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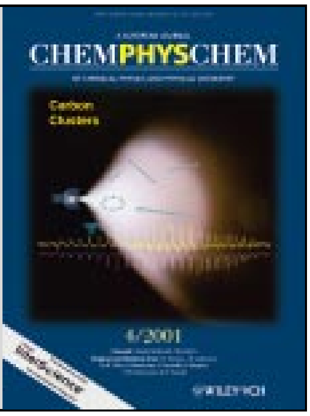
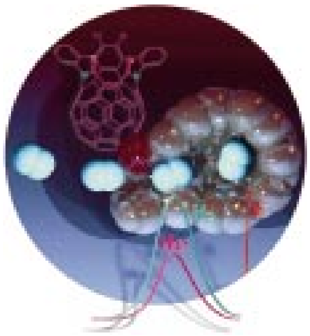
Pages 1321 – 1556

ChemPhysChem 4/2001 is bound in this issue of _Angewandte Chemie._



COVER PICTURE

The cover picture shows the process of hydrogen and helium insertion/expulsion which has been achieved for the first time with an open fullerene derivative (outlined in the background). The experimental activation barrier for helium decomplexation could be obtained and fully agrees with the calculated value (density functional theory). The barrier for H_2 complexation/decomplexation is interestingly almost double that of helium, as illustrated by the energy diagram shown in the foreground. This difference arises from the larger, elongated surface of H_2 undergoing greater van der Waals interaction at the transition state relative to that of helium, even though both atoms have the same radii. More about this process can be found in the article by Rubin, Houk, Saunders, Cross et al. on p. 1543 ff.



Better prediction of the rate constants of radical addition to alkenes is possible by using new, simpler, physically more sensible, but nonlinear, equations. Starting from representative, experimentally and theoretically obtained data sets and clear state-correlation diagrams for radical addition reactions, the controlling factors have been qualified in a new and rigorous manner. The results of this method lead to a partial revision of the existing qualitative rules and show more clearly how the reaction enthalpy, charge transfer, and the steric effects of substituent groups affect the activation energy barrier.

Angew. Chem. **2001**, *113*, 1380–1414

H. Fischer,* L. Radom 1340–1371

Factors Controlling the Addition of Carbon-Centered Radicals to Alkenes—An Experimental and Theoretical Perspective

Keywords: ab initio calculations · additions · kinetics · radical reactions

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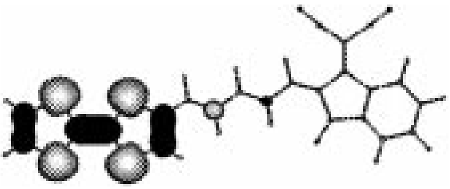
Modified TTF derivatives display not only electrical conductivity but also nonconventional properties, for example, the TTF derivative shown displays nonlinear optical properties. Recent years have witnessed the development of new possibilities for these compounds.



Angew. Chem. **2001**, *113*, 1416–1455

J. L. Segura, N. Martín* 1372–1409

New Concepts in Tetrathiafulvalene Chemistry

Keywords: donor–acceptor systems · electron transfer · materials science · supramolecular chemistry · tetrathiafulvalene

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

Synthesis of Conformationally Locked Carbohydrates: A Skew-Boat Conformation of L-Iduronic Acid Governs the Antithrombotic Activity of Heparin

S. K. Das, J.-M. Mallet, J. Esnault, P.-A. Driguez, P. Duchaussoy, P. Sizun, J.-P. Hèrault, J.-M. Herbert, M. Petitou,* P. Sinaÿ* ◆

Cyclic Dimers of Metalloporphyrins as Tunable Hosts for Fullerenes: A Remarkable Effect of Rhodium(III)

J.-Y. Zheng, K. Tashiro, Y. Hirabayashi, K. Kinbara, K. Saigo,* T. Aida,* S. Sakamoto, K. Yamaguchi

Direct Observation of Surface-Controlled Self-Assembly of Coordination Cages by using Atomic Force Microscopy as a Molecular Ruler

S. A. Levi, P. Guatteri, F. C. J. M. van Veggel, G. J. Vancso, E. Dalcanale,* D. N. Reinhoudt*

Fluorinated Bis(enyl) Ligands through Metal-Induced Dimerization of Fluorinated Allenes

D. Lentz,* S. Willemsen

Probing Guest Geometry and Dynamics through Host-Guest Interactions

T. Kusukawa, M. Yoshizawa, M. Fujita*

The Natural ^{12}C/^{13}C Ratio Allows Classification of Terpenoid Biosynthesis According to the Methylerythritolphosphate or the Mevalonate Pathway: Dynamic Allocation of Resources in Induced Plants

A. Jux, G. Gleixner, W. Boland*

ESSAY

Georg Wittig, what is known today about his work? Certainly the Wittig reaction and dehydrobenzene are mentioned when younger chemists refer to Wittig. However, such pioneering discoveries as the halogen/metal exchange reaction and the directed *ortho*-metalation, as well as the key experiments leading to azaenolates or to complex bases, are associated with Wittig only by some old-timers. This is the reason to refer anew to the significance of Wittig's contributions to the chemistry of the 21st century.

Angew. Chem. **2001**, *113*, 1457–1462

R. W. Hoffmann* 1411–1416

Wittig and His Accomplishments: Still Relevant Beyond His 100th Birthday

Keywords: arenes · biography · metalation · Wittig reactions · ylides

HIGHLIGHTS

Sulfate-reducing bacteria oxidize phosphite (P^{III}) to phosphate (P^{V}). This was established for bacteria isolated from marine sediments. The reaction might form part of a hypothetical phosphate cycle. It is possible that the free energy of oxidation is conserved as energy-rich acylphosphate through a primeval stepwise substrate phosphorylation. In anoxic marine sediments of the Pacific near the Oregon coast a syntrophic community of sulfate reducers and methanogens has been identified, which anaerobically oxidizes methane to CO_2 under the formation of sulfide.

Angew. Chem. **2001**, *113*, 1463–1464

W. Buckel* 1417–1418

Inorganic Chemistry in Marine Sediments

Keywords: archea · bioinorganic chemistry · phosphite oxidation · redox chemistry · sulfate reduction

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This chapter is not yet closed! The synthesis of a vibrationally stable, neutral, and chemically bound ground-state argon compound, along with recent breakthroughs in xenon chemistry, heralds a renaissance in noble gas chemistry.

Angew. Chem. **2001**, *113*, 1465–1467

K. O. Christe* 1419–1421

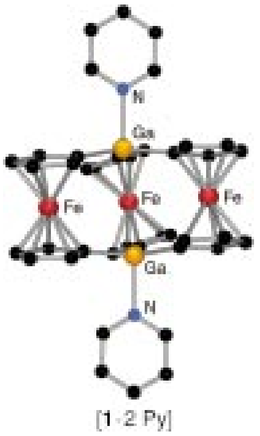
A Renaissance in Noble Gas Chemistry

Keywords: argon · fluorine · hypervalent compounds · noble gases · xenon

COMMUNICATIONS

A molecular carousel, that is the appearance of the structure of the title compound [**1**·2py] (see picture), the first complex of a new structure type prepared by a highly selective condensation reaction from the equally new complex $[Fe(C_5H_4GaMe_2)_2]$. The first gallium bridged [*m.m*]ferrocenophane $[\{Fe(C_5H_4)_2\}_2\{GaMe(C_5H_5N)\}_2]$ is formed as an intermediate; this compound can also be prepared in a planned synthesis and can be converted into [**1**·2py] by warming. The complex [**1**·2py] as well as [**1**·2Et_2O] and [**1**·2DMSO], which were formed by donor exchange, offers various interesting properties, for example, [**1**·2DMSO] can be reversibly oxidized to the mono-, di-, and trication.

Angew. Chem. **2001**, *113*, 1470–1473



[1·2 Py]

P. Jutzi,* N. Lenze, B. Neumann, H.-G. Stammler 1424–1427

$[\{Fe(C_5H_4)_2\}_3\{Ga(C_5H_5N)\}_2]$: A Trinuclear Gallium-Bridged Ferrocenophane with a Carousel Structure

Keywords: carousel structure · electrochemistry · ferrocenophane · gallium · mixed-valent compounds

Encouraged by the international race to sequence the human genome, new approaches to decode single copies of DNA have emerged. These could potentially speed up the sequencing process—if all bases in DNA could be tagged with distinct fluorescent labels. Complete labeling of the pyrimidine bases of one strand, as described here, might be a first solution to this problem.

Angew. Chem. **2001**, *113*, 1473–1476

S. Brakmann,*
S. Löbermann 1427–1429

High-Density Labeling of DNA: Preparation and Characterization of the Target Material for Single-Molecule Sequencing

Keywords: fluorescence · nucleotides · polymerases · sequence analysis

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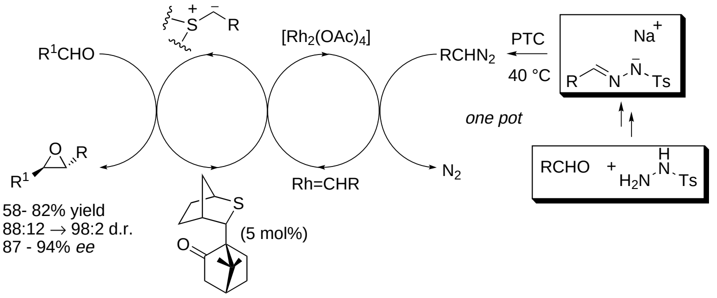
A practical, general, and convergent route to epoxides with control of the relative and absolute stereochemistry has been achieved by generating the reactive intermediate (the diazo compound) in situ from tosylhydrazone salts (see scheme, PTC = phase-transfer catalyst, Ts = toluene-4-sulfonyl). High yields (58–82%), high d.r. (88:12–98:2), and high *ee* values (87–94%) have been obtained using a new class of stable chiral sulfides at low catalyst loading (5 mol%) and $[Rh_2(OAc)_4]$ (0.5 mol%).



Angew. Chem. **2001**, *113*, 1479–1482

V. K. Aggarwal,* E. Alonso, G. Hynd, K. M. Lydon, M. J. Palmer, M. Porcelloni, J. R. Studley 1430–1433

Catalytic Asymmetric Synthesis of Epoxides from Aldehydes Using Sulfur Ylides with In Situ Generation of Diazocompounds

Keywords: asymmetric catalysis · diazo compounds · epoxidation · ylides

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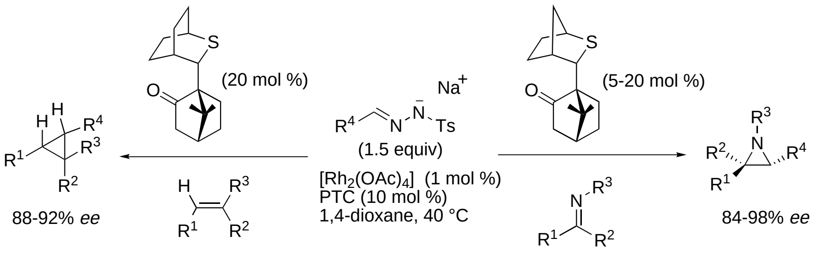
Imines and alkenes can be converted into the corresponding aziridines and cyclopropanes (see scheme, PTC = phase-transfer catalyst, Ts = toluene-4-sulfonyl) in good yield with moderate to high d.r. and high *ee* values using tosylhydrazone salts with catalytic quantities of chiral sulfide (5–20 mol%) and metal catalyst (1 mol%). The process is particularly suited to the synthesis of conformationally locked cyclopropyl amino acids, which can now be prepared in only three steps from commercially available material in 100% *ee*.



Angew. Chem. **2001**, *113*, 1482–1485

V. K. Aggarwal,* E. Alonso, G. Fang, M. Ferrara, G. Hynd, M. Porcelloni 1433–1436

Application of Chiral Sulfides to Catalytic Asymmetric Aziridination and Cyclopropanation with In Situ Generation of the Diazo Compound

Keywords: asymmetric catalysis · aziridination · cyclopropanation · diazo compounds · ylides

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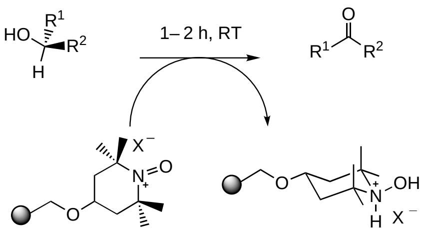
Polymer-supported oxidation of alcohols was conducted very efficiently by employing oxoammonium salts, the reactive intermediates in TEMPO oxidations (TEMPO = 2,2,6,6-tetramethylpiperidinoxyl). These highly reactive salts (see scheme; X = Br, Cl) could be prepared and isolated on the polymeric support, and were used for the conversion of single compounds as well as of complex mixtures of alcohols.



Angew. Chem. **2001**, *113*, 1489–1492

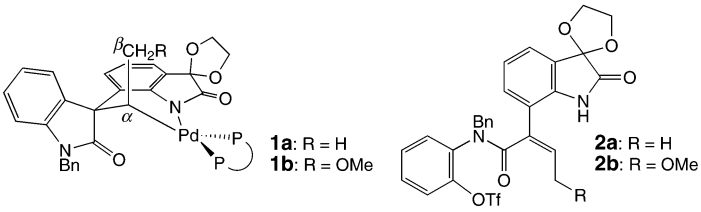
S. Weik, G. Nicholson, G. Jung, J. Rademann* 1436–1439

Oxoammonium Resins as Metal-Free, Highly Reactive, Versatile Polymeric Oxidation Reagents

Keywords: aldehydes · combinatoral chemistry · ketones · oxidations · solid-phase synthesis

1433-7851/01/4008-1326 $ 17.50+.50/0

In spite of containing three conformationally accessible β-H atoms, palladacycle **1a** is an isolable intermediate in the asymmetric Heck cyclization of **2a**. Although **1a** is stable in the presence of the hydrotriflate salt of 1,2,2,6,6-pentamethylpiperidine, it is converted into the oxindole Heck product when exposed to the more acidic hydrotriflate salt of 2,6-di-*tert*-butylpyridine. Heck cyclization of **2b** is also believed to proceed by way of a palladacyclic intermediate **1b**, which in this case undergoes β-methoxide elimination. Bn = benzyl.



1a: R = H
1b: R = OMe

2a: R = H
2b: R = OMe

Angew. Chem. **2001**, *113*, 1485 – 1489

M. Oestreich, P. R. Dennison,
J. J. Kodanko,
L. E. Overman* .... 1439 – 1442

Thwarting β-Hydride Elimination: Capture of the Alkylpalladium Intermediate of an Asymmetric Intramolecular Heck Reaction

Keywords: alkaloids · asymmetric catalysis · cyclization · Heck reactions · palladium

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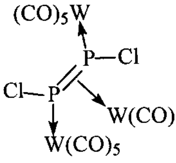
In contrast to the *cis* configuration of N_2F_2, the analogous phosphorus subhalogenides, P_2X_2 (X = F, Cl) adopt a *trans* configuration according to density functional theory calculations. Now for the first time dichlorodiphosphene has been stabilized in the coordination sphere of transition metals in the form of complex **1**.



1

Angew. Chem. **2001**, *113*, 1476 – 1478

U. Vogel, G. Stößer,
M. Scheer* .... 1443 – 1445

Complex Chemical Stabilization of Dichlorodiphosphene

Keywords: density functional calculations · P ligands · phosphene · tungsten

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They exist! Boridecarbides of transition metals. A whole series of Nb compounds was prepared from syntheses in Cu/Al melts with Nb_3B_3C, $Nb_4B_3C_2$, $Nb_7B_4C_4$, and $Nb_7B_6C_3$. Their crystal structures can be explained easily with a simple building-set principle based on the binary components NbC, Nb_2B_3, and Nb_3B_4.

Angew. Chem. **2001**, *113*, 1492 – 1495

H. Hillebrecht,*
K. Gebhardt .... 1445 – 1447

Crystal Structures from a Building Set: The First Boridecarbides of Niobium

Keywords: boridecarbide · niobium · solid-state structures · structure elucidation

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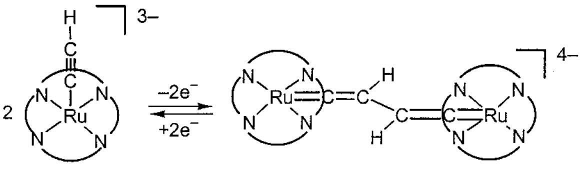
Through a proton-transfer reaction a porphyrinogen assists the transformation of terminal acetylenes into Ru – vinylidenes, which are the entry point to a variety of Ru – carbenes and Ru – cumulenes. The scheme (in which the porphyrinogen is stylized) shows the reversible interconversion of an acetylide into a divinylidene unit.



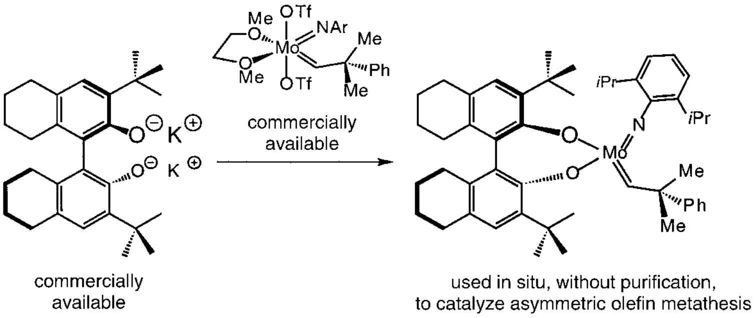
Angew. Chem. **2001**, *113*, 1497 – 1500

L. Bonomo, C. Stern, E. Solari,
R. Scopelliti, C. Floriani* .. 1449 – 1452

Acetylenes Rearranging on Ruthenium – Porphyrinogen and Leading to Vinylidene and Carbene Functionalities

Keywords: carbenes · cumulenes · porphyrinogens · ruthenium · vinylidene complexes

No glove box required! A new chiral catalyst for olefin metathesis is prepared from commercially available materials and is equally or more effective and selective than the previous systems. The new user-friendly catalyst can be prepared in situ (see scheme, Ar = aryl, Tf = trifluoromethanesulfonyl), isolation not needed, outside of a glove box, and delivers reactivity and enantioselectivity levels formerly available only through multiple catalysts.



Angew. Chem. **2001**, *113*, 1500–1504

S. L. Aeilts, D. R. Cefalo,
P. J. Bonitatebus, Jr., J. H. Houser,
A. H. Hoveyda,*
R. R. Schrock* 1452–1456

A Readily Available and User-Friendly Chiral Catalyst for Efficient Enantioselective Olefin Metathesis

Keywords: asymmetric catalysis · chiral complexes · enantioselectivity · metathesis · molybdenum

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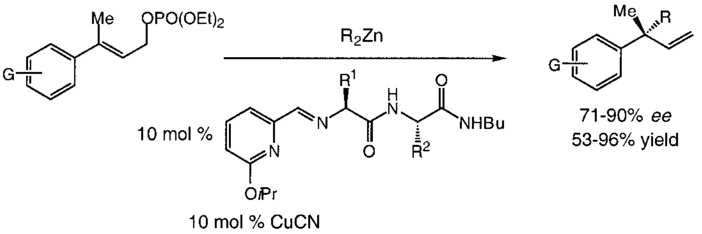
Highest enantioselectivities so far with dialkylzinc reagents! Quaternary carbon centers are formed enantioselectively through a Cu-catalyzed allylic substitution reaction that is promoted by pyridinyl peptide-based ligands in the presence of dialkylzinc reagents (see scheme). The modularity of this new class of chiral ligands is exploited for reactivity and selectivity optimization.



Angew. Chem. **2001**, *113*, 1504–1508

C. A. Luchaco-Cullis, H. Mizutani,
K. E. Murphy,
A. H. Hoveyda* 1456–1460

Modular Pyridinyl Peptide Ligands in Asymmetric Catalysis: Enantioselective Synthesis of Quaternary Carbon Atoms Through Copper-Catalyzed Allylic Substitutions

Keywords: allylic substitutions · asymmetric catalysis · chiral ligands · copper · peptide ligands

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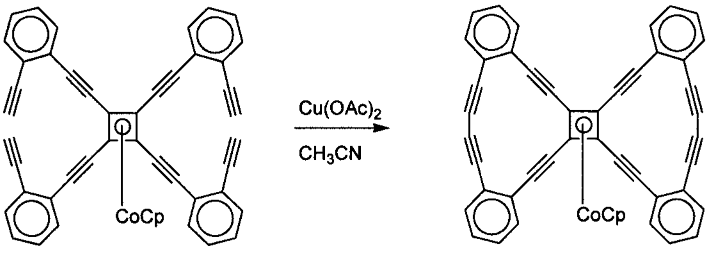
A metamorphosis of the tetraethynyl precursor **1** through double Cu-catalyzed ring closure leads to the corresponding butterfly-shaped cyclobutadiene complexes **2** in high yield (94 %). Single-crystal X-ray diffraction shows that the large organic ligand is distinctly nonplanar with a concave topology. Cp = cyclopentadiene.



1 **2**

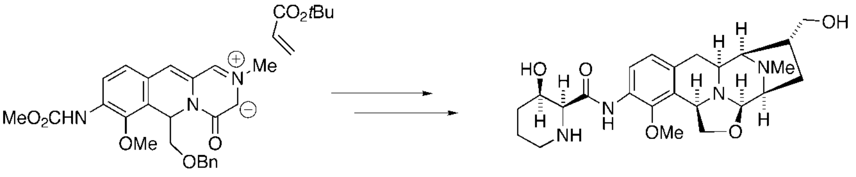
Angew. Chem. **2001**, *113*, 1508–1511

M. Laskoski, G. Roidl, M. D. Smith,
U. H. F. Bunz* 1460–1463

Concave Butterfly-Shaped Organometallic Hydrocarbons?

Keywords: alkyne complexes · alkynes · C–C coupling · cobalt · macrocycles

A new method for the formation of the allylic amine precursor to an azomethine ylide **1** has been developed and exploited in an efficient 1,3-dipolar cycloaddition to afford the key tetracyclic intermediate used in the synthesis of (−)-tetrazomine (**2**). Bn = benzyl.



1 **2**

Angew. Chem. **2001**, *113*, 1511–1513

J. D. Scott, R. M. Williams* 1463–1465

Total Synthesis of (−)-Tetrazomine and Determination of Its Stereochemistry

Keywords: alkaloids • antitumor agents • cycloaddition • natural products • total synthesis

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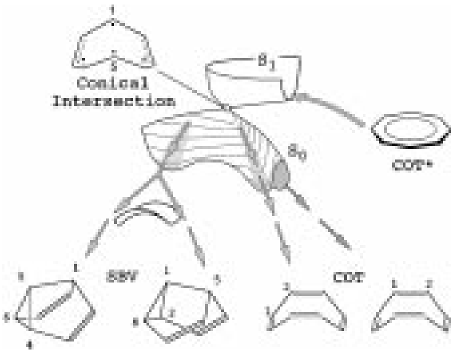
A mechanistic view of the deactivation of photoexcited cycloocta-1,3,5,7-tetraene (COT*) through a novel type of conical intersection (see scheme) is provided by ab initio studies. As a consequence of this deactivation, the formation of semibullvalene (SBV) and of the double-bond-shifted isomer of COT are intrinsically bound. Both gas-phase and solution-phase experimental data are explained.



Angew. Chem. **2001**, *113*, 1514–1516

M. Garavelli,* F. Bernardi, V. Moliner, M. Olivucci* 1466–1468

Intrinsically Competitive Photoinduced Polycyclization and Double-Bond Shift through a Boatlike Conical Intersection

Keywords: ab initio calculations • alkenes • computer chemistry • photochemistry • transition states

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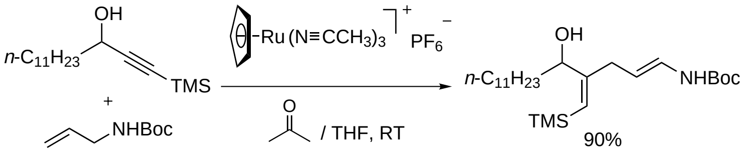
Di- or trisubstituted alkenes of defined geometry, with terminal enamide groups, are formed in an atom-economic three-carbon chain extension of alkynes with allyl amides catalyzed by ruthenium (see, for example, Equation (1); Boc = *tert*-butoxycarbonyl, TMS = trimethylsilyl).



(1)

Angew. Chem. **2001**, *113*, 1516–1519

B. M. Trost,* J.-P. Surivet ... 1468–1471

An Atom-Economic Three-Carbon Chain Extension to Give Enamides

Keywords: alkynes • enamides • ene reactions • homogeneous catalysis • synthetic methods

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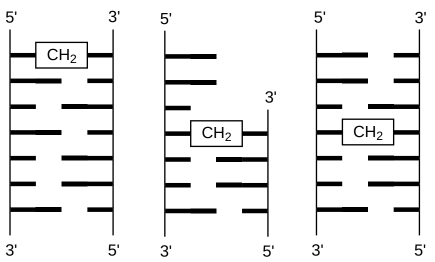
Building bridges: A feasible solid-phase synthesis of antiparallel *n*-, *h*-, and *H*-type DNA oligomers (see picture) has been demonstrated. The oligomers possess a CH_2-bridged base-pair model that should be conformationally flexible, even after base pairing.



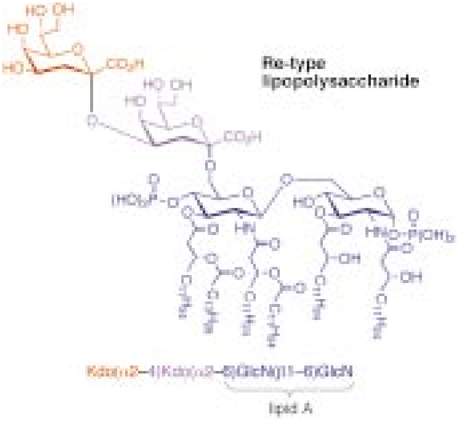
Angew. Chem. **2001**, *113*, 1519–1523

H.-Yu. Li, Y.-L. Qiu, E. Moyroud, Y. Kishi* 1471–1475

Synthesis of DNA Oligomers Possessing a Covalently Cross-Linked Watson–Crick Base Pair Model

Keywords: nucleosides • nucleotides • oligonucleotides • solid-phase synthesis • Watson–Crick base pairs

Three sequential efficient glycosylation reactions starting from D-glucosamine were used in the first total synthesis of *Escherichia coli* Re lipopolysaccharide, which is one of the most simple lipopolysaccharides found on the surface of living bacteria.



Angew. Chem. **2001**, *113*, 1523–1528

H. Yoshizaki, N. Fukuda, K. Sato, M. Oikawa,* K. Fukase, Y. Suda, S. Kusumoto* 1475–1480

First Total Synthesis of the Re-Type Lipopolysaccharide

Keywords: glycolipids · glycosylations · lipopolysaccharides · natural products · total synthesis

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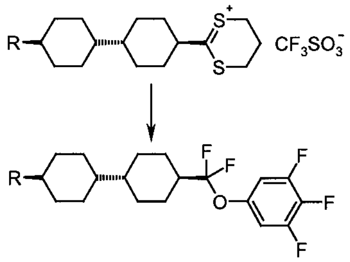
Insertion of a difluorooxymethylene bridge into the mesogenic core structure of phenylcyclohexane-based liquid crystals results in a class of materials that exhibits a surprising and unprecedented improvement of essentially all application-relevant properties (see scheme). A novel synthetic procedure allows the convenient large-scale preparation of a variety of compounds based on α,α-difluoroalkyl ether structures.



Angew. Chem. **2001**, *113*, 1528–1532

P. Kirsch,* M. Bremer, A. Taugerbeck, T. Wallmichrath 1480–1484

Difluorooxymethylene-Bridged Liquid Crystals: A Novel Synthesis Based on the Oxidative Alkoxydifluorodesulfuration of Dithianylium Salts

Keywords: desulfuration · fluorine · liquid crystals · mesogens · sulfur

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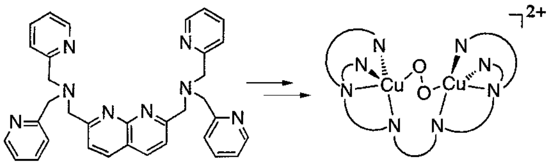
A copper–copper separation of about 2.84 Å is determined by extended X-ray absorption fine structure studies for the (μ-1,2-peroxo)dicopper(II) species **1**, which has only a 1,8-naphthyridine unit as an additional bridge. Complex **1** was prepared by the reaction of O_2 with a dicopper(I) complex formed from BPMAN (see picture).



BPMAN **1**

Angew. Chem. **2001**, *113*, 1532–1535

C. He, J. L. DuBois, B. Hedman,* K. O. Hodgson,* S. J. Lippard* 1484–1487

A Short Copper–Copper Distance in a (μ-1,2-Peroxo)dicopper(II) Complex Having a 1,8-Naphthyridine Unit as an Additional Bridge

Keywords: copper · EXAFS spectroscopy · metal–metal interaction · N ligands · 1,8-naphthyridine · peroxides

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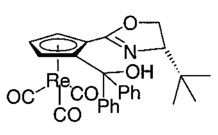
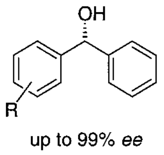


1



2

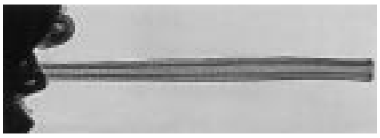
A novel planar chiral cyrhetrene 1 has been identified as an efficient catalyst precursor for the asymmetric synthesis of diarylmethanol compounds **2** by phenylation of aldehydes. Compared to the corresponding ferrocene derivative, the performance of the cyrhetrene is superior or at least equally as good and gives excellent enantioselectivities even with catalyst loadings as low as 2 mol%.

Angew. Chem. **2001**, *113*, 1536–1538

C. Bolm,* M. Kesselgruber, N. Hermanns, J. P. Hildebrand, G. Raabe .. 1488–1490

Application of a Planar Chiral η^5-Cyclopentadienylrhenium(I)tricarbonyl Complex in Asymmetric Catalysis: Highly Enantioselective Phenyl Transfer to Aldehydes

Keywords: asymmetric catalysis · diarylmethanols · rhenium · zinc



Anodization of aluminum with H_2SO_4 on an Si substrate results in the formation of individual alumina nanotubes (ANTs). The picture shows an ANT with a length of 650 nm and internal and external diameters of 12 and 35 nm, respectively. Detailed studies by transmission electron microscopy revealed that the ANTs are completely detached cells of the porous anodized aluminum film.

Angew. Chem. **2001**, *113*, 1538–1541

L. Pu,* X. Bao, J. Zou,
D. Feng 1490–1493

Individual Alumina Nanotubes

Keywords: aluminum · electrochemistry · nanostructures · oxidations · silicon

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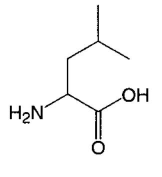
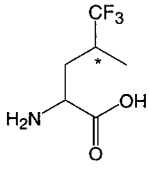
Fluorination of the hydrophobic core of a coiled-coil protein significantly improved its stability toward thermal and chemical denaturation. 5′,5′,5′-Trifluoroleucine (**2**) was efficiently incorporated into a leucine-zipper protein in place of leucine (**1**) during *E. coli* biosynthesis. The fluorinated variant maintained stable secondary and tertiary structures under conditions that caused denaturation of the “wild-type” protein.



1



2

Angew. Chem. **2001**, *113*, 1542–1544

Y. Tang, G. Ghirlanda, W. A. Petka,
T. Nakajima, W. F. DeGrado,
D. A. Tirrell* 1494–1496

Fluorinated Coiled-Coil Proteins Prepared In Vivo Display Enhanced Thermal and Chemical Stability

Keywords: biosynthesis · circular dichroism · fluorine · helical structures · protein structures

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Immobile solvated ions such as $NH_4^+ \cdot NH_3$ act as kinetic traps that prevent the proton-transfer reaction between H_3O^+ and NH_3 on ice surfaces at 85–140 K reaching thermodynamic equilibrium. A combination of Cs^+ reactive ion scattering and mass spectrometry showed that all species of the reaction (NH_3, NH_4^+, H_2O, and H_3O^+) coexist on ice. This result indicates that metastable species can be produced and kinetically stabilized on ice surfaces such that they may contribute to the chemistry of stratospheric and interstellar ice particles.

Angew. Chem. **2001**, *113*, 1545–1548

S.-C. Park, K.-W. Maeng, T. Pradeep,*
H. Kang* 1497–1500

Unique Chemistry at Ice Surfaces: Incomplete Proton Transfer in the H_3O^+–NH_3 System

Keywords: ice surface · ion–molecule reactions · mass spectrometry · protonations

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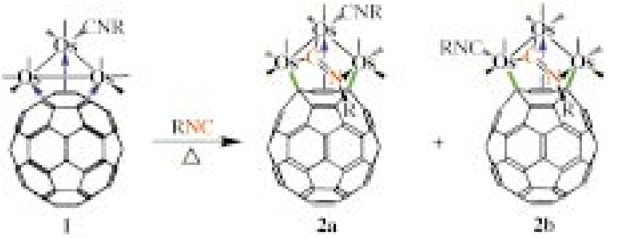
A boat-shaped 1,4-cyclohexadiene-like ring is present in the C_{60} molecule with a novel σ-type μ_3-η^1,η^2,η^1 bonding mode in the clusters **2a** and **2b**. The change in coordination mode was induced by insertion of an RNC ligand into an Os–Os bond of the π-type C_{60} complex **1**. R = $CH_2C_6H_5$.



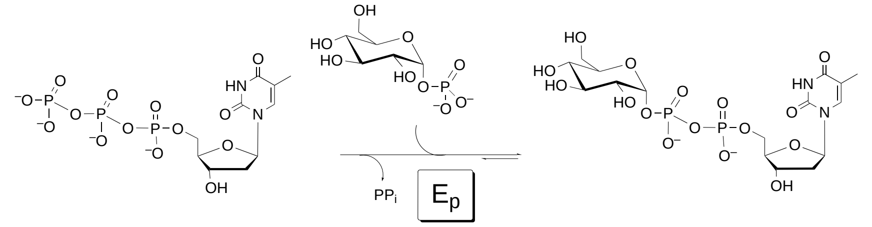
Angew. Chem. **2001**, *113*, 1548–1550

H. Song, K. Lee, C. H. Lee, J. T. Park,*
H. Y. Chang, M.-G. Choi ... 1500–1502

First Example of the μ_3-η^1,η^2,η^1-C_{60} Bonding Mode: Ligand-Induced Conversion of π to σ C_{60}–Metal Complexes

Keywords: cluster compounds · fullerenes · osmium

The exploitation of a unique thymidylyltransferase (E_p) allows the rapid syntheses of thymidine and uridine 5′-(aminodeoxy-α-D-hexopyranosyl diphosphates), 5′-(acetamidodeoxy-α-D-hexopyranosyl diphosphates), and even 5′-(aminodideoxy-α-D-hexopyranosyl diphosphates), which are amino analogues of the products from the native reaction of E_p (see scheme).



Angew. Chem. **2001**, *113*, 1550–1553

J. Jiang, J. B. Biggins,
J. S. Thorson* 1502–1505

Expanding the Pyrimidine Diphosphosugar Repertoire: The Chemoenzymatic Synthesis of Amino- and Acetamidoglucopyranosyl Derivatives

Keywords: enzyme catalysis · glycosyl phosphate · nucleotides · synthetic methods · transferases

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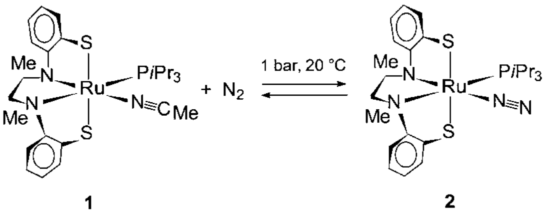
N_2 coordination to the nitrogenase Fe_7MoS_9 cofactor is considered a key step of biological N_2 fixation, however, modeling this step with metal–sulfur complex fragments under mild conditions has remained a long-standing challenge. The title complex **2** represents a first example, forming from N_2 and the precursor CH_3CN complex **1** under standard conditions [Eq. (1)].



(1)

Angew. Chem. **2001**, *113*, 1553–1555

D. Sellmann,* B. Hautsch, A. Rösler,
F. W. Heinemann 1505–1507

$[Ru(N_2)(PiPr_3)(\text{'}N_2Me_2S_2\text{'})]$: Coordination of Molecular N_2 to Metal Thiolate Cores under Mild Conditions

Keywords: dinitrogen complexes · N ligands · nitrogen fixation · ruthenium · S ligands

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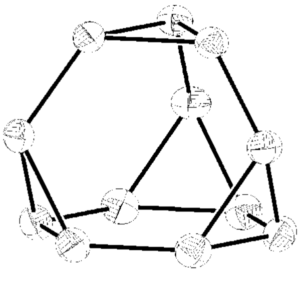
The largest isolated clusters of Group 14 elements, giant truncated tetrahedra of Ge_{12}^{12-} (see picture), are found in the title compound. $RbLi_7Ge_8$, which is an electronically balanced, saltlike Zintl phase, was synthesized by heating the corresponding stoichiometric mixture of elements.



Angew. Chem. **2001**, *113*, 1555–1558

S. Bobev, S. C. Sevov* 1507–1510

Synthesis and Characterization of $RbLi_7Ge_8$ with Isolated *closo*-$[Li_4Ge_{12}]^{8-}$ Ions, Lithium-Capped Truncated Tetrahedra of Ge_{12}^{12-}

Keywords: cluster compounds · germanium · lithium · solid-state structures · Zintl phases

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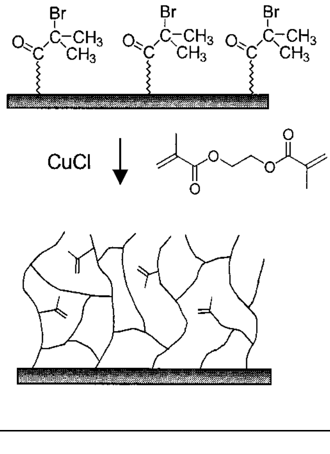
Ambient-temperature atom transfer radical polymerization of ethyleneglycol dimethacrylate from a surface yields homogeneous, cross-linked polymer films (see scheme). The absence of polymerization in solution in this "living" procedure avoids physisorption and gives uniform, cross-linked films with controlled thicknesses from 3 to 300 nm.



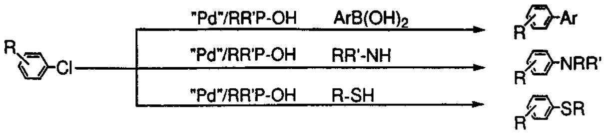
Angew. Chem. **2001**, *113*, 1558–1560

W. Huang, G. L. Baker,*
M. L. Bruening* 1510–1512

Controlled Synthesis of Cross-Linked Ultrathin Polymer Films by Using Surface-Initiated Atom Transfer Radical Polymerization

Keywords: atom transfer radical polymerization · radicals · surface chemistry · thin films

Rapid and regioselective oxidative addition of unactivated aryl chlorides in the presence of bases can be achieved by using metal complexes of phosphinous acid (RR′POH), for which air-stable phosphine oxides (RR′P(O)H) serve as ideal ligand precursors. Such processes can be incorporated into efficient catalytic cycles for a variety of C–C, C–N, and C–S bond-forming processes (see scheme, Ar = aryl).



Angew. Chem. **2001**, *113*, 1561–1564

G. Y. Li* 1513–1516

The First Phosphine Oxide Ligand Precursors for Transition Metal Catalyzed Cross-Coupling Reactions: C–C, C–N, and C–S Bond Formation on Unactivated Aryl Chlorides

Keywords: combinatorial chemistry · cross-coupling · homogeneous catalysis · palladium · phosphine oxides

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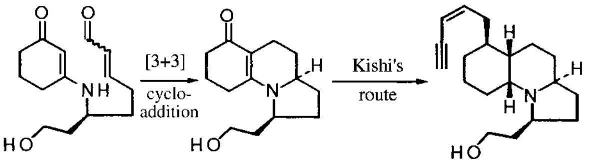
Complex piperidinyl heterocycles (for example, **2**) were accessed by using a novel intramolecular formal [3+3] cycloaddition reaction of vinylogous amides tethered with enals (for example, **1**). This method has been applied to a formal total synthesis of (+)-gephyrotoxin (**3**).



1 **2** **3**

Angew. Chem. **2001**, *113*, 1564–1566

L.-L. Wei, R. P. Hsung,* H. M. Sklenicka, A. I. Gerasyuto 1516–1518

A Novel and Highly Stereoselective Intramolecular Formal [3+3] Cycloaddition Reaction of Vinylogous Amides Tethered with α,β-Unsaturated Aldehydes: A Formal Total Synthesis of (+)-Gephyrotoxin

Keywords: alkaloids · amides · cycloaddition · electrocyclic reactions · synthetic methods

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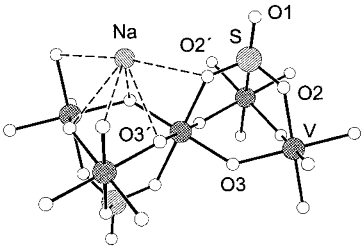
A dominant ferromagnetic exchange interaction propagates about the magnetic sites of the Kagomé lattice of the title compound through the bridging hydroxy groups (see section of the structure). This is at variance with the antiferromagnetic exchange observed for jarosite and its derivatives. The ferromagnetism probably arises from the d^2 electron count of the V^{III} centers.



Angew. Chem. **2001**, *113*, 1567–1569

D. Grohol, D. Papoutsakis, D. G. Nocera* 1519–1521

$NaV_3(OH)_6(SO_4)_2$: A Kagomé-Type Vanadium(III) Compound with Strong Intralayer Ferromagnetic Interactions

Keywords: ferromagnetism · hydrothermal synthesis · jarosite · magnetic properties · vanadium

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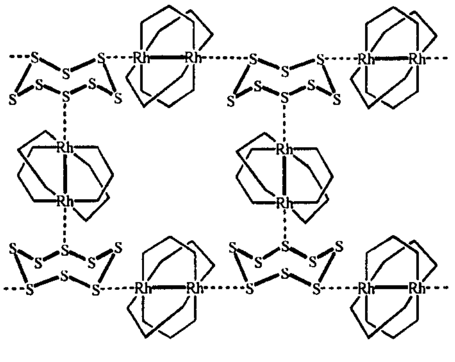
Coordination of neutral S_8 molecules by transition metal centers has been structurally confirmed for the first time. The monoadduct $[Rh_2(O_2CCF_3)_4](S_8)$ is a one-dimensional polymer with an alternating chain of dirhodium(II) tetra(trifluoroacetate) and bidentate S_8 rings, whereas $[Rh_2(O_2CCF_3)_4]_3(S_8)_2$ is a pseudo-two-dimensional ribbon in which all cyclo-S_8 ligands act in a tridentate fashion (see picture).



Angew. Chem. **2001**, *113*, 1569–1571

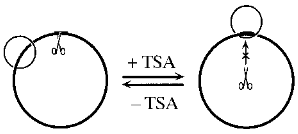
F. A. Cotton,* E. V. Dikarev, M. A. Petrukhina 1521–1523

Neutral Cyclooctasulfur as a Polydentate Ligand: Supramolecular Structures of $[Rh_2(O_2CCF_3)_4]_n(S_8)_m$ (n:m = 1:1, 3:2)

Keywords: carboxylato ligands · rhodium · S ligands · structure elucidation · supramolecular chemistry

Catenation of a circular oligonucleotide to a supercoiled plasmid can be achieved in high yields by means of ligand-induced triple-helix formation. The noncovalent interactions in this supramolecular structure can be modulated by a triplex-stabilizing agent (TSA; see picture). The circular oligonucleotide represents a noncovalent anchor for plasmid functionalization.

Angew. Chem. **2001**, *113*, 1571–1574



T. Roulon, C. Hélène,
C. Escudé* 1523–1526

A Ligand-Modulated Padlock Oligonucleotide for Supercoiled Plasmids

Keywords: catenanes · DNA structures · helical structures · oligonucleotides · supramolecular chemistry

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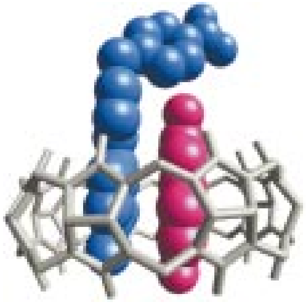
Two different molecules are selectively included in cucurbit[8]uril to form a stable 1:1:1 ternary complex, which has been characterized by X-ray crystallography (see picture). The inclusion of a hetero-guest pair (a pyridinium derivative (blue) and 2,6-dihydroxynaphthalene (magenta)) in the molecular host is driven and stabilized by a charge-transfer interaction between the electron-rich and electron-deficient guests.

Angew. Chem. **2001**, *113*, 1574–1577



H.-J. Kim, J. Heo, W. S. Jeon, E. Lee,
J. Kim, S. Sakamoto, K. Yamaguchi,
K. Kim* 1526–1529

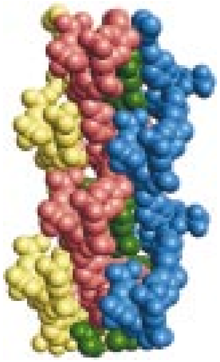
Selective Inclusion of a Hetero-Guest Pair in a Molecular Host: Formation of Stable Charge-Transfer Complexes in Cucurbit[8]uril

Keywords: charge transfer · host–guest chemistry · inclusion compounds · structure elucidation · supramolecular chemistry

---

Coordination-driven assembly based on manganese(II) centers and flexible 1,3-bis(4-pyridyl)propane leads to the solid-state formation of electronically neutral, self-templated homochiral helices (see picture), closed ring structures, and racemic mixtures of helices depending upon the presence or absence of guests such as benzene and 1,2-diphenylethane.

Angew. Chem. **2001**, *113*, 1577–1580



F. M. Tabellion, S. R. Seidel, A. M. Arif,
P. J. Stang* 1529–1532

Template and Guest Effects on the Self-Assembly of a Neutral and Homochiral Helix

Keywords: crystal engineering · helical structures · host–guest chemistry · manganese · supramolecular chemistry

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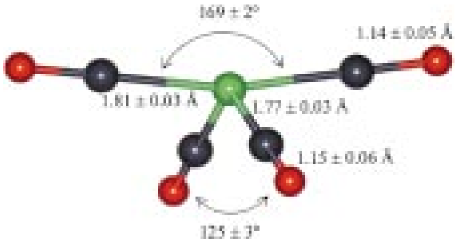
The temporal diffraction–difference approach of the ultrafast electron diffraction (UED) technique was used to determine the molecular structure of the transient [Fe(CO)$_4$] (see picture) formed during the elimination of CO ligands from [Fe(CO)$_5$]. The results clearly show that the major product, up to 200 ps, is the transient [Fe(CO)$_4$] which is formed in the $^1A_1$ state, rather than the ground $^3B_2$ state.

Angew. Chem. **2001**, *113*, 1580–1584



H. Ihee, J. Cao,
A. H. Zewail* 1532–1536

Ultrafast Electron Diffraction of Transient [Fe(CO)$_4$]: Determination of Molecular Structure and Reaction Pathway

Keywords: carbonyl ligands · electron diffraction · iron · laser spectroscopy · intermediates

Twist and shout! By restricting conformation, 2,6-biarylpyridines can be induced to “speak” to us through increased fluorescence emission. In combination with induced charge transfer, this allows these simple fluorophores to reveal otherwise silent binding events to alkali metal and alkaline earth cations through brightening and color change (see picture; from left to right: no metal, Li^+, Mg^{2+}, and Ca^{2+}).

Angew. Chem. **2001**, *113*, 1584 – 1586

J. V. Mello, N. S. Finney* .... 1536 – 1538

Dual-Signaling Fluorescent Chemosensors Based on Conformational Restriction and Induced Charge Transfer

Keywords: coordination chemistry · fluorescence spectroscopy · molecular recognition · sensors

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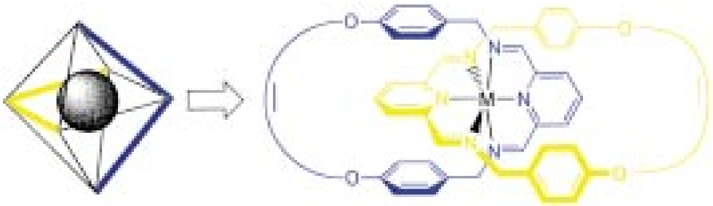
The shape of rings to come: The first members of a new family of simple-to-prepare octahedral analogues of the tetrahedral Sauvage catenates are described (see scheme). M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}.



Angew. Chem. **2001**, *113*, 1586 – 1591

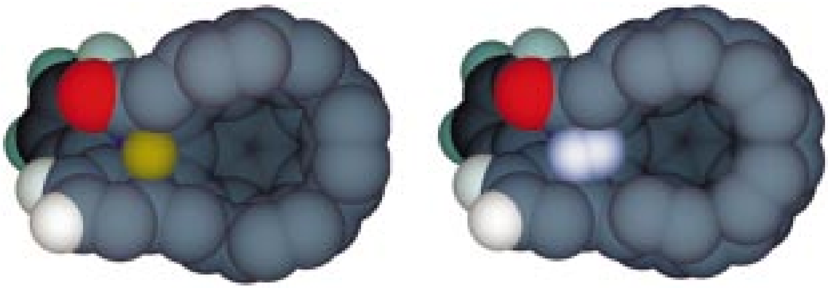
D. A. Leigh,* P. J. Lusby, S. J. Teat, A. J. Wilson, J. K. Y. Wong . 1538 – 1543

Benzylic Imine Catenates: Readily Accessible Octahedral Analogues of the Sauvage Catenates

Keywords: catenanes · catenates · coordination modes · self-assembly · template synthesis

---

A “molecular surgery” approach has been used to create an opening within a fullerene cage that is large enough to allow atoms and small molecules to pass through. The thermodynamics for the insertion of He and H_2 into the open fullerene (left and right pictures, respectively) as well as their escape have been studied by NMR spectroscopy and theoretical methods.



Angew. Chem. **2001**, *113*, 1591 – 1594

Y. Rubin,* T. Jarrosson, M. D. Bartberger, K. N. Houk,* G. Schick, M. Saunders,* R. J. Cross* .... 1543 – 1546

Insertion of Helium and Molecular Hydrogen Through the Orifice of an Open Fullerene

Keywords: density functional calculations · fullerenes · helium · host – guest chemistry · hydrogen

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

* Author to whom correspondence should be addressed

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