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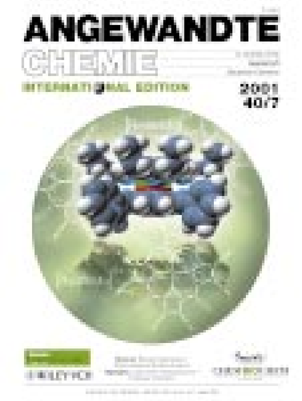
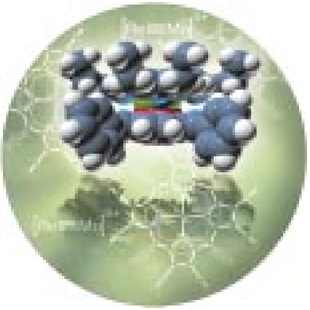


ChemBioChem* 4/2001 is bound in this issue of *Angewandte Chemie.

COVER PICTURE

The cover picture shows the metalloporphyrin heterodimer $[(\mathrm{tpp})\mathrm{Mo}\overset{4}{-}\mathrm{Re}(\mathrm{oep})]^+$ with the novel $[\mathrm{Mo}\overset{4}{-}\mathrm{Re}]^{5+}$ core. The core represents the first example of a quadruple bond between elements of different triads, thus proving that heterometallic quadruple bonds are not limited to the Group 6 metals. From the space-filling model it is clear that there is no interaction between the stabilizing porphyrin ligands. The ORTEP plot in a projection along the Re–Mo axis emphasizes the perfectly eclipsed geometry of the porphyrins, which is unambiguous proof of the existence of the quadruple bond in the solid state. The diamagnetism and large magnetic anisotropy of the cation, as determined by ^{1}H NMR spectroscopy, indicate that the quadruple bond is retained in solution. A logical and well-defined synthetic route was used to synthesize the dimer, and can be extended to other metalloporphyrins to generate further novel quadruple bonds (the picture was generated by Marina Boulan, St. Petersburg, Russia), full details are reported by J. P. Collman et al. on p. 1271 ff.



An atomistic view of electrochemistry? Modern surface-science techniques applied to single-crystal electrodes with structurally well-defined surfaces allow electrochemists to study the metal/electrolyte interface and simple electrochemical reactions at a level of sophistication unheard of some twenty years ago.

Angew. Chem. **2001**, *113*, 1198 – 1220

D. M. Kolb* .... 1162 – 1181

Electrochemical Surface Science

Keywords: electrochemistry · scanning tunneling microscopy · surface analysis · surface structure

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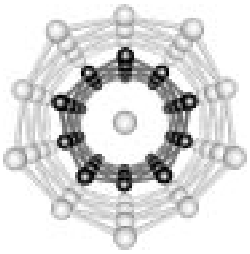
Variety and individuality are characteristics of the crystal structures of the subhalides that can be obtained through the partial oxidation of the intermetallic phases of bismuth and an electron-rich transition metal. The spatial extent of the intermetallic structural region is mainly determined by the degree of oxidation. This results in "porous" and low-dimensional metals (see picture) as well as ionic and molecular cluster compounds.



Angew. Chem. **2001**, *113*, 1222 – 1234

M. Ruck* .... 1182 – 1193

From the Metal to the Molecule—Ternary Bismuth Subhalides

Keywords: bismuth · cluster compounds · intermetallic phases · low-dimensional metals · subvalent compounds

VIPs

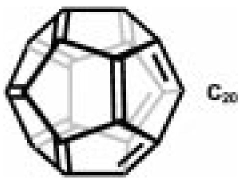
The following communications are "Very Important Papers" in the opinion of two referees. They will be published shortly (those marked with a diamond will be published in the next issue). Short summaries of these articles can be found on the *Angewandte Chemie* homepage at the address http://www.angewandte.com

The 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	G. Y. Li*	◆
Modular Pyridinyl Peptide Ligands in Asymmetric Catalysis: Enantioselective Synthesis of Quaternary Carbon Atoms Through Cu-Catalyzed Allylic Substitutions	C. A. Luchaco-Cullis, H. Mizutani, K. E. Murphy, A. H. Hoveyda*	◆
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	
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*	
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*	

1433-7851/01/4007-1146 $ 17.50+.50/0

HIGHLIGHTS

Minifullerenes, bizarre cages, and highly reactive guests are currently causing a stir in fullerene chemistry. An example is C_{20}, recently generated in the gas phase, which constitutes the smallest conceivable classical fullerene.



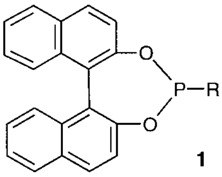
Angew. Chem. **2001**, *113*, 1235–1237

A. Hirsch* 1195–1197

New Cages and Unusual Guests: Fullerene Chemistry Continues To Excite

Keywords: aromaticity • cage compounds • fullerenes

Much better than their reputation are the rhodium(I) complexes of monophosphorus ligands, which were believed to be unsuitable for use in highly enantioselective hydrogenation reactions and have lain dormant and forgotten for 30 years. Now values of >99% *ee* have been reached in the hydrogenation of standard substrates when the ligand used is the binaphthol derivative **1**. As the synthesis of the monodentate ligands is often simpler than that of the more common diphosphorus ligands, a new and promising area of application has been opened up.



1

Angew. Chem. **2001**, *113*, 1237–1240

I. V. Komarov, A. Börner* .. 1197–1200

Highly Enantioselective or Not?—Chiral Monodentate Monophosphorus Ligands in the Asymmetric Hydrogenation

Keywords: asymmetric catalysis • chelate complexes • hydrogenation • P ligands • phosphanes

CORRESPONDENCE

"[To bring] … the essence of the world … [in each possible relation and from each point of view] to the clear and abstract perception of reason". This is, according to Arthur Schopenhauer, the assignment of philosophy, and in Wallau's interpretation, exactly this is accomplished by the logic of science established by Karl Popper for the field of empirical science. Therefore, its rejection by Jerome Berson in his essay "Kekulé Escapes, Popper Notwithstanding" is unfounded. This is a claim that Berson refutes in his reply.

Angew. Chem. **2001**, *113*, 1241–1243

Angew. Chem. **2001**, *113*, 1244–1245

W. M. Wallau* 1201–1203

Kekulé Escapes, Popper As Well

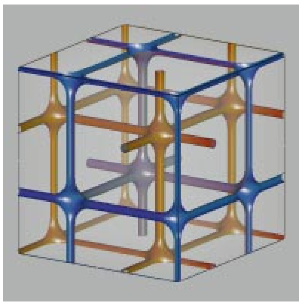
J. A. Berson* 1204–1205

Reply

Keywords: correspondence • falsification criterion • Kekulé, August • philosophy of science • Popper, Karl

COMMUNICATIONS

Two distinct channel systems are present in a polymer–inorganic nanocomposite, the structure of which is based on a bicontinuous plumber's nightmare (a regular array of completely interconnected tubes; see picture). Calcination at high temperatures leads to a metal oxide containing mesoporous silica-type material with promise for application in separation technology and catalysis.



Angew. Chem. **2001**, *113*, 1248–1251

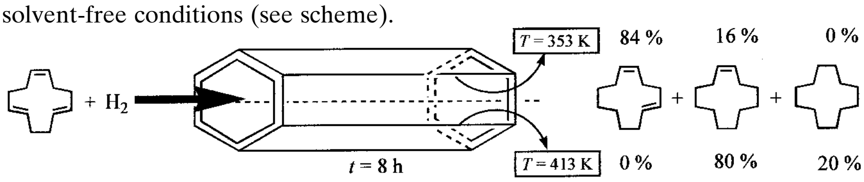
A. C. Finnefrock, R. Ulrich,
A. Du Chesne, C. C. Honeker,
K. Schumacher, K. K. Unger,
S. M. Gruner, U. Wiesner* .. 1208–1211

Metal Oxide Containing Mesoporous Silica with Bicontinuous "Plumber's Nightmare" Morphology from a Block Copolymer–Hybrid Mesophase

Keywords: block copolymers • mesophases • mesoporous materials • nanostructures • organic–inorganic hybrid composites

1433-7851/01/4007-1147 $ 17.50+.50/0

The point of attachment of bimetallic Ru_6Sn particles which are anchored to the pore walls of a highly dispersed high-area mesoporous silica is found to be the tin atom, as indicated by in situ and ex situ measurements. This catalyst displays high activity for the low-temperature, selective hydrogenation of cyclic polyenes under solvent-free conditions (see scheme).



Angew. Chem. **2001**, *113*, 1251 – 1255

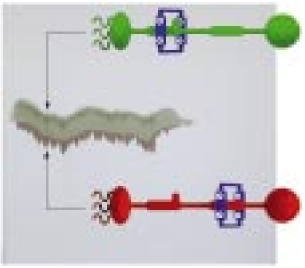
S. Hermans, R. Raja, J. M. Thomas,*
B. F. G. Johnson,* G. Sankar,
D. Gleeson .... 1211 – 1215

Solvent-Free, Low-Temperature, Selective Hydrogenation of Polyenes using a Bimetallic Nanoparticle Ru – Sn Catalyst

Keywords: cycloalkenes · hydrogenation · mesoporous materials · ruthenium · supported catalysts

---

Separation of the two translational isomers by preparative thin-layer chromatography (see picture) and a kinetic study of their interconversion are possible when a central barrier is inserted between two stations on the rod section in the dumbbell component of a [2]rotaxane. This switchable [2]rotaxane incorporates a monopyrrolotetrathiafulvalene unit and a 1,5-dioxynaphthalene ring system within its rod section and the tetracationic cyclobis(paraquat-*p*-phenylene) as its ring component.



Angew. Chem. **2001**, *113*, 1256 – 1261

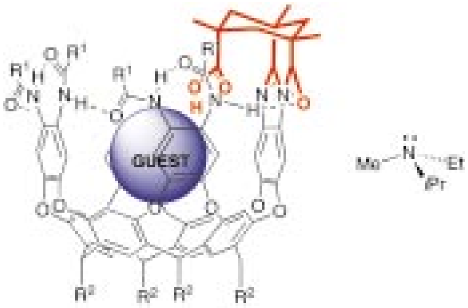
J. O. Jeppesen, J. Perkins, J. Becher,*
J. F. Stoddart* .... 1216 – 1221

Slow Shuttling in an Amphiphilic Bistable [2]Rotaxane Incorporating a Tetrathiafulvalene Unit

Keywords: isomerization · rotaxanes · self-assembly · supramolecular chemistry · tetrathiafulvalene

---

An introverted carboxy functionality of the cavitand shown, significantly alters the dynamics of nitrogen inversion of guest molecules, as well as the hydrogen bonding and guest tumbling in the inner recess. For example, NMR experiments indicate that N-inversion of ethylmethylisopropylamine is several orders of magnitude slower in the cavitand than the rate observed in solution.



Angew. Chem. **2001**, *113*, 1261 – 1262

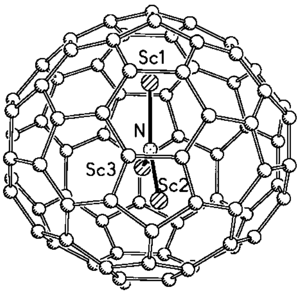
P. L. Wash, A. R. Renslo,
J. Rebek, Jr.* .... 1221 – 1222

Isolation of an Acid/Base Complex in Solution Puts the Brakes on Nitrogen Inversion

Keywords: amines · cavitands · host – guest systems · kinetics · nitrogen inversion

---

The unfavorable D_{3h} isomer of the C_{78} fullerene cage is present in $Sc_3N@C_{78}$, an endohedral fullerene which has been prepared by the trimetallic nitride template process. The crystal structure of the fullerene – porphyrin adduct $Sc_3N@C_{78} \cdot [Co(oep)] \cdot 1.5\,C_6H_6 \cdot 0.3\,CHCl_3$ (oep = octaethylporphyrin) shows that the scandium atoms are located over the centers of the [6,6] ring junctions of pyracylene patches on the inner surface of the fullerene (see picture).



Angew. Chem. **2001**, *113*, 1263 – 1265

M. M. Olmstead, A. de Bettencourt-Dias,
J. C. Duchamp, S. Stevenson, D. Marciu,
H. C. Dorn,* A. L. Balch* .. 1223 – 1225

Isolation and Structural Characterization of the Endohedral Fullerene $Sc_3N@C_{78}$

Keywords: fullerenes · nitrides · scandium · structure elucidation

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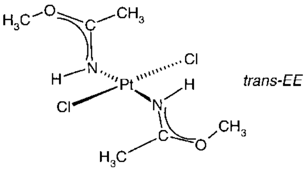
1,2-Intrastrand chelation is not unique for cisplatin adducts of nucleic acids, but is also possible for Pt complexes having a *trans* geometry. This possibility is demonstrated by the formation of an unprecedented cross-link of a *trans*-Pt-iminoether complex (*trans-EE*, see picture) with the A(N3) and G(N7) positions of the ribonucleotide r(ApG).



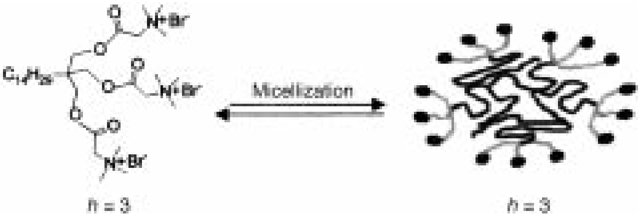
Angew. Chem. **2001**, *113*, 1266 – 1268

Y. Liu, C. Pacifico, G. Natile,
E. Sletten* .... 1226 – 1228

Antitumor *trans* Platinum Complexes can Form Cross-Links with Adjacent Purine Groups

Keywords: antitumor agents · bioinorganic chemistry · coordination chemistry · NMR spectroscopy · nucleotides

Folding of hydrocarbon chains and reduction in micelle size are observed as the number of headgroups (*h*) on the new single-chain cationic surfactants increases from (*h* = 1) to bident (*h* = 2) or trident (*h* = 3, see picture). The aggregation number is dramatically decreased and the fractional charge on the micelle increases with the increase in the charge at the headgroup.



Angew. Chem. **2001**, *113*, 1278–1282

J. Haldar, V. K. Aswal, P. S. Goyal,
S. Bhattacharya* 1228–1232

Molecular Modulation of Surfactant Aggregation in Water: Effect of the Incorporation of Multiple Headgroups on Micellar Properties

Keywords: chain structures · micelles · small-angle neutron scattering · surfactants · viscoelasticity

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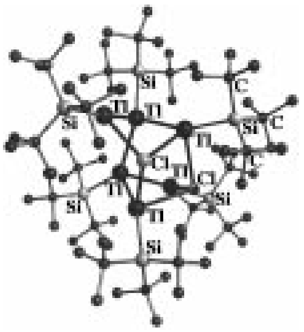
The largest Tl clusters to date with covalently linked Tl atoms are contained in the title compounds obtained from $TlCl_3$ and two molar equivalents of $NaSi\mathit{t}Bu_3$ in THF at −78°C. The structure of $(Si\mathit{t}Bu_3)_6Tl_6Cl_2$, which contains two Tl_3Cl four-membered rings linked through the central Tl atoms and the Cl atoms, is depicted.



Angew. Chem. **2001**, *113*, 1275–1278

N. Wiberg,* T. Blank, H.-W. Lerner,
D. Fenske, G. Linti 1232–1235

$R^*_4Tl_3Cl$ and $R^*_6Tl_6Cl_2$ ($R^* = Si\mathit{t}Bu_3$)—The First Compounds with Larger Clusters Containing Covalently Linked Thallium Atoms

Keywords: cluster compounds · silicon · structure elucidation · thallium

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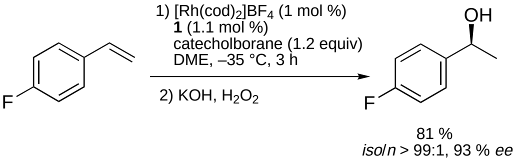
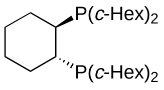
A double [2,3] sigmatropic rearrangement enables the fast synthesis of novel C_2-symmetrical 1,2-diphosphanes in good yields. These phosphanes (for example, **1**; *c*-Hex = cyclohexyl) are highly efficient ligands for the rhodium-catalyzed asymmetric hydroboration of a wide variety of styrenes (see scheme). cod = 1,5-cyclooctadiene; DME = 1,2-dimethoxyethane.





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Angew. Chem. **2001**, *113*, 1272–1275

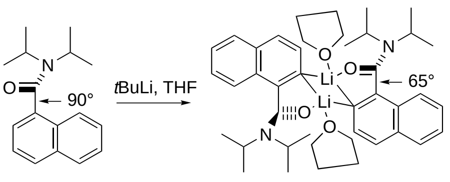
S. Demay, F. Volant,
P. Knochel* 1235–1238

New C_2-Symmetrical 1,2-Diphosphanes for the Efficient Rhodium-Catalyzed Asymmetric Hydroboration of Styrene Derivatives

Keywords: asymmetric catalysis · hydroboration · P ligands · phosphanes · rearrangement · rhodium

---

Despite the near-perpendicular arrangement of the amide group and aromatic ring in many tertiary aromatic amides, *ortho*-lithiation is still a very straightforward process. The first X-ray crystal structures of *ortho*-lithiated amides reveal why: the angle of twist is lessened to some degree, and the lithium ion lies far from the plane of the aromatic ring, with stabilization of the strained structure being achieved by dimerization (see scheme).



Angew. Chem. **2001**, *113*, 1282–1285

J. Clayden,* R. P. Davies,
M. A. Hendy, R. Snaith†,
A. E. H. Wheatley* 1238–1240

The First Crystallographic Evidence for the Structures of *ortho*-Lithiated Aromatic Tertiary Amides

Keywords: amides · lithiation · *ortho*-metalation · solid-state structures

Atoms, bonds, clusters: The reaction of a metastable GaBr solution with trisyllithium (LiC($SiMe_3$)$_3$) led to a novel cluster unit: two tetrahedral Ga_4R_3 units are linked through a Ga–Ga bond to give the Ga_8R_6 cluster (R = C($SiMe_3$)$_3$; see picture; Ga: dark blue, C: light blue, $SiMe_3$: not shown), which contains the prototype of a localized metal–metal bond.

Angew. Chem. **2001**, *113*, 1287–1290

A. Schnepf, R. Köppe,
H. Schnöckel* 1241–1243

A Ga_8R_6 Cluster as an Ideal Model for a Metal–Metal Bond?

Keywords: ab initio calculations • cluster compounds • gallium • metal–metal interactions

A “cracking” good performance: Cycloalkanes, which are easily accessible from the surplus aromatic products of petrochemistry, can be converted under hydrogen into a steamcracker feed consisting mainly of *n*-alkanes. The highest yields are obtained on zeolite H-ZSM-5 with tiny amounts of noble metals—a catalyst with a new type of cracking performance.

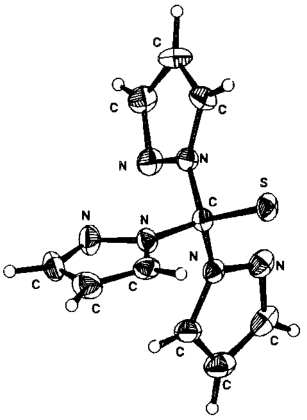
Angew. Chem. **2001**, *113*, 1268–1272

A. Raichle, Y. Traa, F. Fuder, M. Rupp,
J. Weitkamp* 1243–1246

Haag–Dessau Catalysts for Ring Opening of Cycloalkanes

Keywords: cycloalkanes • Haag–Dessau catalysts • heterogeneous catalysis • petrochemistry • zeolites

Trifluoromethylthiolate $[CF_3S]^-$, which contains activated C–F bonds, can act not only as a nucleophile but also can undergo nucleophilic substitution by Me_3Si-Az (Az = pyrazolyl, 1,2,4-triazolyl, imidazolyl) leading to the corresponding tris(azolyl)methylthiolates $[(Az)_3CS]^-$ (the structure of the anion with Az = pyrazoyl is shown), a potential new class of scorpionates. Tetrapyrrolemethane was isolated from the reaction with trimethylsilylpyrrole.



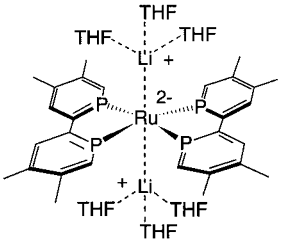
Angew. Chem. **2001**, *113*, 1285–1287

M. Müller, E. Lork,
R. Mews* 1247–1249

Tris(azolyl)methylthiolates: Another New Scorpionate Class?

Keywords: C–F activation • N ligands • S nucleophiles • scorpionates • thiolates

Two partially reduced ligands and a d^8-configured Ru^0 center are shown by extended Hückel calculations to be present in a ruthenium complex containing a dianionic Ru(2–) center stabilized by the 2,2′-biphosphinine ligand. The ruthenium complex shown (and its iron analogue) adopts a square-planar geometry which is quite unusual for a ML_4 complex having a formal d^{10} electronic configuration.



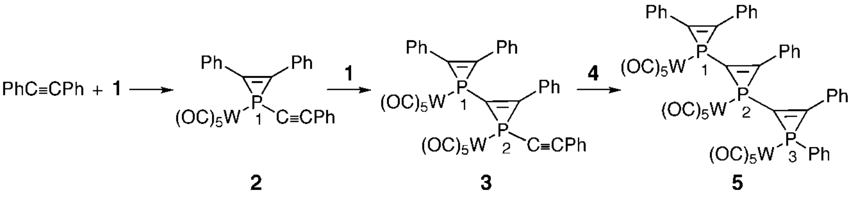
Angew. Chem. **2001**, *113*, 1291–1293

P. Rosa, N. Mézailles, L. Ricard,
F. Mathey, P. Le Floch,*
Y. Jean 1251–1253

Dianionic Iron and Ruthenium(2–) Biphosphinine Complexes: A Formal d^{10} Ruthenium Complex with a Square Planar Geometry

Keywords: electronic structure • iron • P ligands • phosphinines • ruthenium

No end in sight: the mono-, bi-, and triphosphirenes **2**, **3**, and **5**, respectively, are prepared by a simple iterative method (see scheme; **1** = [Ph≡CPW(CO)$_5$], **4** = [PhPW(CO)$_5$]); these oligomers offer numerous possibilities in coordination chemistry and catalysis. They can serve to create numerous other classes of polyphosphine chains by ring opening or ring expansion of the phosphirene units.



Angew. Chem. **2001**, *113*, 1293–1295

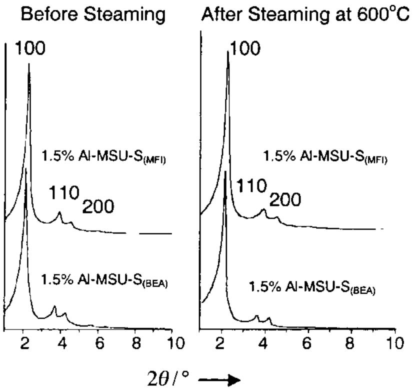
N. H. Tran Huy,* L. Ricard,
F. Mathey* 1253–1255

Stepwise Building of Polyphosphirene Chains

Keywords: oligomers • P ligands • phosphirenes • small ring systems • tungsten

Protozeolitic nanoclusters or "zeolite seeds" templated by quaternary ammonium ions are shown to be effective precursors for the assembly of an improved class of aluminosilicate mesostructures, denoted MSU-S, which retain well-expressed hexagonal X-ray diffraction patterns and open mesopores even after exposure to steam at 600°C (see picture).

Angew. Chem. **2001**, *113*, 1295–1298



Y. Liu, W. Zhang,
T. J. Pinnavaia* 1255–1258

Steam-Stable MSU-S Aluminosilicate Mesostructures Assembled from Zeolite ZSM-5 and Zeolite Beta Seeds

Keywords: aluminosilicates · heterogeneous catalysis · mesophases · supramolecular chemistry · zeolites

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Self-assembly of preformed aluminosilicate nanoclusters in the presence of templating micella provides a route to strongly acidic, hydrothermally stable mesoporous aluminosilicates with ordered hexagonal structures (MAS-5). Results show that the materials are similar to Beta zeolite and are highly active for the catalytic cracking of 1,3,5-triisopropylbenzene.

Angew. Chem. **2001**, *113*, 1298–1302

Z. Zhang, Y. Han, L. Zhu, R. Wang,
Y. Yu, S. Qiu,* D. Zhao,
F.-S. Xiao* 1258–1262

Strongly Acidic and High-Temperature Hydrothermally Stable Mesoporous Aluminosilicates with Ordered Hexagonal Structure

Keywords: aluminosilicates · heterogeneous catalysis · mesophases · zeolites

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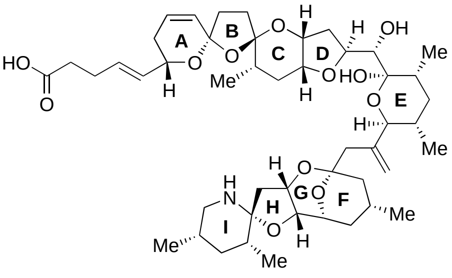
As a causative agent of food poisonings, azaspiracid (1), a novel marine toxin isolated from the mussel *Mytilus edulis*, challenges the synthetic chemist with an intricate array of acetal and ketal structures. The construction of the FGHI ring system of azaspiracid was achieved by means of a key $BF_3 \cdot Et_2O$-catalyzed cyclization to form the HI spirocycle. A final chemoselective intramolecular ketalization with $Hg(OAc)_2$ formed the G ring, to afford the N-protected FGHI as a single diastereomer.

Angew. Chem. **2001**, *113*, 1302–1305



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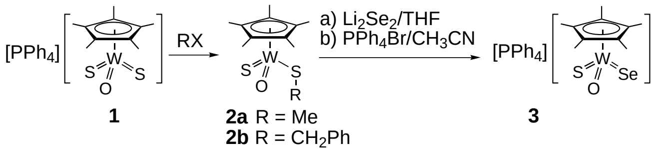
K. C. Nicolaou,* P. M. Pihko,
N. Diedrichs, N. Zou,
F. Bernal 1262–1265

Synthesis of the FGHI Ring System of Azaspiracid

Keywords: cyclization · natural products · spiro compounds · synthesis design

---

Oxygen, sulfur, and selenium all coordinate to the same tungsten atom in the mixed-chalcogenido complex $[PPh_4][Cp^*W(O)(S)(Se)]$ (**3**; $Cp^* = C_5Me_5$), which has been prepared by the reaction of $[Cp^*W(O)(S)(SR)]$ (R = Me (**2a**), CH_2Ph (**2b**)) with Li_2Se_2 followed by cation exchange (see scheme). This unique mixed-chalcogenide complex is thermodynamically stable, and does not exhibit chalcogen-exchange reactions in solution.



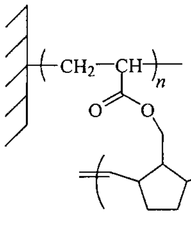
Angew. Chem. **2001**, *113*, 1306–1308

H. Kawaguchi, K. Tatsumi* 1266–1268

Synthesis of a Cp* Complex of Tungsten with Three Different Chalcogenido (O^{2-}, S^{2-}, and Se^{2-}) Ligands

Keywords: chalcogens · chiral complexes · selenium · sulfur · tungsten

1433-7851/01/4007-1151 $ 17.50+.50/0



Controlling the adhesion: a poly(norbornenylmethylene acrylate) coating was electrografted onto various conducting substrates, in a subsequent step, an initiator of ring-opening metathesis polymerization (ROMP) was attached to the norbornene pendant groups, and norbornene was polymerized, so forming a strongly adhering coating (see picture). This strategy which combines the "electrografting from" method and the more classical "grafting from" copolymerization is a novel powerful way to control adhesion, thickness, and the chemical properties of organic coatings.

Angew. Chem. **2001**, *113*, 1308–1311

C. Detrembleur, C. Jérôme, M. Claes, P. Louette, R. Jérôme* 1268–1271

Combination of Electrografting and Ring-Opening Metathesis Polymerization: An Efficient Way to Prepare Polynorbornene Brushes on Conducting Substrates

Keywords: coatings · electrochemistry · metathesis · polymer films · polymerization

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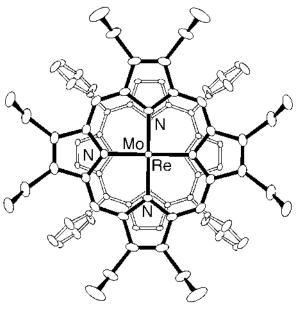
Heterometallic quadruple bonds are very rare and although known since 1974, have been restricted to the $\text{Cr}\overset{4}{-}\text{Mo}$ and the $\text{Mo}\overset{4}{-}\text{W}$ cores. Now the synthesis and structure of a quadruply bonded Mo-Re heterodimer, [(tetraphenylporphyrin)-$\text{Mo}\overset{4}{-}\text{Re}$(octaethylporphyrin)]PF$_6$, is reported (see picture). This complex proves that quadruple bonds can exist between elements from different triads.



Angew. Chem. **2001**, *113*, 1311–1314

J. P. Collman,* R. Boulatov, G. B. Jameson 1271–1274

The First Quadruple Bond Between Elements of Different Groups

Keywords: metalloporphyrins · metal–metal interactions · molybdenum · quadruple bonds · rhenium

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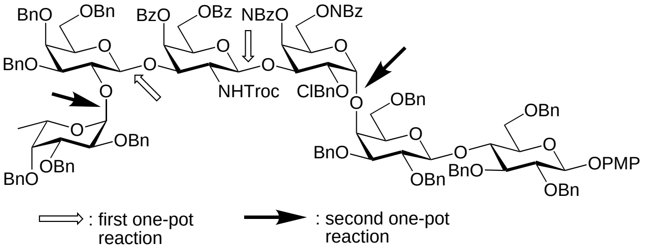
Designer saccharides: The cancer antigen Globo H hexasaccharide has been synthesized from designed building blocks in a rapid, stereoselective, and high-yielding manner by using the reactivity-based one-pot strategy (see scheme) guided by the OptiMer computer program. Bn = benzyl, Bz = benzoyl, ClBn = *ortho*-chlorobenzyl, NBz = *para*-nitrobenzoyl, NHTroc = 2,2,2-trichloroethylcarbamate, PMP = *para*-methoxyphenyl.



Angew. Chem. **2001**, *113*, 1314–1317

F. Burkhart, Z. Zhang, S. Wacowich-Sgarbi, C.-H. Wong* 1274–1277

Synthesis of the Globo H Hexasaccharide Using the Programmable Reactivity-Based One-Pot Strategy

Keywords: combinatorial chemistry · Globo H · oligosaccharides · one-pot synthesis · synthetic methods

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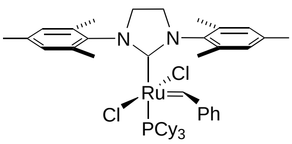
Electronic and steric properties of the substituents on the amide nitrogen atom govern the yield and rate of the cross-metathesis between a variety of α,β-unsaturated amides and olefins with **1** as the catalyst. This influence is the result of deactivation of the catalyst by chelation of the carbonyl group to the metal. However, an increase in catalyst loading compensates for the chelation effect.



1

Angew. Chem. **2001**, *113*, 1317–1319

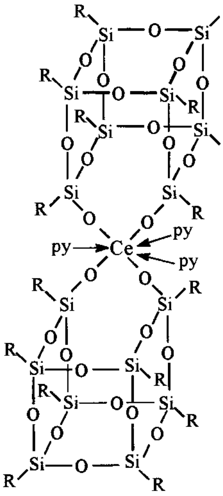
T.-L. Choi, A. K. Chatterjee, R. H. Grubbs* 1277–1279

Synthesis of α,β-Unsaturated Amides by Olefin Cross-Metathesis

Keywords: amides · chelates · cross-coupling · metathesis · ruthenium

1433-7851/01/4007-1152 $ 17.50+.50/0

The diamagnetic Ce^{IV} complex 1 is the main product of the reaction of the Ce^{III} compounds $[Ce\{N(SiMe_3)_2\}_3]$ or $CeCl_3$ with two equivalents of the polyhedral silsesquioxane $(c\text{-}C_6H_{11})_8Si_8O_{11}(OH)_2$ in the presence of pyridine (py). Compound **1** is a potential homogeneous analogue of silica-supported rare earth metal catalysts, and its novel synthesis may open routes to other metallasilsesquioxanes. R = cyclohexyl.



1

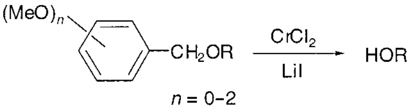
Angew. Chem. **2001**, *113*, 1319–1321

Y. K. Gun'ko,* R. Reilly,
F. T. Edelmann,*
H.-G. Schmidt 1279–1281

The First Ce^{IV} Metallasilsesquioxane Complex: $[Ce\{(c\text{-}C_6H_{11})_8Si_8O_{13}\}_2(py)_3]$

Keywords: catalysts · cerium · O ligands · silicon

$CrCl_2$/LiI selectively cleave benzyl ethers and methoxy-substituted benzyl ethers (see scheme) in the order: $C_6H_5CH_2OR < 4\text{-}MeOC_6H_4CH_2OR < 3,4\text{-}(MeO)_2C_6H_3CH_2OR < 2,6\text{-}(MeO)_2C_6H_3CH_2OR$. In contrast, $C_6H_5CH_2OR$ is more readily cleaved than $2,6\text{-}(MeO)_2C_6H_3CH_2OR$ during catalytic hydrogenolysis while $3,4\text{-}(MeO)_2C_6H_3CH_2OR$ is cleaved faster than $2,6\text{-}(MeO)_2C_6H_3CH_2OR$ with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ).



Angew. Chem. **2001**, *113*, 1321–1323

J. R. Falck,* D. K. Barma, R. Baati,
C. Mioskowski 1281–1283

Differential Cleavage of Arylmethyl Ethers: Reactivity of 2,6-Dimethoxybenzyl Ethers

Keywords: chemoselectivity · chromium · cleavage reactions · protecting groups · reductions

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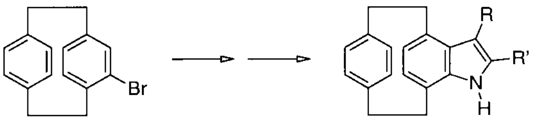
Fancy drug candidates: The first preparation of indoloparacyclophanes is reported through the use of the Buchwald variant of the Fischer indole synthesis (see scheme). Receptor binding studies clearly demonstrated that the double-layered molecular scaffold can serve as an effective arylbioisostere.



Angew. Chem. **2001**, *113*, 1323–1325

B. Ortner, R. Waibel,
P. Gmeiner* 1283–1285

Indoloparacyclophanes: Synthesis and Dopamine Receptor Binding of a Novel Arylbioisostere

Keywords: bioisosteres · cyclophanes · Fischer indolization · indoles · receptors

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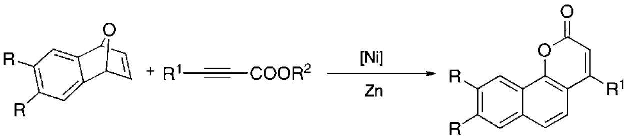
7-Oxabenzonorbornadienes bearing various substituents react with propiolates in the presence of $[NiBr_2(dppe)]$ (dppe = bis(diphenylphosphanyl)ethane) as a catalyst precursor and zinc powder to give benzocoumarin derivatives [Eq. (1)]. The one-pot reactions proceed at 80°C in acetonitrile, and the products are obtained in good yields with high regio- and stereoselectivity.



(1)

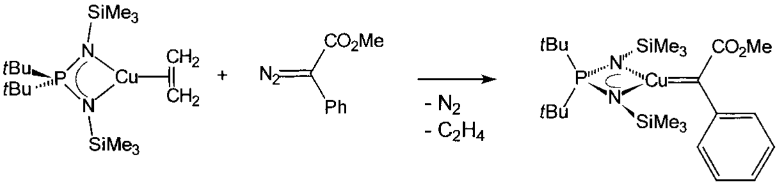
Angew. Chem. **2001**, *113*, 1326–1328

D. K. Rayabarapu, T. Sambaiah,
C.-H. Cheng* 1286–1288

Nickel-Catalyzed Highly Regio- and Stereoselective Cyclization of Oxanorbornenes with Alkyl Propiolates: A Novel Method for the Synthesis of Benzocoumarin Derivatives

Keywords: alkenes · coumarins · cyclization · nickel

A tailor-made copper ethylene complex was used to prepare solutions of highly reactive copper(I) carbene complexes of the d^{10}-ML$_3$ type which are active in olefin cyclopropanation and have been characterized unambigously in situ [Eq. (1)]. Electronic and structural features of this novel class of compounds were determined by NMR spectroscopy.



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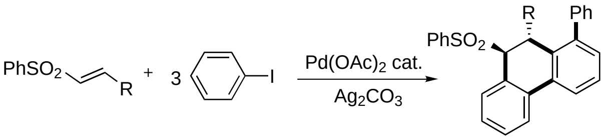
Angew. Chem. **2001**, *113*, 1328–1330

B. F. Straub, P. Hofmann* .. 1288–1290

Copper(I) Carbenes: The Synthesis of Active Intermediates in Copper-Catalyzed Cyclopropanation

Keywords: carbene complexes · copper · cyclopropanation · diazo compounds · N ligands

Four C–C bonds are formed in a single step by an intermolecular four-component cascade pathway. 1-Phenyl-9-phenylsulfonyl-9,10-dihydrophenanthrenes are formed in the palladium-catalyzed Heck-like reaction of α,β-unsaturated phenyl sulfones with three equivalents of iodobenzene in the presence of Ag$_2$CO$_3$ [Eq. (1)].



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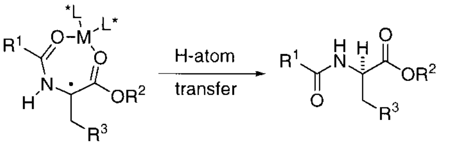
Angew. Chem. **2001**, *113*, 1331–1333

P. Mauleón, I. Alonso,
J. C. Carretero* 1291–1293

Unusual Palladium-Catalyzed Cascade Arylation of α,β-Unsaturated Phenyl Sulfones under Heck Reaction Conditions

Keywords: Heck reaction · metallacycles · palladium · phenanthrenes · sulfones

Glycine radicals derived from conjugate radical additions to dehydroalanines complexed to chiral Lewis acids (L*) undergo enantioselective H-atom transfer to furnish α-amino acids (see scheme). A variety of amino acids with *ee* values ranging from 27–85% can be prepared with good chemical efficiency.



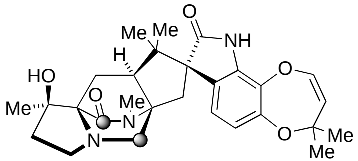
Angew. Chem. **2001**, *113*, 1333–1336

M. P. Sibi,* Y. Asano,
J. B. Sausker 1293–1296

Enantioselective Hydrogen Atom Transfer Reactions: Synthesis of *N*-Acyl-α-Amino Acid Esters

Keywords: amino acids · enantioselectivity · hydrogen transfer · Lewis acids · radical reactions

Looking for the right path: An advanced metabolite involved in the biosynthesis of paraherquamide A (**1**) has been synthesized in a doubly ^{13}C-labeled form and shown to be incorporated into the potent anthelminthic alkaloid **1** by *Penicillium fellutanum*. The results are discussed in terms of a unified biogenesis of the paraherquamides and VM55599.



1

● = ^{13}C

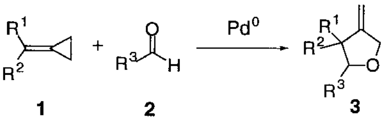
Angew. Chem. **2001**, *113*, 1336–1338

E. M. Stocking, J. F. Sanz-Cervera,
R. M. Williams* 1296–1298

Studies on the Biosynthesis of Paraherquamide: Synthesis and Incorporation of a Hexacyclic Indole Derivative as an Advanced Metabolite

Keywords: biosynthesis · Diels–Alder reaction · isotopic labeling · metabolites · natural products

Multiply substituted tetrahydrofuran rings can be prepared by the [3+2] cycloaddition of alkylidenecyclopropanes **1** with aldehydes **2** [Eq. (1)]. In this reaction, the distal bond of the cyclopropane ring is cleaved, and 3-methylenetetrahydrofuran derivatives **3** are produced in good yields.



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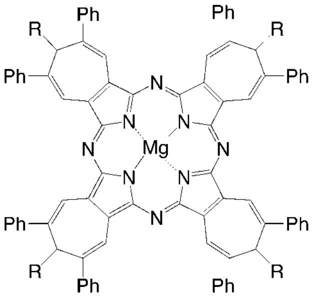
Angew. Chem. **2001**, *113*, 1338–1340

I. Nakamura, B. H. Oh, S. Saito,
Y. Yamamoto* 1298–1300

Novel [3+2] Cycloaddition of Alkylidenecyclopropanes with Aldehydes Catalyzed by Palladium

Keywords: aldehydes · cycloaddition · heterocycles · palladium · synthetic methods

Both the size and symmetry of the π-conjugated systems change during dehydrogenation/hydrogenation cycles of a phthalocyanine analogue fused with four cycloheptatriene rings (see picture, R = H or Ph).



Angew. Chem. **2001**, *113*, 1340–1343

N. Kobayashi,* T. Nonomura,
K. Nakai 1300–1303

A Seven-Membered Carbon-Ring-Fused Phthalocyanine Analogue in which the π System Changes during Dehydrogenation/Hydrogenation Cycles

Keywords: dehydrogenation · hydrogenation · phthalocyanines · redox chemistry

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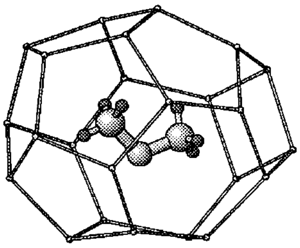
Filling space with a host of cages: completely hydrophobic interactions between organic molecules and water are present in the novel clathrate hydrate that has dimethyl ether guests in three different cages. One of these cages is the previously unreported tetrakaidecahedron ($4^1 5^{10} 6^3$) and is shown in the picture along with an ecapsulated dimethyl ether molecule.



Angew. Chem. **2001**, *113*, 1343–1345

K. A. Udachin, C. I. Ratcliffe,
J. A. Ripmeester* 1303–1305

A Dense and Efficient Clathrate Hydrate Structure with Unusual Cages

Keywords: clathrates · host–guest systems · hydrates · supramolecular chemistry · water

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A simple hydride-transfer mechanism to produce alkyl cations occurs when isolated protonated hydrogen peroxide ($HOOH_2^+$) attacks the C–H bonds of alkanes (except methane) [Eq. (1)]. The chemical properties of $HOOH_2^+$, which may serve as a model of the central catalytic motif of key biological systems, have been studied for the first time.

$$RH + HOOH_2^+ \longrightarrow R^+ + 2\,H_2O \qquad (1)$$

Angew. Chem. **2001**, *113*, 1345–1349

Å. M. Leere Øiestad, A. C. Petersen,
V. Bakken, J. Vedde,
E. Uggerud* 1305–1309

The Oxidative Power of Protonated Hydrogen Peroxide

Keywords: C–H activation · ion–molecule reactions · oxidation · peroxides · protonation

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

* Author to whom correspondence should be addressed

BOOKS

WEB SITES

CORRIGENDUM

In the description of the cover picture of Issue 4 on p. 637 it should say Mes* = 2,4,6-tBu$_3$C$_6$H$_2$ instead of Mes* = 2,4,6-tBu$_3$C$_6$H$_3$.

SERVICE

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