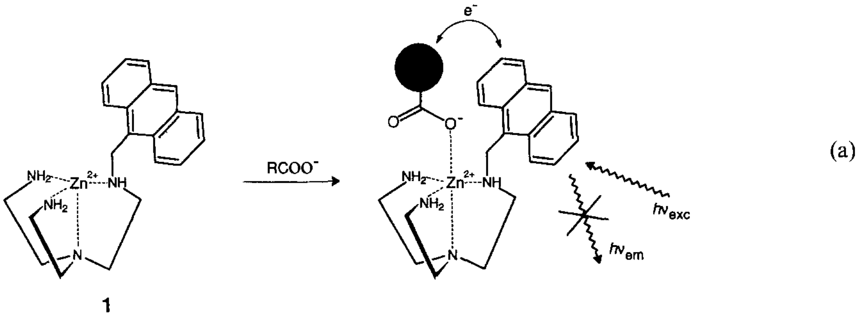
Enantiomeric excesses of up to 99% have been obtained in Heck reactions of cyclic olefins with (phosphanyldihydrooxazole)Pd catalysts [Eq. (a)]. In contrast to analogous (BINAP)Pd-catalyzed reactions, essentially no isomerization of the products by C=C bond migration is observed.



O. Loiseleur, P. Meier, A. Pfaltz* 200–202

Chiral Phosphanyldihydrooxazoles in Asymmetric Catalysis: Enantioselective Heck Reactions

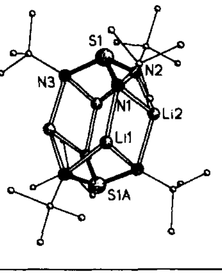
Aromatic carboxylate ions bearing an acceptor or donor substituent are recognized by the Zn^{II}-containing receptor **1**, and their binding is signaled through quenching of the fluorescence of the appended anthracene unit [Eq. (a)]. Quenching of the fluorophore is induced by an electron transfer to or from the substituent. R = aryl.



G. De Santis, L. Fabbrizzi,* M. Licchelli, A. Poggi, A. Taglietti 202–204

Molecular Recognition of Carboxylate Ions Based on the Metal–Ligand Interaction and Signaled through Fluorescence Quenching

Two dianionic caps, linked by four lithium atoms, characterize the structure of the Li salt **1** of the tripodal ligand $[S(NtBu)_3]^{2-}$. On addition of THF to **1**, one lithium atom leaves the inner region and coordinates to only two N atoms and a THF molecule. Oxidation of white **1** with O_2 or iodine leads to a dark blue, stable radical monoanion.

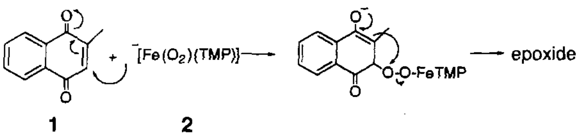


1

R. Fleischer, S. Freitag, F. Pauer, D. Stalke* 204–206

$[S(NtBu)_3]^{2-}$—A Cap-Shaped Dianion, Isoelectronic with the Sulfite Ion and Oxidizable to a Stable Radical Anion

Direct oxygen transfer to an olefinic bond is possible from the Fe^{III} complex **2** if the double bond is electron-deficient as in **1** [Eq. (a)]. Complex **2** is analogous to intermediates proposed for cytochrome P450 type enzymes.

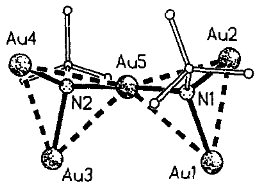


(a)

M. F. Sisemore, J. N. Burstyn, J. S. Valentine* 206–208

Epoxidation of Electron-Deficient Olefins by a Nucleophilic Iron(III) Peroxo Porphyrinato Complex, Peroxo(tetramesitylporphyrinato)ferrate(1−)

A "bowtie-shaped" Au$_5$ moiety (structure shown on the right, PPh$_3$ ligands on the terminal Au centers have been omitted) is the characteristic structural feature of the title complex. This is formed in high yield by the reaction of [AuCl(PPh$_3$)] with [tBuNHLi] (1:1 equiv) in toluene. The cation can be regarded as the next homologue of cations of the type [(AuPPh$_3$)$_3$NR]$^+$ and is the largest structurally characterized imidogold(I) species to date.

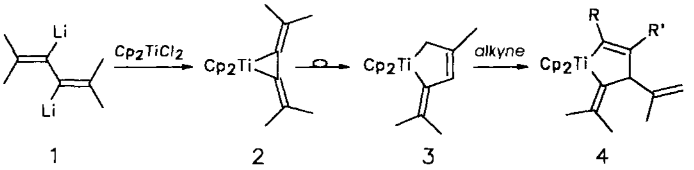


R. E. Allan, M. A. Beswick, M. A. Paver, P. R. Raithby, A. Steiner, D. S. Wright* 208–209

Synthesis and Structure of the Bis(imido)gold Complex [Au$^{\text{I}}_5$(NtBu)$_2$(PPh$_3$)$_4$]$^+$Cl$^-$·2C$_6$H$_5$CH$_3$; a Higher Homologue of the Organotris(triphenylphosphaneaurio)ammonium Ions

---

A whole range of titanacycles can be prepared from the dilithio compound **1** and titanocene dichloride. The initial product in the reaction, radialene **2**, rearranges immediately into titanacyclopentene **3**. Cyclopentenes like **4** arise from the reaction of **3** with alkynes.

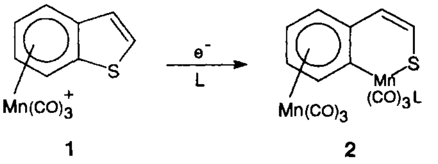


A. Maercker,* A. Groos 210–212

Synthesis of the First Titana[3]radialene and Its Ring Enlargement to a Titanacyclopentene

---

A highly nonplanar metallacyclic ring with a nucleophilic sulfur atom is contained in the binuclear complex **2**, which is formed by reduction of the benzothiophene complex **1** in the presence of additional ligands (L = CO, P(OMe)$_3$, P(OEt)$_3$). This reaction, which proceeds by the insertion of manganese into the S–C(aryl) bond, is of interest in the context of catalytic desulfurization of fossil fuels.



C. A. Dullaghan, S. Sun, G. B. Carpenter, B. Weldon, D. A. Sweigart* 212–214

Model Compounds for the Homogeneous Hydrodesulfurization of Benzothiophene: Insertion of Manganese into the S–C(aryl) Bond

---

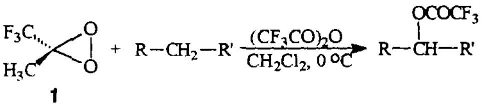
A multicomponent molecular recognition process leads to a self-assembled "quaternary" supramolecular complex formed from porphyrins and an "unusual" poly(A·A·U) triple helix. The formation of this superstructure is promoted by porphyrin aggregation and a number of recognition processes (Watson–Crick and Hoogsteen pairing, coulombic interactions, and stacking interactions).

R. Lauceri, T. Campagna, A. Contino, R. Purrello* 215–216

Poly(A·A·U) Triple Helix Formation Promoted by Porphyrin Assembly

---

The initially formed alcohols do not oxidize further when primary and secondary C–H bonds are oxidized by dioxirane **1** in the presence of a large excess of trifluoroacetic anhydride. The reactions (a) proceed with excellent yields under very mild conditions. R = alkyl, aryl; R′ = H, alkyl, aryl.

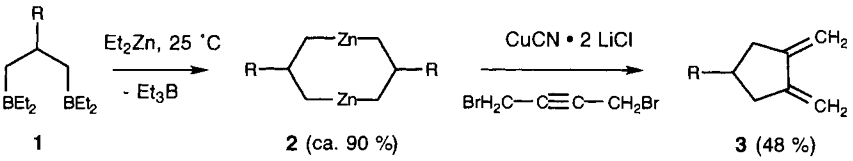


$$\mathbf{1} + \text{R-CH}_2\text{-R'} \xrightarrow[\text{CH}_2\text{Cl}_2,\ 0\,^\circ\text{C}]{(\text{CF}_3\text{CO})_2\text{O}} \text{R-}\overset{\text{OCOCF}_3}{\overset{|}{\text{CH}}}\text{-R'} \qquad \text{(a)}$$

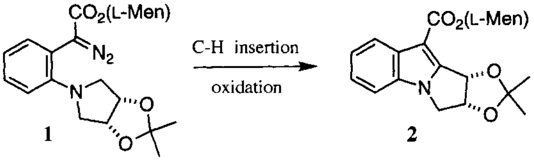
G. Asensio,* R. Mello, M. E. González-Núñez, G. Castellano, J. Corral 217–218

A General and Efficient Method for the Monohydroxylation of Alkanes

Excellent yields of 1,5-dizincacyclooctanes 2 (R = H, Bu) are readily available from the reaction of 1,3-bis(diethylboryl)propanes **1** with diethylzinc. After transmetalation with Cu^I salts, the heterocycles **2** react with electrophiles (allylic and propargylic bromides, benzoyl chloride, etc.) in satisfactory to good yields; the reaction with 1,4-dibromo-2-butyne leads to the bis(methylene)cyclopentane **3** (R = Bu).



A microtiter plate was used to set up 96 different conditions for the asymmetric C–H insertion reaction of diazo compound **1** which leads to the heterocycle **2**. This high throughput catalyst screening process unearthed a superior set of conditions, and a new silver-based catalyst for the reaction. L-Men = L-Menthyl.



* Author to whom correspondence should be addressed

BOOKS

ANGEWANDTE CHEMIE

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1996
35/1
Pages 1–116

COVER PICTURE

The cover picture shows a space-filling model of the anionic cesocene triple-decker complex $[Cp_3Cs_2]^-$. The Cs centers in this strongly bent molecule are highly ionic. The chemistry of anionic metallocenes of main group elements is a rapidly growing field and such metallocenes are structurally as well as theoretically of interest. Mixing cyclopentadienyl alkali metal compounds with cyclopentadienyl anions results in degradation of the CpMCpM polymer chains into smaller units such as $[Cp_2M]^-$ and $[Cp_3M_2]^-$. A structural comparison of these alkali metallocene complexes with the isovalent neutral alkaline earth metallocenes gives additional information on the still not well-understood bonding characteristics. The picture was painted by Peter Brinkmann, Universität Konstanz, using a technique that combines pastels and watercolors. Chemetall GmbH, Frankfurt/Main (Germany), is kindly acknowledged for providing the funding for the color print. Further details on the structure of this complex are reported by S. Harder and M. H. Prosenc on p. 97ff.

REVIEWS

Contents

The advantages of solid-phase synthesis have been recognized by organic chemists, who have adapted numerous well-known reactions for application with immobilized substrates. For example, a polymeric support may act as a protecting group for one functional group of a compound while a second functional group is derivatized. In other applications combinatorial syntheses on supports provide access to libraries of nonpeptides from collections of building blocks. This strategy is essential for supplying new compounds for modern automated screening assays used in the search and optimization of lead structures for drugs.

J. S. Früchtel, G. Jung* 17–42

Organic Chemistry on Solid Supports

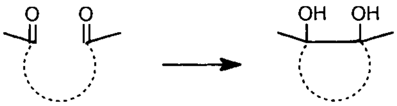
Mutual stimulation of ideas in biochemistry, medical practice, and inorganic chemistry has led to the discovery of many molecular details of the biological functions of copper, an essential element in nature. Copper probably became significantly bioavailable only rather late in the evolution of life. This and the unique redox and coordination properties closely link the redox pair Cu^{II}/Cu^{I} with the metabolism of O_2 and with radical ligands.

W. Kaim,* J. Rall 43–60

Copper—A "Modern" Bioelement

HIGHLIGHTS

Even 130 years after its discovery, the pinacol coupling [Eq. (a)] still has plenty of new variants. New reagents have been developed that are suitable not only for the elegant synthesis of 1,2-diols but also for the formation of amino alcohols. This powerful reaction has been used in numerous natural product syntheses.



(a)

T. Wirth* 61–63

"New" Reagents for the "Old" Pinacol Coupling Reaction

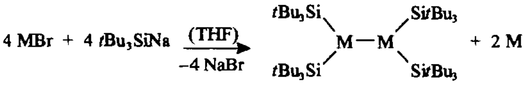
The arrangement of the pore openings serves as a template for the positions of the branchings in the isomerization of *n*-alkanes—this is the explanation proposed by Martens et al. (*Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2528) to rationalize their results in the isomerization of *n*-heptadecane on the zeolite ZSM-22. This reaction would thereby be the first example of key–lock catalysis on the *external* surface of a zeolite.

S. Ernst* 63–64

Selective Catalytic Reactions at the External Surface of Zeolite Crystals

COMMUNICATIONS

Deep violet (tBu$_3$Si)$_4$In$_2$ (1) and black-green (tBu$_3$Si)$_4$Tl$_2$ (2) are formed from MBr and tBu$_3$SiNa in THF at −78 °C [Eq. (a)]. The M atoms of **1** (decomp. 125 °C) and **2** (decomp. 52 °C) are each coordinated by two Si atoms and one M atom in a trigonal-planar fashion, and the two Si$_2$MM planes are orthogonal.



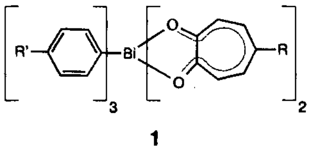
$$4\,\mathrm{MBr} + 4\,t\mathrm{Bu_3SiNa} \xrightarrow[-4\,\mathrm{NaBr}]{\mathrm{(THF)}} (t\mathrm{Bu_3Si})_2\mathrm{M{-}M}(\mathrm{Si}t\mathrm{Bu_3})_2 + 2\,\mathrm{M} \qquad \text{(a)}$$

1 (M = In); 2 (M = Tl)

N. Wiberg,* K. Amelunxen, H. Nöth, M. Schmidt, H. Schwenk 65–67

Tetrasupersilyldiindium(*In–In*) and Tetrasupersilyldithallium(*Tl–Tl*): (tBu$_3$Si)$_2$M–M(SitBu$_3$)$_2$ (M = In, Tl)

Extremely air- and moisture-stable seven-coordinate Bi$^{\mathrm{V}}$ complexes 1 are obtained readily from di(acetato)tri(aryl)bismuth(v) and tropolone derivatives. The Bi atom in **1** resides in a distorted pentagonal-bipyramidal environment. Thus, stable Bi$^{\mathrm{V}}$ complexes are now available for biological and medicinal activity studies.



1

U. Dittes, B. K. Keppler,* B. Nuber 67–68

Synthesis and Structure of Seven-Coordinate Bismuth(v) Complexes with Benzenoid and Non-Benzenoid Arene Ligands: Tri(aryl)tropolonatobismuth(v) Complexes

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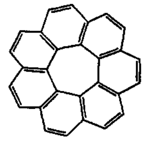
A remarkably simple synthesis of [7]circulene **1** via an ethano-bridged hexahelicene intermediate is described. Cyclic voltammetry reveals that **1** is easier to oxidize and reduce than coronene. The results of ab initio calculations for coronene, **1**, and its radical ions are consistent with the experimental findings.

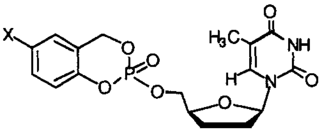


1

K. Yamamoto,* H. Sonobe, H. Matsubara, M. Sato, S. Okamoto, K. Kitaura* 69–70

Convenient New Synthesis of [7]Circulene

A nonenzymatic, hydrolytic tandem reaction selectively releases the 5'-phosphorylated derivatives of the antiviral active nucleoside analogues ddT and d4T from the nucleoside phosphotriesters **1** and **2**. The hydrolysis of **1** and **2** can be controlled by varying the substituents X. Consequently, compounds of type **1** and **2** should, in principle, be suitable prodrugs of phosphorylated nucleosides.



1 (**2**: nucleoside = d4T)

C. Meier* 70–72

2-Nucleos-5'-*O*-yl-4*H*-1,3,2-benzodioxaphosphinin-2-oxides—A New Concept for Lipophilic, Potential Prodrugs of Biologically Active Nucleoside Monophosphates

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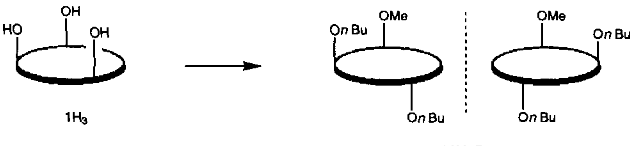
The shoe fits! The association constants for the complexes formed from the chiral host compound (−)-*anti*-1MeBu$_2$ [shown in Eq. (a)] and chiral alkylammonium ions such as L-phenylalanine ethyl ester are up to 6.7 times greater than those with the (+) isomer of the host. *anti*-1MeBu$_2$ is prepared in two steps from the homooxacalix[3]arene 1H$_3$ [Eq. (a)].



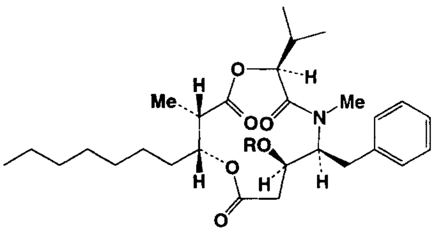
(a)

anti-1MeBu$_2$

K. Araki, K. Inada, S. Shinkai* 72–74

Chiral Recognition of α-Amino Acid Derivatives with a Homooxacalix[3]arene: Construction of a Pseudo-C_2-Symmetrical Compound from a C_3-Symmetrical Macrocycle

Tumor cells can develop resistance towards the drugs administered in chemotherapy. Hapalosin (**1**, R = H), a cyclodepsipeptide whose total synthesis has now been achieved, can inhibit this resistance. The constitution and configuration of the compound have been confirmed by its synthesis. It should now be possible to carry out detailed structure–function studies.



1

A. K. Ghosh,* W. Liu, Y. Xu,
Z. Chen 74–76

A Convergent, Enantioselective Total Synthesis of Hapalosin: A Drug with Multidrug-Resistance Reversing Activity

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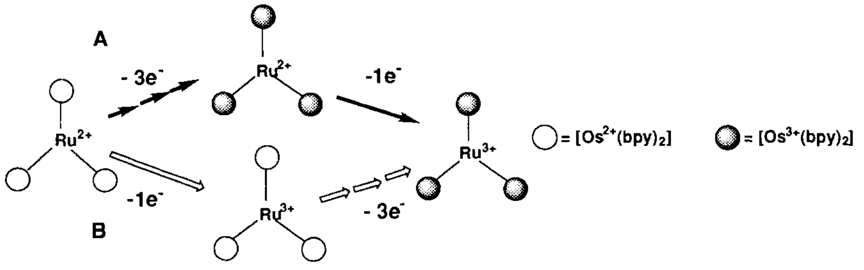
Protonation and deprotonation of Brönsted basic sites in the tetranuclear $RuOs_3$ complex shown schematically below results in switching between two oxidation patterns **A** and **B**. In the deprotonated $Ru^{III}Os_3^{II}$ complex obtained after one-electron oxidation, electron transfer from the peripheral Os^{II} atoms to the central Ru^{III} site is induced by the addition of protons. bpy = 2,2′-bipyridine, — = 2,2′-bis(benzimidazol-2-yl)-4,4′-bipyridine.



M. Haga,* M. M. Ali,
R. Arakawa 76–78

Proton-Induced Switching of Electron Transfer Pathways in Dendrimer-Type Tetranuclear $RuOs_3$ Complexes

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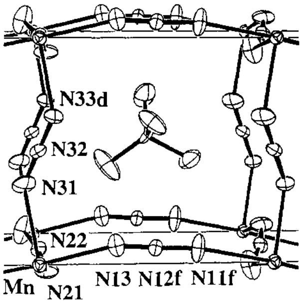
Manganese(II) nitrate and tetramethylammonium azide react to give the title compound in which the azido groups function as end-to-end bridging ligands in all spatial directions, and whose structure can be described as corresponding to a distorted perovskite (section of the structure shown on the right). At higher temperatures the compound undergoes a reversible phase transition to a pseudocubic phase.



F. A. Mautner, R. Cortés, L. Lezama,
T. Rojo* 78–80

$[N(CH_3)_4][Mn(N_3)_3]$: A Compound with a Distorted Perovskite Structure through Azido Ligands

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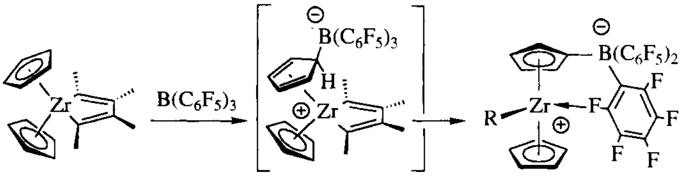
A potential starting material for the development of new catalysts, the zirconocene–betaine complex **3** was obtained from the zirconocene derivative **1** by functionalization of a Cp ligand (via **2**). Analogous reactions with metallocenes containing titanium, zirconium, or hafnium are relatively unexplored. R = CMe=CMe–CMe=CHMe.



1 **2** **3**

J. Ruwwe, G. Erker,*
R. Fröhlich 80–82

Formation of a Zirconocene–Betaine System by Electrophilic Substitution with $B(C_6F_5)_3$ at a Cyclopentadienyl Ligand

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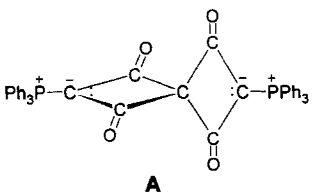
Quantitatively and in one step, the heterocumulenes O=C=C=C=O and Ph_3P=C=C=O form spirobis(cyclobutanedione) **A** in a double [2+2]cycloaddition. The bis(ylidic) structure was confirmed by spectroscopy and X-ray crystallography.

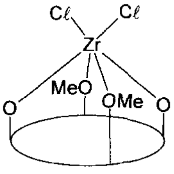


A

L. Pandolfo,* G. Facchin,* R. Bertani,
P. Ganis,* G. Valle 83–85

Heterocumulenes: Reaction of C_3O_2 with Ketenylidenetriphenylphosphorane; Synthesis and Structure of a Spirobis(cyclobutanedione)

Distorted into an ellipse, the calix[4]arene units in novel complexes of type **1** bind the hexacoordinate Zr center. In complex **1**, which is prepared in two steps by reaction of BuLi, calixarene, and $ZrCl_4$, the $ZrCl_2$ unit can be replaced by $Zr(alkyl)_2$, Zr(alkyl), Zr(butadiene), and Zr(ketone) moieties. These reactions provide access to organometallic fragments bonded to a polyoxo matrix.

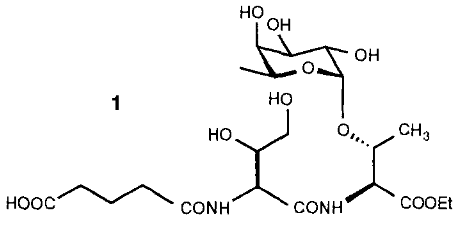


1

L. Giannini, E. Solari, A. Zanotti-Gerosa, C. Floriani,* A. Chiesi-Villa, C. Rizzoli 85–87

The Organometallic Chemistry of Zirconium on an Oxo Surface Provided by *p-tert*-Butylcalix[4]arene

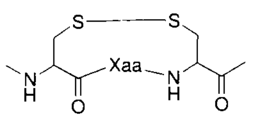
The same biological activity as the antigen determinant sialyl Lewis^x was shown by the fucopeptide **1** in a binding assay with E-selectin. In the design of this mimetic the type and spatial arrangement of the functional groups essential for the interaction between sialyl Lewis^x and E-selectin were considered. Fucopeptide **1**, which may have potential as an antiinflammatory agent, was synthesized from L-fucose, L-threonine, (2*S*,3*R*)-2-amino-3,4-dihydroxybutyric acid, and glutarate.



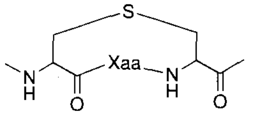
S.-H. Wu, M. Shimazaki, C.-C. Lin, L. Qiao, W. J. Moree, G. Weitz-Schmidt, C.-H. Wong* 88–90

Synthesis of Fucopeptides as Sialyl Lewis^x Mimetics

The labile disulfide bridge between cysteine residues in naturally occurring peptides can be replaced by lanthionine, as demonstrated by the synthesis of conformationally constrained dipeptide mimetics (see below) based on *β*,*β*-dimethylcyclolanthionines. Their structural features indicate that they represent a novel family of peptidomimetics.



peptide chain with disulfide bridge

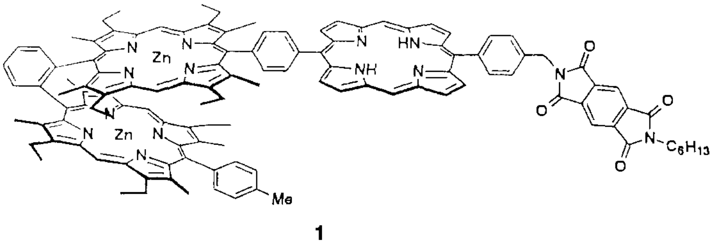


lanthionine-modified peptide chain

H. Shao, C.-W. Lee, Q. Zhu, P. Gantzel, M. Goodman* 90–92

β,*β*-Dimethylcyclolanthionines, New Constrained Dipeptide Mimetics: Synthesis, Crystal Structures, and Conformational Studies

Without a doubt, photochemically induced electron transfer in **1** proceeds stepwise. Triad **1** is one of the latest models of the photosynthetic reaction center. The rates of the individual steps in the electron transfer relay have been determined by ultrafast laser spectroscopy.

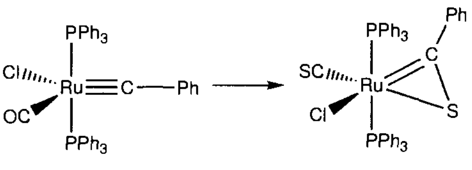


1

A. Osuka,* S. Nakajima, T. Okada,* S. Taniguchi, K. Nozaki, T. Ohno, I. Yamazaki, Y. Nishimura, N. Mataga* 92–95

A Sequential Electron-Transfer Relay in Diporphyrin–Porphyrin–Pyromellitimide Triads Analogous to That in the Photosynthetic Reaction Center

Electrophilic attack by the carbon atom of the heterocumulene at the ruthenium center characterizes the cycloadditions between the ruthenium alkylidyne complex **1** and CO_2, CS_2, or MeNCS. One of the products, the thiobenzoyl complex **2**, has been structurally characterized by X-ray diffraction.

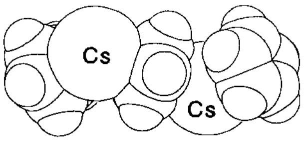


1 **2**

R. B. Bedford, A. F. Hill,* A. J. P. White, D. J. Williams 95–97

Cycloadditions of Ruthenium Alkylidyne Complexes with Carbonyl or Thiocarbonyl Compounds

The strongly bent triple-decker structure shown on the right is exhibited by the anion in $[Cp_3Cs_2][PPh_4]$, which is obtained as a red crystalline compound by the reaction of CpCs with PPh_4Cl. The coordination sphere of the Cs cation is filled by additional intermolecular interactions with neighboring $[Cp_3Cs_2]^+$ ions and $[PPh_4]^-$ ions.



S. Harder,* M. H. Prosenc 97–99

The Heaviest Alkali Metallocene: Structure of an Anionic Cesocene Triple-Decker

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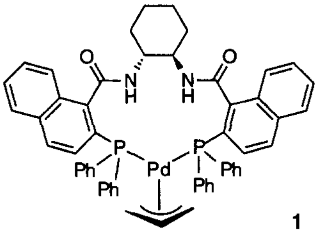
A quantitative synthesis with an enantiomeric ratio of 99:1 has been achieved for the important building block vinylglycinol. The crucial concept lay in sculpting the chiral pocket in catalyst **1** by restricting bond rotations in its chiral-inducing ligand.



1

B. M. Trost,* R. C. Bunt 99–102

On Ligand Design for Catalytic Outer Sphere Reactions: A Simple Asymmetric Synthesis of Vinylglycinol

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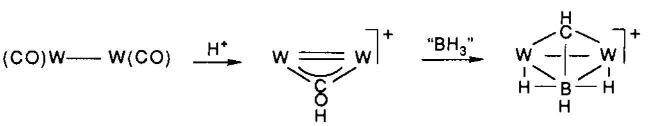
The reduction of a carbonyl to a methylidyne ligand in the reaction sequence below proceeds readily via the unsaturated hydroxycarbyne complex $[W_2(\mu\text{-COH})(CO)_2(\mu\text{-dppm})Cp_2]^+$, the unexpected protonation product of a neutral carbonyl complex. dppm = $Ph_2PCH_2PPh_2$.

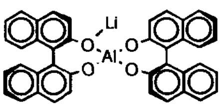


M. A. Alvarez, C. Bois, M. E. García, V. Riera, M. A. Ruiz* 102–104

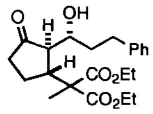
O-Protonation at a Neutral Ditungsten Carbonyl Dimer to Give a Stable Hydroxycarbyne Complex

---

Two types of metal are essential for some reactions! The first efficient catalyst for asymmetric tandem Michael–aldol reactions is the heterobimetallic complex **1**, which is easily prepared from $LiAlH_4$ and (*R*)-2,2′-dihydroxy-1,1′-binaphthyl. The cascade reaction of diethyl methylmalonate, cyclopentenone, and 3-phenylpropanal affords the three-component adduct **2** in 64% yield and 91% *ee*.



1



2

T. Arai, H. Sasai, K.-i. Aoe, K. Okamura, T. Date, M. Shibasaki* 104–106

A New Multifunctional Heterobimetallic Asymmetric Catalyst for Michael Additions and Tandem Michael–Aldol Reactions

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Since it can be removed under extremely mild conditions and with complete selectivity by choline esterase, the solubilizing choline ester function is advantageous for high-yielding peptide syntheses. This enzyme-labile protecting group was employed in the synthesis of the S-palmitoylated and S-farnesylated C-terminal lipohexapeptide of the human N-*Ras* protein.

M. Schelhaas, S. Glomsda, M. Hänsler, H.-D. Jakubke,* H. Waldmann* 106–109

Enzymatic Synthesis of Peptides and *Ras* Lipopeptides Employing Choline Ester as a Solubilizing, Protecting, and Activating Group

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* Author to whom correspondence should be addressed

BOOKS