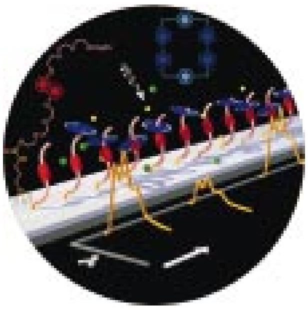
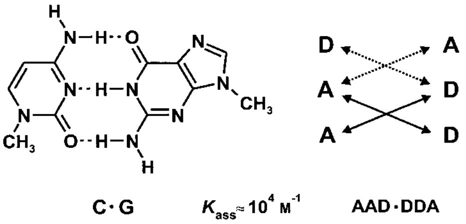
COVER PICTURE

The cover picture shows linear motor molecules in action on a silicate support. Under the spotlight, tethered threadlike polyether chains (pink) intercepted by electron-donating naphthalene units (red) doff and don electron-accepting cyclobis(paraquat-*p*-phenylene) girdles (blue). Their risque actions are revealed by the luminescence of the naphthalene units when the girdles are removed. The temporal sequence (left to right) shows the bare thread donning a girdle and then doffing it under the influence of light. The action is attentively monitored by the luminescence spectra; the intensity increases when the girdle is doffed and is quenched when it is donned. More about this process is reported by Zink, Stoddart, and co-workers on p. 2447 ff.



REVIEW

The combined strength of weak interactions at the molecular level can be used to build thermodynamically stable structures with exciting new properties. This review describes the characteristic traits of a new type of organic synthesis which uses the formation of hydrogen bonds between a H-bond donor (D) and an acceptor (A) group, such as in the AAD · DDA module 1-methylcytosine · 9-methylguanine (see scheme).



Angew. Chem. **2001**, *113*, 2446–2492

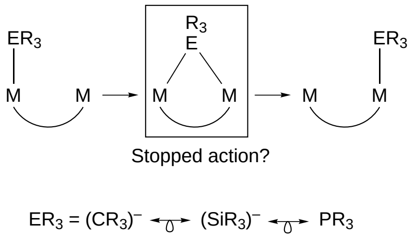
L. J. Prins, D. N. Reinhoudt,
P. Timmerman* 2382–2426

Noncovalent Synthesis Using Hydrogen Bonding

Keywords: hydrogen bonds · molecular recognition · noncovalent interactions · self-assembly · supramolecular chemistry

MINIREVIEW

Unusual bonding modes and reactivity of familiar ligands in organometallic and coordination chemistry, such as alkyl, silyl, and phosphane ligands, have become increasingly apparent in recent years. This contribution highlights the similarities between ostensibly unrelated systems (isolobal principle; see scheme) and summarizes their relevance both to fundamental molecular chemistry and catalysis.



Angew. Chem. **2001**, *113*, 2493–2500

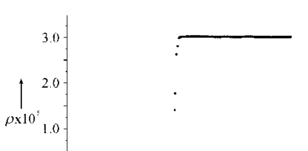
P. Braunstein,* N. M. Boag .. 2427–2433

Alkyl, Silyl, and Phosphane Ligands—Classical Ligands in Nonclassical Bonding Modes

Keywords: alkyl ligands · bridging ligands · cluster compounds · dinuclear complexes · P ligands · Si ligands

HIGHLIGHTS

It was a sensation, when in January this year the message went around the world that magnesium diboride MgB_2, known for fifty years, becomes superconducting below the relatively moderate temperature of 39 K (see picture). The commercially available compound was simply overlooked during the search for new superconductors over the past decades.



Angew. Chem. **2001**, *113*, 2501–2503

J. Köhler* 2435–2437

Superconductivity in MgB_2 at 39 K—A Sensational and Curious Discovery

Keywords: borides · magnesium · superconductivity

In the era of genomics and proteomics the functional characterization of gene products (proteins, metabolites) plays an important role. The simple introduction of double-stranded RNA into cells promotes the specific degradation of messenger RNA that encodes a particular protein, and so allows the analysis of the protein's function.

Angew. Chem. **2001**, *113*, 2503 – 2505

U. Schepers, T. Kolter* .... 2437 – 2439

RNA Interference: A New Way to Analyze Protein Function

Keywords: functional genomics · gene silencing · gene technology · nucleic acids · proteins

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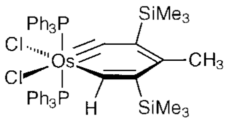
Organometallic chemistry still provides startling surprises! A stable, structurally characterized metallabenzyne (see picture) is the latest addition to the list of exotic organometallic species.



Angew. Chem. **2001**, *113*, 2506 – 2507

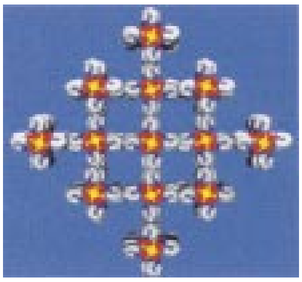
W. R. Roper* .... 2440 – 2441

First Metallabenzenes and now a Stable Metallabenzyne

Keywords: carbene ligands · carbyne ligands · metallabenzynes · metallacycles · osmium

COMMUNICATIONS

Eight-coordinate metal-ion nodes are linked through 4,4-bipyridine-*N*,*N*′-dioxide (L) ligands to form the first examples of eight- and seven-connected coordination networks. Thus, whereas $[La(L)_4](CF_3SO_3)_3$ adopts an eight-connected body-centered hypercubic CsCl-like lattice (see picture), $[La(L)_4](BPh_4)(ClO_4)_2$ shows eight-coordinate, but seven-connected, nodes linked in an unprecedented $4^{17}6^2$ topology.



Angew. Chem. **2001**, *113*, 2510 – 2513

D.-L. Long, A. J. Blake, N. R. Champness,* C. Wilson, M. Schröder* .... 2444 – 2447

Unprecedented Seven- and Eight-Connected Lanthanide Coordination Networks

Keywords: coordination chemistry · crystal engineering · lanthanum · solid-state reactions · supramolecular chemistry

VIPs

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

The Reaction Mechanism of the Enzyme-Catalyzed Central Cleavage of *β*,*β*-Carotene to Retinal	M. G. Leuenberger, C. Engeloch-Jarret, W.-D. Woggon*	◆
Activation, Tuning, and Immobilization of Homogeneous Catalysts in an Ionic Liquid/Compressed CO_2 Continuous-Flow System	A. Bösmann, G. Franció, E. Janssen, M. Solinas, W. Leitner,* P. Wasserscheid*	◆
Synthetic seco Forms of (−)-Diazonamide A	J. Li, X. Chen, A. W. G. Burgett, P. G. Harran*	◆
Targeting Molecular Recognition: Exploring the Dual Role of Functional Pseudo-Prolines in the Design of SH3 Ligands	G. Tuchscherer,* D. Grell, Y. Tatsu, P. Durieux, J. Fernandez-Carneado, B. Hengst, C. Kardinal, S. Feller*	
Synthesis of the C1 – C13 Fragment of Kendomycin: Atropisomerism around a C-Aryl Glycosidic Bond	H. J. Martin,* M. Drescher, H. Kählig, S. Schneider, J. Mulzer*	

1433-7851/01/4013-2368 $ 17.50+.50/0

Two surface-tethered nanomachines have been constructed at a supramolecular level by employing cylinders of the π-electron deficient tetracationic cyclophane, cyclobis(paraquat-*p*-phenylene) (blue), inside which polyether pistons incorporating π-electron rich dioxynaphthalene units (red and pink) can be induced to move when reductants are supplied either by chemicals or from a light source with 9-anthracenecarboxylic acid (yellow) as the photosensitizer and ethylenediaminetetraacetate (green) as a sacrificial reagent.

Angew. Chem. **2001**, *113*, 2513 – 2517

S. Chia, J. Cao, J. F. Stoddart,*
J. I. Zink* .... 2447 – 2451

Working Supramolecular Machines Trapped in Glass and Mounted on a Film Surface

Keywords: molecular machines · pseudorotaxanes · sol – gel processes · supramolecular chemistry

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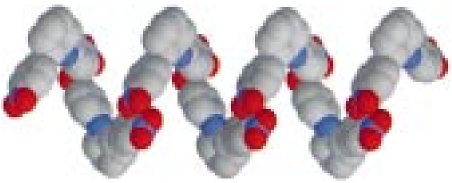

The crystallization solvent exerts a critical control of the nonlinear optical properties of helical superstructures in molecular crystals based on *N*,*N*′-bis(4-nitrophenyl)-(1*R*,2*R*)-diaminocyclohexane. While crystallization from ethyl acetate resulted in mutually orthogonal helices with different handedness, crystallization from ethyl acetate/hexane or acetyl acetone/hexane resulted in the formation of helical motifs (see picture) of a single-handedness oriented in one direction. The latter showed a strong solid-state second harmonic generation capability.

Angew. Chem. **2001**, *113*, 2517 – 2521

P. Gangopadhyay,
T. P. Radhakrishnan* .... 2451 – 2455

Helical Superstructures of a C_2-Symmetric Molecule Exhibiting Strong Second Harmonic Generation in the Solid State

Keywords: chirality · helical structures · nonlinear optics · structure determination

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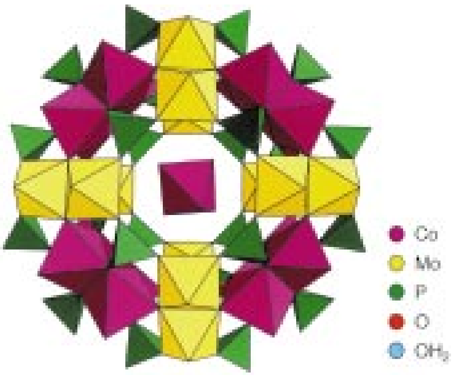


Four tetramers of Mo^{V} centers and four tetramers of Co^{II} centers, linked by phosphate groups around a central isolated $[Co(H_2O)_6]^{2+}$ octahedron form the key structural unit (see picture) in the molybdenum(v) cobaltophosphates **1** and **2**, which were prepared by hydrothermal synthesis. These units are connected to produce two-dimensional structures in which the cobalt atoms are antiferromagnetically coupled.

$[(Mo_2O_4)_8(HPO_4)_{14}(PO_4)_{10}\{Co_{22}Cl_2(H_2O)_{42}\}]\cdot 28\,H_2O$ **1**

$[(Mo_2O_4)_8(HPO_4)_{14}(PO_4)_{10}\{Co_{19}Na_4(H_2O)_{34}\}]\cdot 14\,H_2O$ **2**

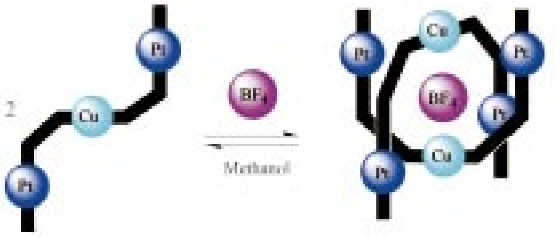
Angew. Chem. **2001**, *113*, 2521 – 2523

C. du Peloux, A. Dolbecq, P. Mialane,
J. Marrot, E. Rivière,
F. Sécheresse* .... 2455 – 2457

A New Family of Layered Molybdenum(v) Cobalto-Phosphates Built up of $[H_{14}(Mo_{16}O_{32})Co_{16}(PO_4)_{24}(H_2O)_{20}]^{10-}$ Wheels

Keywords: cobalt · magnetic properties · molybdenum · polyoxometalates · solid-state structures

New balls please! Reaction of $Cu(BF_4)_2$ with $[(dach)Pt^{II}]$ (dach = *trans* (±)-1,2-diaminocyclohexane) and bis(ethylthio)methylenepropanedioate (BETMP) gave $[\{(dach)Pt(BETMP)\}_2Cu(BF_4)_2]$ (**1**; shown schematically). Dimerization of **1** in methanol leads to the first inorganic "tennis ball" **2** [Eq. (1)]. A BF_4^- ion is encapsulated in the cavity of **2**.



1 2

(1)

Angew. Chem. **2001**, *113*, 2524–2526

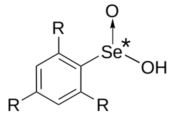
K. M. Kim,* J. S. Park, Y.-S. Kim,
Y. J. Jun, T. Y. Kang, Y. S. Sohn,
M.-J. Jun* 2458–2460

The First Inorganic "Tennis Ball" Encapsulating an Anion

Keywords: anions · host-guest systems · self-assembly · supramolecular chemistry

---

Bulky alkyl substituents on the benzene ring stabilize optically active areneseleninic acids **1**, which were obtained for the first time by chiral resolution on an optically active HPLC column, against racemization. Racemization was found to proceed via achiral seleninate anions with extrusion of a proton, at least under high-dilution conditions.



1

R = Me, Et, *i*Pr

Angew. Chem. **2001**, *113*, 2526–2528

T. Shimizu, I. Watanabe,
N. Kamigata* 2460–2462

Optically Active Seleninic Acids: Optical Resolution and Stability

Keywords: circular dichroism · enantiomer resolution · liquid chromatography · selenium

---

The Te bridges of the $[Co_9(CO)_8Te_6]$ cube of **1** serve as anchors for three $Cp'_2Nb(CO)$ ($Cp' = tBuC_5H_4$) and three $Cr(CO)_5$ fragments (see picture). This new principle allows the synthesis and structural comparison of clusters with 122–124 metal valence electrons.

$[\{Cp'_2Nb(CO)\}_3Co_9(CO)_8Te_6 \cdot 3\,Cr(CO)_5]$ **1**

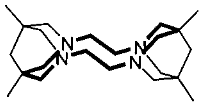
Angew. Chem. **2001**, *113*, 2529–2531

H. Brunner, A. C. Stückl, J. Wachter,*
R. Wanninger, M. Zabel 2463–2465

$[\{(tBuC_5H_4)_2Nb(CO)\}_3Co_9(CO)_8Te_6 \cdot 3\,Cr(CO)_5]$: Unusual Stabilization of a Cubic Body-Centered Metal Telluride Cluster by Peripheral Complex Fragments

Keywords: cluster compounds · cobalt · niobocene · tellurium

The absorption maximum of the orange-colored copper(II) complex of the cyclam derivative L, which has two 3,7-diazabicyclo[3.3.1]nonane units (see picture), occurs at 390 nm. This is the lowest value for a copper(II) tetraamine known so far, and indicates an extremely strong ligand field. This maximum is shifted by 110 nm (5740 cm^{-1}, 68 kJ mol^{-1}) to lower wavelengths than that of the parent compound $[Cu(cyclam)]^{2+}$; cyclam = 1,4,8,11-tetraazacyclotetradecane.



L

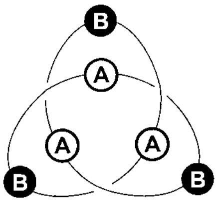
Angew. Chem. **2001**, *113*, 2556–2559

P. Comba,* H. Pritzkow,
W. Schiek 2465–2468

A Very Rigid Bis-bispidine Tetraazamacrocycle and Its Unusual Copper(II) Complex

Keywords: copper · N ligands · UV/Vis spectroscopy

By comparison of experimental and theoretical CD curves the absolute configurations of chromatographically baseline-separated enantiomers of new trefoil molecular knots could be determined (see schematic representation). From the results of syntheses with differently substituted starting materials, conclusions can be drawn about the knot-formation mechanism.



Angew. Chem. **2001**, *113*, 2534–2537

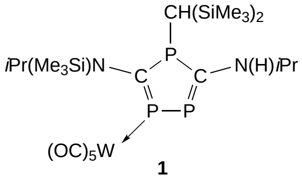
F. Vögtle,* A. Hünten, E. Vogel,
S. Buschbeck, O. Safarowsky, J. Recker,
A.-H. Parham, M. Knott, W. M. Müller,
U. Müller, Y. Okamoto,* T. Kubota,
W. Lindner, E. Francotte,
S. Grimme* 2468–2471

Novel Amide-Based Molecular Knots: Complete Enantiomeric Separation, Chiroptical Properties, and Absolute Configuration

Keywords: circular dichroism • enantiomer resolution • molecular knots • supramolecular chemistry • template synthesis

---

Surprisingly selective is the preparation of the novel 1,3,4-triphosphole complex **1** by insertion of a phosphaalkyne into a 1*H*-diphosphirene complex. NMR spectroscopic experiments and quantum-mechanical calculations indicate a small P-inversion barrier for the σ^3-phosphorus center in **1** as well as new possibilities of "π-tuning".



1

Angew. Chem. **2001**, *113*, 2531–2534

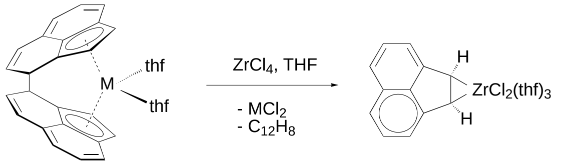
R. Streubel,* U. Schiemann, P. G. Jones,
J. Grunenberg, H.-M. Schiebel,
D. Gudat* 2471–2474

Synthesis of the First 1,3,4-Triphosphole Complex

Keywords: inversion • phosphaalkynes • phosphorus heterocycles • ring expansion

---

A ligand-splitting transmetalation: The ansa-metalloacenes $[(\eta^5\text{-}C_{12}H_8)_2M(thf)_2]$ (M = Yb, Ca) react with $ZrCl_4$ or Me_3SiCl unexpectedly by splitting the ansa-bisacenyl ligand, leading to the formation of the zirconacycle $[(\eta^2\text{-}C_{12}H_8)ZrCl_2(thf)_3]$ (**1**) [Eq. (1)] and the 1,2-bistrimethylsilylacenaphthene $(Me_3Si)C_{12}H_8$, respectively.



(1)

M = Yb, Ca

1, 60-85%

Angew. Chem. **2001**, *113*, 2540–2543

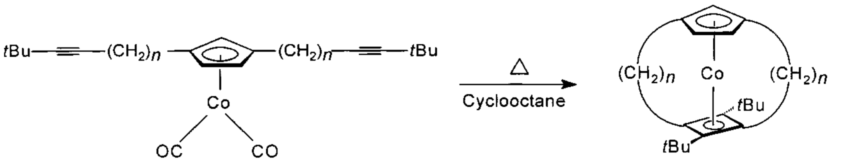
I. L. Fedushkin,* T. V. Petrovskaya,
M. N. Bochkarev,* S. Dechert,
H. Schumann* 2474–2477

Unexpected Splitting of ansa-Ytterboacene and ansa-Calcoacene: Formation of $[(\eta^2\text{-}C_{12}H_8)ZrCl_2(thf)_3]$ and $(Me_3Si)_2C_{12}H_8$

Keywords: ansa compounds • lanthanides • metallacycles • metallocenes • zirconium

---

The template-controlled synthesis of π ligands offers new methods for synthesizing endohedral metallocenophanes. This strategy allows the assembly of previously inaccessible bridged metallocenes, for example, the doubly bridged cobaltocenes **2**, prepared from **1**, n = 3, 4, 5.



1 **2**

Angew. Chem. **2001**, *113*, 2559–2562

G. Scholz, R. Gleiter,*
F. Rominger 2477–2479

A New Strategy for Synthesizing Endohedral Metallocenophanes

Keywords: alkynes • cobalt • cyclophanes • template synthesis

A Highly active, time stable, and water resistant, Hombikat TiO_2 supported Mn catalyst has been developed for the selective reduction of NO by NH_3 [Eq. (1)]. The analogous Cu and Cr supported catalysts also provide 100 % N_2 selectivity at $\leq 120\,^\circ C$. Lewis acidity, redox properties, and a high surface metal oxide concentration are essential for good catalytic performance.

$$4NO + 4NH_3 + O_2 \xrightarrow[80-180\ ^\circ C]{\text{Mn/Hombikat TiO}_2} 4N_2 + 6H_2O \qquad (1)$$

Angew. Chem. **2001**, *113*, 2537–2540

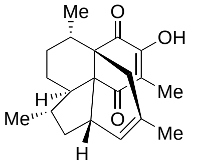
P. G. Smirniotis,* D. A. Peña,
B. S. Uphade 2479–2482

Low-Temperature Selective Catalytic Reduction (SCR) of NO with NH_3 by Using Mn, Cr, and Cu Oxides Supported on Hombikat TiO_2

Keywords: ammonia · heterogeneous catalysis · manganese · nitrogen oxides

---

Colombian corals of the species *Pseudopterogorgia elisabethae* produce the title compound, colombiasin A (**1**). This structurally novel, biologically active tetracyclic compound has now been synthesized for the first time in racemic form. Preliminary studies toward the asymmetric total synthesis of both enantiomers indicate that the determination of the absolute stereochemistry can be expected soon.



1

Angew. Chem. **2001**, *113*, 2543–2547

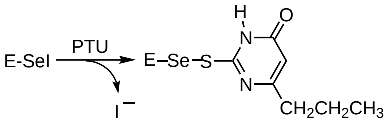
K. C. Nicolaou,* G. Vassilikogiannakis,
W. Mägerlein, R. Kranich ... 2482–2486

Total Synthesis of Colombiasin A

Keywords: cycloadditions · natural products · polycycles · quinones · total synthesis

---

The proposed mechanism of iodothyronine deiodinase inhibition by the thiourea-derived drugs 6-*n*-propylthiouracil (PTU) and 6-methylthiouracil is supported by experimental evidence. Model reactions with sterically or coordinatively stabilized organoselenyl iodides as enzyme-mimetic substrates (E-SeI; see scheme) support the proposal that PTU reacts not with the enzyme but with the enzyme–SeI intermediate containing a covalent Se–I bond, and suggest that the Se–I bond is kinetically activated by basic amino acid groups such as histidine.



Angew. Chem. **2001**, *113*, 2547–2550

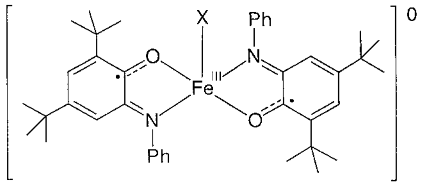
W.-W. du Mont,* G. Mugesh,
C. Wismach, P. G. Jones 2486–2489

Reactions of Organoselenenyl Iodides with Thiouracil Drugs: An Enzyme Mimetic Study on the Inhibition of Iodothyronine Deiodinase

Keywords: antithyroid drugs · deiodinases · enzyme inhibitors · selenium · selenoenzymes

---

The halide ligand determines the ground state for the complexes **1**. The chloride complex has a pure $S_t = 3/2$ state, the iodide complex a pure $S_t = 1/2$ state, and the bromide complex contains both spin-state isomers ($S_t = 3/2$ and $1/2$) in a 1:1 ratio. Strong intramolecular antiferromagnetic exchange coupling between the Fe^{III} ion, which in the chloride complex has a high-spin ($S_{Fe} = 5/2$) state and in the iodide complex an intermediate-spin ($S_{Fe} = 3/2$) state, and the two π radicals leads to observed ground states, S_t.



1, X = Cl, Br, I

Angew. Chem. **2001**, *113*, 2552–2555

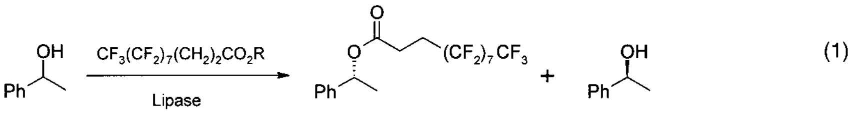
H. Chun, T. Weyhermüller, E. Bill,
K. Wieghardt* 2489–2492

Tuning the Electronic Structure of Halidobis(*o*-imino-benzosemiquinonato)-iron(III) Complexes

Keywords: electronic structure · iron · Moessbauer spectroscopy · radical ligands

---

No chromatography is necessary to separate a racemic alcohol into its enantiomers. A highly fluorinated acyl residue was tranferred in an enantiomer-selective manner onto a racemic alcohol in the presence of a lipase [Eq. (1)]. The labeled enantiomer was separated from the unlabeled one by a simple but very efficient partition between fluorous and organic phases.



Angew. Chem. **2001**, *113*, 2550–2552

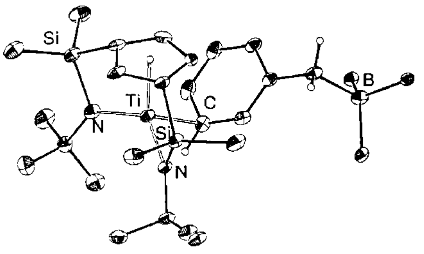
B. Hungerhoff, H. Sonnenschein,
F. Theil* 2492–2494

Separation of Enantiomers by Extraction Based on Lipase-Catalyzed Enantiomer-Selective Fluorous-Phase Labeling

Keywords: enantiomer resolution · enzyme catalysis · hydrolases · kinetic resolution · perfluorinated solvents

Doubly bridged di(silyl-η-amido)cyclopentadienyltitanium and -zirconium complexes and their related cations as the $[(PhCH_2)B(C_6F_5)_3]^-$ salts have been isolated (see structure of the Ti derivative). The neutral benzylzirconium complex was a very efficient catalyst in the presence of methylaluminoxane for producing high molecular weight polyethylene and ethylene-1-hexene copolymers.

Angew. Chem. **2001**, *113*, 2563–2565



J. Cano, P. Royo,* M. Lanfranchi,
M. A. Pellinghelli,
A. Tiripicchio 2495–2497

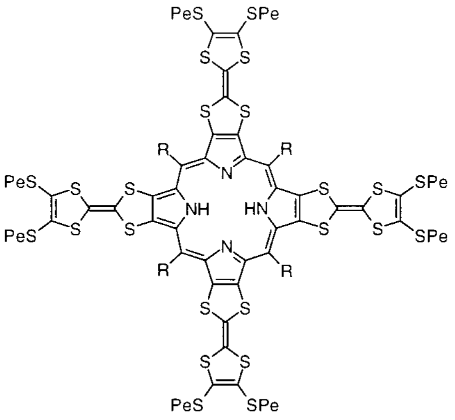
A New Type of Doubly Silylamido-Bridged Cyclopentadienyl Group 4 Metal Complexes

Keywords: catalysts • N ligands • polymerization • titanium • zirconium

---

Two efficient synthetic routes to the first tetrathiafulvaleno-annelated porphyrins are reported. These novel porphyrin systems (see picture; Pe = pentyl) have been characterized by using a variety of techniques including EPR spectroscopy, cyclic voltammetry, and mass spectrometry. Langmuir–Blodgett films obtained from the porphyrins were used to carry out structural studies by using X-ray diffraction and atomic force microscopy.

Angew. Chem. **2001**, *113*, 2565–2568



J. Becher,* T. Brimert, J. O. Jeppesen,
J. Z. Pedersen, R. Zubarev, T. Bjørnholm,
N. Reitzel, T. R. Jensen, K. Kjaer,
E. Levillain 2497–2500

Tetrathiafulvaleno-Annelated Porphyrins

Keywords: cyclic voltammetry • EPR spectroscopy • Langmuir–Blodgett films • porphyrinoids • tetrathiafulvalenes

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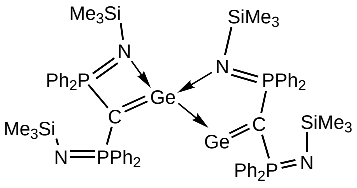
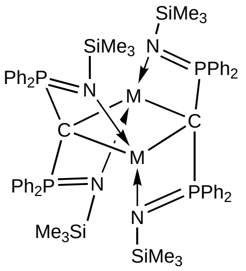
Low-valent metallavinylidenes $:M=C<$ are scarce owing to the low stability of such species. Compound **1**, prepared from $[CH(Ph_2P=NSiMe_3)_2Li(thf)]$ and $GeCl_2\cdot$dioxane, represents the first stable bis(germavinylidene). The dimetallacyclobutanes **2** (M = Pb, Sn) were also prepared—they are believed to form by dimerization of the intermediate metallavinylidenes.



1



2

Angew. Chem. **2001**, *113*, 2569–2571

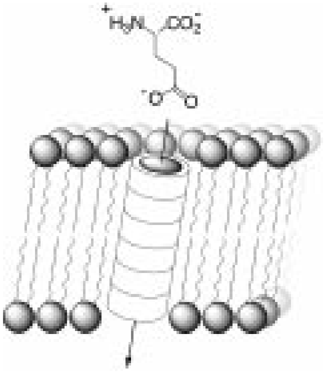
W.-P. Leung,* Z.-X. Wang, H.-W. Li,
T. C. W. Mak 2501–2503

Bis(germavinylidene) $[(Me_3SiN{=}PPh_2)_2C{=}Ge\rightarrow Ge{=}C(Ph_2P{=}NSiMe_3)]$ and 1,3-Dimetallacyclobutanes $[M\{\mu^2\text{-}C(Ph_2P{=}NSiMe_3)_2\}]_2$ (M = Sn, Pb)

Keywords: germanium • lead • tin • vinylidene ligands

Transported to the other side: Cyclic D,L-α-peptides self-assemble in lipid bilayers into transmembrane ion channels that may allow efficient transport of glutamic acid (see picture). The molecular transport is size/shape selective, as evidenced by the high transport rates observed with cyclodecapeptide-based transmembrane pores but not with the smaller cyclooctapeptide analogue.

Angew. Chem. **2001**, *113*, 2571–2574

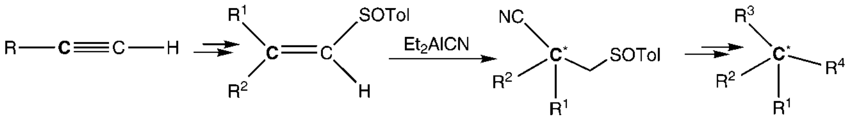


J. Sánchez-Quesada, H. Sun Kim,
M. R. Ghadiri * 2503–2506

A Synthetic Pore-Mediated Transmembrane Transport of Glutamic Acid

Keywords: ion-channels • molecular transport • nanotubes • peptides • self-assembly

Terminal alkynes are easily transformed into enantiomerically enriched compounds containing tertiary and quaternary carbon atoms. Sulfinylation followed by reduction (or alkylation) and hydrocyanation of the resulting vinyl sulfoxides with Et_2AlCN provides nitriles bearing the chiral center, which can in turn undergo reaction to form the desired products (see reaction scheme). Tol = 4-tolyl.



Angew. Chem. **2001**, *113*, 2575–2577

J. L. García Ruano,*
M. Cifuentes García, N. M. Laso,
A. M. Martín Castro,
J. H. Rodríguez Ramos* ... 2507–2509

Stereoselective Hydrocyanation of Alkenyl Sulfoxides as a Method to Highly Enantiomerically Enriched Compounds with Tertiary and Quaternary Chiral Carbon Atoms

Keywords: aluminum · asymmetric synthesis · hydrocyanation · sulfoxides · sulfur

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The substituents at the *peri* positions of dehydro[14]annulenes **1** have a dramatic effect on the stability of these macrocycles, and lead to derivatives that are stable even at elevated temperatures (up to 190°C).

1

Angew. Chem. **2001**, *113*, 2577–2580

G. J. Palmer, S. R. Parkin,
J. E. Anthony* 2509–2512

Synthesis of a Remarkably Stable Dehydro[14]annulene

Keywords: alkynes · annulenes · conjugation · macrocycles

Different intramolecular dynamics of HNO_3 at different levels of internal excitation can be used to represent connected logic gates. An ultrafast IR–UV double-resonance experiment, where the time delay between the two pulses can be operationally set to a positive or negative value, is used to present an equivalent logic circuit and its Boolean structure.

Angew. Chem. **2001**, *113*, 2580–2582

T. Witte, C. Bucher, F. Remacle,
D. Proch, K. L. Kompa,
R. D. Levine* 2512–2514

IR-UV Double-Resonance Photodissociation of Nitric Acid ($HONO_2$) Viewed as Molecular Information Processing

Keywords: computer chemistry · molecular devices · molecular electronics · photochemistry · UV/Vis spectroscopy

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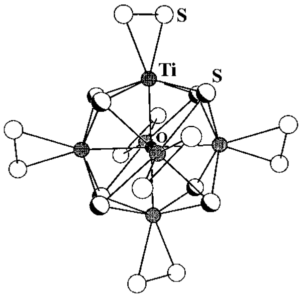
The zero-dimensional cluster compound $K_4Ba[Ti_6OS_8(S_2)_6]$ has been synthesized from a reactive flux similar to that of K_2S_n and Ti used in the synthesis of the one-dimensional compound $K_4Ti_3S_{14}$, but augmented by the deliberate introduction of TiO_2. The picture shows the structure of the $[Ti_6OS_8(S_2)_6]^{6-}$ ion.



Angew. Chem. **2001**, *113*, 2583–2584

F. Q. Huang, J. A. Ibers* 2515–2516

Oxide Addition to a Reactive Polysulfide Flux: Synthesis of $K_4Ba[Ti_6OS_{20}]$ Containing Isolated $[Ti_6OS_8(S_2)_6]^{6-}$ Clusters

Keywords: cluster compounds · interstitial atoms · reactive flux method · solid-state reactions · titanium

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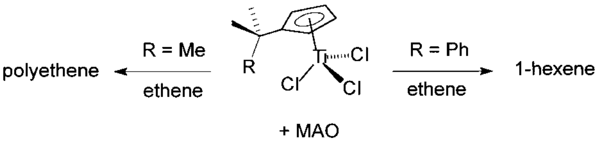
A drastic ligand effect was observed in the catalytic ethene conversion by the substituted mono(cyclopentadienyl)titaniumtrichloride/methylalumoxane (MAO) catalysts shown. The catalyst with R = Me produces polyethene, whereas the catalyst with R = Ph selectively trimerizes ethene to 1-hexene. This switch in catalyst performance appears to be the result of a hemilabile behavior of the cyclopentadienyl ligand with the pendant arene group, involving reversible coordination of the arene moiety.



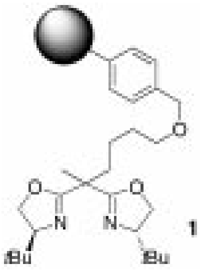
Angew. Chem. **2001**, *113*, 2584–2587

P. J. W. Deckers, B. Hessen,*
J. H. Teuben 2516–2519

Switching a Catalyst System from Ethene Polymerization to Ethene Trimerization with a Hemilabile Ancillary Ligand

Keywords: ethene · homogeneous catalysis · ligand effects · titanium · trimerization

The polystyrene-supported bis-oxazoline 1 forms a complex with copper(II)triflate that is a highly effective catalyst for the heterogeneously catalyzed enantioselective Mukaiyama aldol reaction of silylthioketene acetals with methyl pyruvate (ca. 90% yield, ca. 90% *ee*). The catalyst can be recovered by simple filtration and reused several times without a decline in enantioselectivity.



1

Angew. Chem. **2001**, *113*, 2587–2589

S. Orlandi, A. Mandoli, D. Pini, P. Salvadori* 2519–2521

An Insoluble Polymer-Bound Bis-Oxazoline Copper(II) Complex: A Highly Efficient Heterogeneous Catalyst for the Enantioselective Mukaiyama Aldol Reaction

Keywords: aldol reaction · asymmetric catalysis · copper · heterogeneous catalysis · solid-phase synthesis

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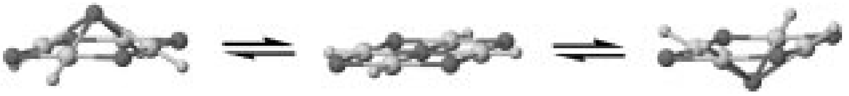
Halide ions act as the template for the self-assembly of tetrapalladium macrocyclic pyramidal structures. These undergo easy inversion in which the halide ion apparently jumps across the macrocycle (see scheme).



Angew. Chem. **2001**, *113*, 2589–2592

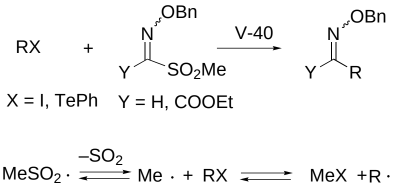
C. Bartolomé, R. de Blas, P. Espinet,* J. M. Martín-Álvarez, F. Villafañe 2521–2524

Self-Assembly of Pyramidal Tetrapalladium Complexes with a Halide at the Apex

Keywords: fluxionality · halogens · metallacycles · palladium · self-assembly

---

A simple strategy involving thermal decomposition of the methanesulfonyl radical into the methyl radical and the subsequent transfer of an iodine atom or phenyl telluride group was used to develop a tin-free radical acylation reaction (see scheme; V-40 = 1,1′-azobis(cyclohexane-1-carbonitrile). The key was finding reaction conditions under which the I or PhTe transfer is faster than the direct addition of the alkyl radical to the methanesulfonyl oxime ether.



Angew. Chem. **2001**, *113*, 2592–2594

S. Kim,* H.-J. Song, T.-L. Choi, J.-Y. Yoon 2524–2526

Tin-Free Radical Acylation Reactions with Methanesulfonyl Oxime Ether

Keywords: acylation · C–C coupling · radical reactions · synthetic methods

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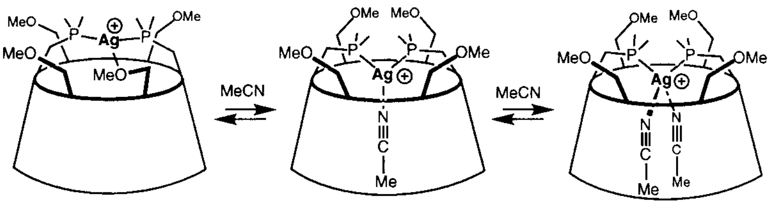
A multitopic cavity equipped with two phosphorus and four oxygen donor atoms has been successfully used for the covalent entrapment of organometallic fragments. The α-cyclodextrin–silver complex **1** is able to reversibly host one or two acetonitrile ligands.



1

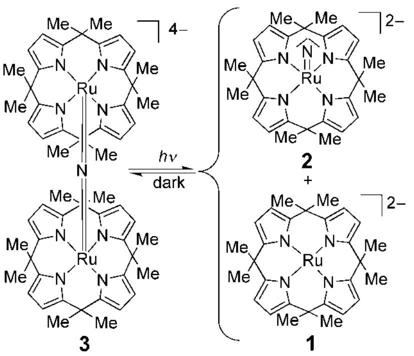
Angew. Chem. **2001**, *113*, 2594–2597

E. Engeldinger, D. Armspach,* D. Matt* 2526–2529

Cyclodextrin Cavities as Probes for Ligand-Exchange Processes

Keywords: coordination chemistry · cyclodextrins · P ligands · silver

Tunable electrophilicity/nucleophilicity by means of the redox properties of the Ru $\equiv$ N group and reversible interconversion of mononuclear and dinuclear species as a result of the photolability of the Ru=N=Ru group are characteristic of the nitrido derivatives of Ru porphyrinogens. For example, **2**, the product of reversible reduction of a Ru $\equiv$ N precusor, reacts with **1** in the dark to form **3**, which undergoes photocleavage to **1** and **2**.



Angew. Chem. **2001**, *113*, 2597–2599

L. Bonomo, E. Solari, R. Scopelliti, C. Floriani* 2529–2531

Ruthenium Nitrides: Redox Chemistry and Photolability of the Ru–Nitrido Group

Keywords: N ligands · photochemistry · porphyrinogens · redox chemistry · ruthenium

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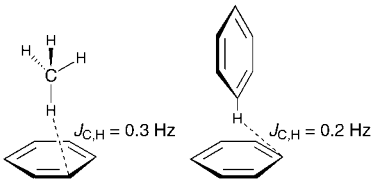
A small but detectable intermolecular spin–spin coupling ($J_{C,H}$) is predicted by density functional calculations on van der Waals bonded dimers like methane–benzene and benzene–benzene, as shown in the picture.



Angew. Chem. **2001**, *113*, 2600–2602

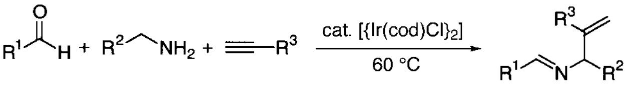
A. Bagno,* G. Saielli, G. Scorrano 2532–2534

DFT Calculation of Intermolecular Nuclear Spin–Spin Coupling in van der Waals Dimers

Keywords: ab initio calculations · density functional calculations · NMR spectroscopy · spin–spin coupling · van der Waals dimers

---

C–H bond activation of imines by an iridium complex is the decisive step in the three-component coupling reaction of an aldehyde, an amine, and an alkyne [Eq. (1)]. The aldehyde and amine initially react to provide an imine, which in turn reacts with the alkyne to form the coupling product.

 (1)

Angew. Chem. **2001**, *113*, 2602–2604

S. Sakaguchi, T. Kubo, Y. Ishii* 2534–2536

A Three-Component Coupling Reaction of Aldehydes, Amines, and Alkynes

Keywords: aldehydes · alkynes · amines · C–H activation · cross-coupling

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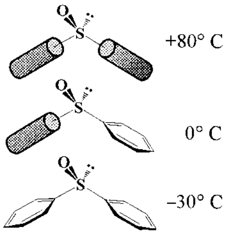
The formally enantiotopic phenyl rings of Ph$_2$SO (C_s symmetry) display different rotation rates about the Ph–S bonds in the crystalline state. For example, at 0°C one phenyl ring rotates (see picture; cylinder represents rotating phenyl ring), whereas the other does not. Two distinct barriers (13.0 and 14.0 kcal mol^{-1}) were determined by solid-state NMR spectroscopy.



Angew. Chem. **2001**, *113*, 2604–2608

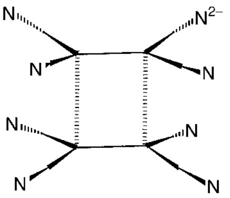
D. Casarini,* L. Lunazzi,* A. Mazzanti 2536–2540

Unprecedented Detection of Distinct Barriers Involving Formally Enantiotopic Substituents: Phenyl Rotation in Solid Diphenyl Sulfoxide

Keywords: chirality · NMR spectroscopy · stereodynamics · sulfoxides · X-ray diffraction

---

Attractive interaction with the cation overcomes the electrostatic repulsion between two tetracyanoethylene radical anions, [TCNE]$^{\bullet-}$, and leads to the formation of a diamagnetic dimer [TCNE]$_2^{2-}$ (see picture), for example, in [K(glyme)]$_2$[TCNE]$_2$. The bonding is described as two-electron, four-center bonding arising from π*–π* overlap. Crystallographic as well as spectroscopic (IR and UV/Vis) features of this bonding are observed.



Angew. Chem. **2001**, *113*, 2608–2613

J. J. Novoa,* P. Lafuente, R. E. Del Sesto, J. S. Miller* 2540–2545

Exceptionally Long (≥2.9 Å) C–C Bonds between [TCNE]$^-$ Ions: Two-Electron, Four-Center π*–π* C–C Bonding in π-[TCNE]$_2^{2-}$

Keywords: pi*–pi* bonding · radical ions · self-assembly · supramolecular interactions · tetracyanoethylene

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

* Author to whom correspondence should be addressed

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