COVER PICTURE

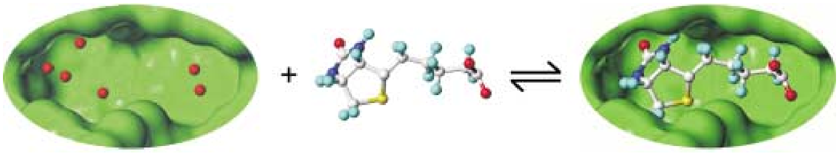
The cover picture shows the interior of a red-figure kylix (440–430 BC, British Museum London) which shows the brilliant exploits of Theseus, the Greek mythology hero. In the center, Theseus is shown defeating the infamous Minataur within the labyrinth. On the right, the hero raises his hand against Sciron, below whom the turtle is visible. Next clockwise, are shown the bull of Marathon, the punishment of Sinis, the slaying of the sow Phaea, the battle of Cercyon, and finally the punishment of Procrustes. The labors of Theseus are no different from the accomplishments of today's synthetic chemists working in total synthesis. One such endeavor, the total synthesis of the CP molecules with its challenges, twists and turns, and dead-ends, but also its rewards, is compared to the conquest of the Minotaur by Theseus in the Review by K. C. Nicolaou and P. S. Baran on p. 2678 ff.

REVIEWS

H. Gohlke, G. Klebe* 2644–2676

Approaches to the Description and Prediction of the Binding Affinity of Small-Molecule Ligands to Macromolecular Receptors

Biological activity at the molecular level involves the binding of a small-molecule ligand to a macromolecular receptor, usually a protein, in aqueous solution (see scheme). Enthalpic and entropic contributions arising from inter- and intramolecular effects determine the affinity of both binding partners towards each other. Affinity as a key element in life sciences—how well is this quantity understood today?



Angew. Chem. **2002**, *114*, 2764–2798

Keywords: binding affinity · calorimetry · drug research · protein–ligand interactions · scoring function

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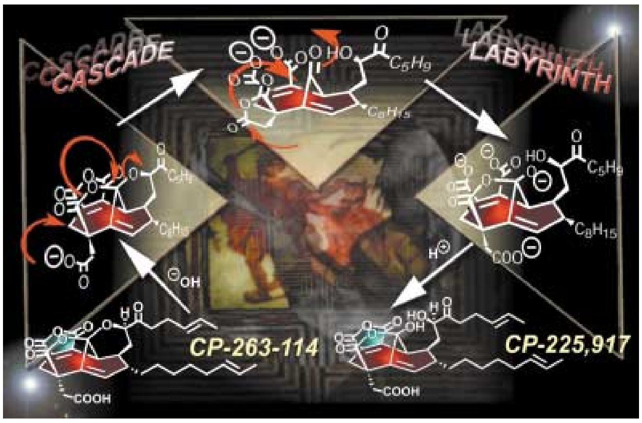
K. C. Nicolaou,* P. S. Baran 2678–2720

The CP Molecule Labyrinth: A Paradigm of How Endeavors in Total Synthesis Lead to Discoveries and Inventions in Organic Synthesis

Total synthesis programs directed toward complex molecules may take the form of unrelentless campaigns in which the synthetic chemist is faced with unprecedented challenges and unforeseen obstacles, but which often lead to invaluable fundamental knowledge and powerful new technologies. Here the authors describe one of the most arduous and rewarding endeavors in total synthesis of modern times—the synthesis of the CP molecules (see scheme)—and compare it to the Greek mythology's Labyrinth and the conquest of the Minotaur by Theseus.



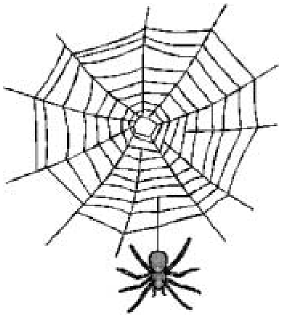
Angew. Chem. **2002**, *114*, 2800–2843

Keywords: CP molecules · natural products · organic synthesis · synthetic methods · total synthesis

HIGHLIGHTS

Transgenic goats to spin webs! The silk of spider nets (see picture) possesses unique mechanical properties. By using suitable microbiological methods, a structurally similar fiber protein has recently been prepared that, after spinning, exhibits comparable strength and elasticity to natural spider silk. The American firm Nexia Biotechnology plans to use transgenic goats to express this silk protein in their milk.

Angew. Chem. **2002**, *114*, 2845 – 2847



S. Kubik* .... 2721 – 2723

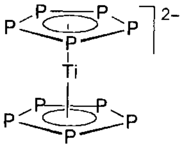
High-Performance Fibers from Spider Silk

Keywords: gene technology · mechanical properties · polymers · protein design · spider silk

---

The P_5 rings of the first inorganic metallocene, $[Ti(\eta^5\text{-}P_5)_2]^{2-}$ (see picture) are generated from white phosphorus in a selective reaction. The steric and electronic properties of these rings provide the remarkable stability of this unprecedented sandwich complex.

Angew. Chem. **2002**, *114*, 2847 – 2848



H. Sitzmann* .... 2723 – 2724

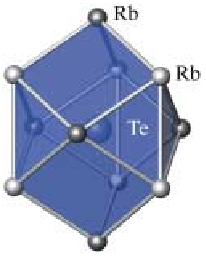
The Decaphosphatitanocene Dianion—A New Chapter in the Chemistry of Naked Polyphosphorus Ligands

Keywords: cyclopentadienyl ligands · metallocenes · phosphorus · P ligands · sandwich complexes · titanium

COMMUNICATIONS

At least four different polymorphic forms are possible for the previously uncharacterized compound Rb_2Te. One form is a metastable phase at room temperature and two are high-temperature phases; in one of the latter, the Te atoms are coordinated in the form of an Edshammar polyhedron (see picture). Rb_2Te is therefore unique within the di(alkali metal) monotellurides.

Angew. Chem. **2002**, *114*, 2849 – 2854



K. Stöwe,* S. Appel .... 2725 – 2730

Polymorphic Forms of Rubidium Telluride Rb_2Te

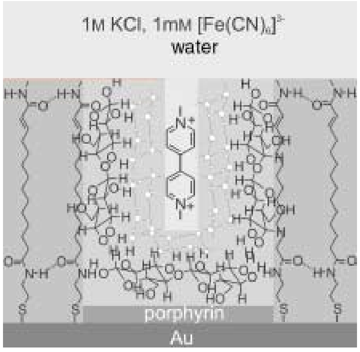
Keywords: polymorphism · rubidium · solid-state structures · structure elucidation · tellurium

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.org

Atom-Transfer Tandem Radical Cyclization Reactions Promoted by Lewis Acids	D. Yang, S. Gu, H.-W. Zhao, N.-Y. Zhu	◆
Metallabenzenes and Valence Isomers: Synthesis and Characterization of a Platinabenzene	V. Jacob, T. J. R. Weakley, M. M. Haley*	
Stereoselective Synthesis of β-D-Mannopyranosides with Reactive Mannopyranosyl Donors Possessing a Neighboring Electron-Withdrawing Group	R. R. Schmidt,* A. A.-H. Rahmann, S. Jonke E. S. H. El Ashry*	◆

In hydrophobic nanometer clefts in membranes, ridge molecules, such as cellobiose, can be anchored for months. They do not diffuse into the neighboring bulk water and electrolytes from the bulk water do not penetrate the immobilized layer. In the presence of dimethyl viologen, cycling of the Au electrode potential causes the viologen molecules to stir the anchored molecules out of the cleft and into the bulk water (see picture: the bulk water phase does not penetrate the hydrate layer but the viologen molecules can).



Angew. Chem. **2002**, *114*, 2855–2859

G. Li, K. Doblhofer,
J.-H. Fuhrhop* 2730–2734

Irreversible Adsorption of Cellobiose, Ascorbic Acid, and Tyrosine to Hydrophobic Surfaces in Water and Their Separation by Molecular Stirring

Keywords: cyclic voltammetry · membranes · nanostructures · self-assembly

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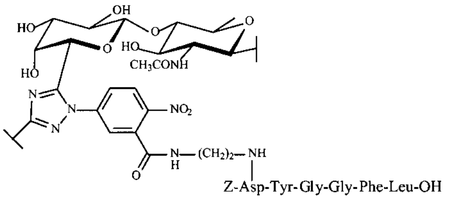
Carbohydrate coupling at any desired peptide carboxylate moiety is possible with a highly selective biocatalytic route for the synthesis of carbohydrate–peptide conjugates (see picture).



Angew. Chem. **2002**, *114*, 2859–2863

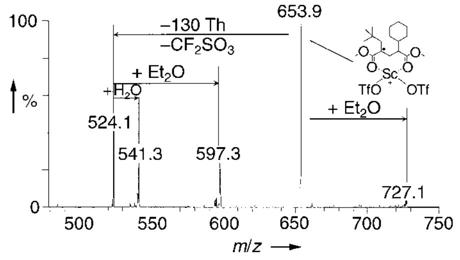
N. Wehofsky, R. Löser, A. Buchynskyy,
P. Welzel, F. Bordusa* 2735–2738

Synthesis of Neo-Peptidoglycans: An Unexpected Activity of Proteases

Keywords: chemoenzymatic synthesis · enzyme catalysis · glycopeptides · proteases · substrate mimetics

---

A useful tool for the investigation of synthetically important tributyltin-mediated radical chain reactions is electrospray ionization mass spectrometry (ESIMS). A microreaction system is coupled online to the ESI source. Transient radicals were detected unambiguously by using MS/MS methods (see picture).



Angew. Chem. **2002**, *114*, 2863–2866

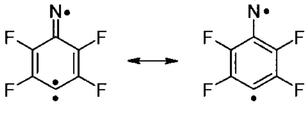
J. Griep-Raming, S. Meyer, T. Bruhn,
J. O. Metzger* 2738–2742

Investigation of Reactive Intermediates of Chemical Reactions in Solution by Electrospray Ionization Mass Spectrometry: Radical Chain Reactions

Keywords: carbocations · mass spectrometry · radicals · reactive intermediates · scandium

---

Elements of a carbene and a nitrene are linked by a common delocalized π electron in the molecule described here (see picture). The organic high-spin molecule with a quartet ground state could be photochemically generated and spectroscopically characterized in an argon matrix at 3 K.



Angew. Chem. **2002**, *114*, 2873–2876

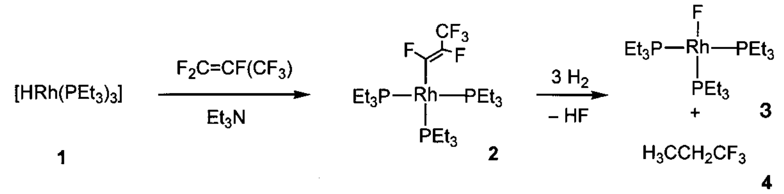
H. H. Wenk, W. Sander* 2742–2745

2,3,5,6-Tetrafluorophenylnitren-4-yl: A Quartet-Ground-State Nitrene Radical

Keywords: density functional calculations · high-spin molecules · matrix isolation · nitrenes · radicals

---

Rapid and regioselective C–F bond activation of hexafluoropropene occurs on reaction with **1**. Treatment of the resulting complex **2** with hydrogen yields the rhodium fluoro complex **3** and 1,1,1-trifluoropropane (**4**).



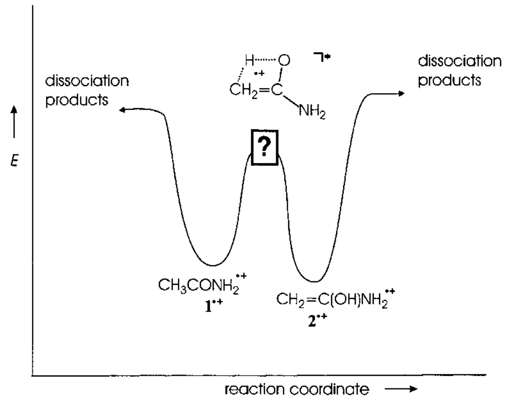
Angew. Chem. **2002**, *114*, 2870–2873

T. Braun,* D. Noveski, B. Neumann,
H.-G. Stammler 2745–2748

Conversion of Hexafluoropropene into 1,1,1-Trifluoropropane by Rhodium-Mediated C–F Activation

Keywords: alkenes · C-F activation · fluorinated ligands · fluorine · rhodium

By using a new "titration" technique, the activation barrier for the strictly unimolecular 1,3-hydrogen migration $\mathbf{1}^{\bullet+} \rightarrow \mathbf{2}^{\bullet+}$ has been determined (0.74 ± 0.06 eV; see reaction profile). With this technique the internal energy of $\mathbf{1}^{\bullet+}$ is controlled by variable photoionization of acetamide and the chemistry of the resulting enol ion $\mathbf{2}^{\bullet+}$ is then probed by structure-specific ion – molecule reactions.



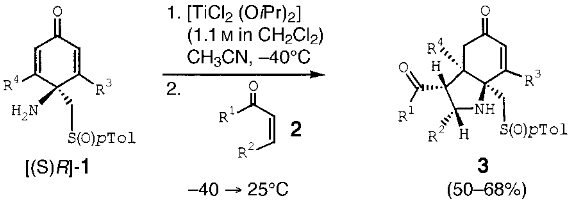
Angew. Chem. **2002**, *114*, 2867 – 2870

D. Schröder,* J. Loos, R. Thissen, O. Dutuit, P. Mourgues, H.-E. Audier, C. Lifshitz, H. Schwarz ...... 2748 – 2751

Barrier Height Titration by Tunable Photoionization Combined with Chemical Monitoring: Unimolecular Keto/Enol Tautomerization of the Acetamide Cation Radical

Keywords: electron transfer • hydrogen transfer • mass spectrometry • photoionization • tautomerism

New stereogenic centers are generated in the $[TiCl_2(O\mathit{i}Pr)_2]$-catalyzed reaction of [(S)*R*]-[(*p*-tolylsulfinyl)methyl]-*p*-quinamines **1** with *α*,*β*-unsaturated ketones **2** to give hydroindole-substituted systems **3** in a domino process. Up to four stereogenic centers are formed in the reaction of cycloalkenones and up to five when acyclic enones (2 equiv) are used.



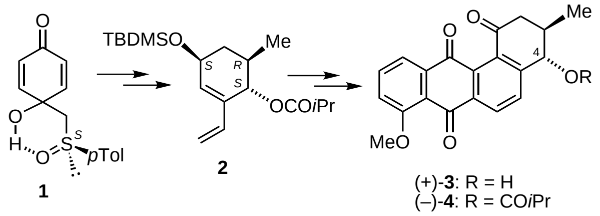
Angew. Chem. **2002**, *114*, 2877 – 2879

M. C. Carreño,* M. Ribagorda, G. H. Posner .... 2753 – 2755

Titanium-Promoted Stereoselective Synthesis of Hydroindolones from *p*-Quinamines by Domino Conjugate Additions

Keywords: Michael addition • nitrogen heterocycles • quinamines • sulfoxides • titanium

The tetracyclic skeleton of C4-oxygenated angucyclinone-type antibiotics rubiginones A_2 ((+)-**3**) and C_2 ((–)-**4**) is constructed by Diels – Alder reaction of a racemic sulfinyl-substituted methyl juglone and the enantiopure vinyl cyclohexene **2**, which is prepared in nine steps and in 26 % overall yield from sulfinyl-substituted *p*-quinol **1**. TBDMS = *tert*-butyldimethylsilyl.



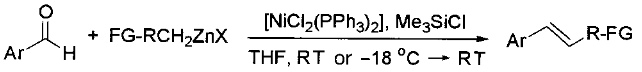
Angew. Chem. **2002**, *114*, 2879 – 2881

M. C. Carreño,* M. Ribagorda, Á. Somoza, A. Urbano* .... 2755 – 2757

Enantioselective Total Synthesis of Angucyclinone-Type Antibiotics Rubiginones A_2 and C_2

Keywords: antibiotics • asymmetric synthesis • cycloaddition • quinones • sulfoxides

Stereoselective alkenylated compounds are formed from the reaction of organozinc halides and aldehydes (see scheme; FG = functional group). Under mild conditions, and in the presence of a silylating agent, the Ni-catalyzed procedure gives *E*-alkenes and *E*-stilbenes in excellent yield.



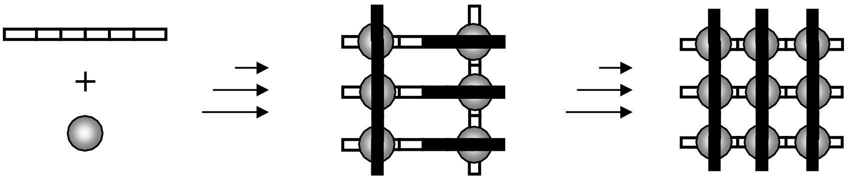
Angew. Chem. **2002**, *114*, 2881 – 2884

J.-X. Wang,* Y. Fu, Y. Hu ... 2757 – 2760

Carbon – Carbon Double-Bond Formation from the Reaction of Organozinc Reagents with Aldehydes Catalyzed by a Nickel(II) Complex

Keywords: aldehydes • alkenes • homogeneous catalysis • nickel • organozinc reagents

A [3 × 3] Ag^+_9 metallogrid self-assembles by a highly complex mechanism involving several intermediates, which may be generated at different metal/ligand stoichiometries. Extensive NMR spectroscopic studies have allowed the unraveling of the structure of these species and have revealed that the final grid entity presents high structural robustness and that the last assembly step (see scheme) occurs with strong cooperativity.



Angew. Chem. **2002**, *114*, 2884 – 2888

A. Marquis, J.-P. Kintzinger, R. Graff,
P. N. W. Baxter, J.-M. Lehn* 2760 – 2764

Mechanistic Features, Cooperativity, and Robustness in the Self-Assembly of Multicomponent Silver(I) Grid-Type Metalloarchitectures

Keywords: complexation mechanism · cooperative effects · self-assembly · silver · supramolecular chemistry

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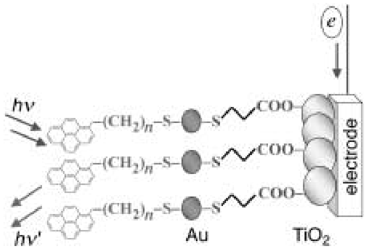
Suppressing the charge-transfer quenching with an externally applied electrochemical bias results in a fluorescence enhancement of a fluorophore (pyrene) on a gold nanoparticle surface (see scheme). At positive bias the fluorophore is totally quenched on the gold surface while at negative bias (less than – 0.5 V) it becomes highly fluorescent.



Angew. Chem. **2002**, *114*, 2888 – 2891

P. V. Kamat,* S. Barazzouk,
S. Hotchandani .... 2764 – 2767

Electrochemical Modulation of Fluorophore Emission on a Nanostructured Gold Film

Keywords: fluorescence · gold nanoparticles · nanostructures · organic – inorganic hybrid composites · spectroelectrochemistry

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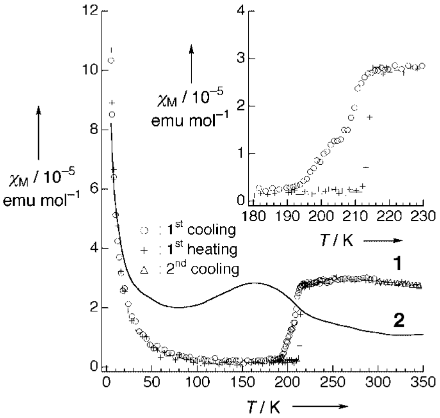
Chains change: Novel valence-ordering structures of the ground states of MMX chain compounds, $[Pt_2(RCS_2)_4I]_\infty$ (**1**: R = *n*Bu, **2**: R = Et), are determined by low-temperature crystal-structure analyses to be $\text{-}Pt^{2+}\text{-}Pt^{3+}\text{-}I^-\text{-}Pt^{3+}\text{-}Pt^{2+}\text{-}I^-\text{-}$. Magnetic susceptibility measurements of **1** (see graph) revealed an abrupt drop in magnitude from a 1D antiferromagnetic spin system to a spin-singlet state accompanying a first-order phase-transition around 210 K. This result is in contrast to the spin degree of freedom of **2** that survived down to 2 K.



Angew. Chem. **2002**, *114*, 2891 – 2895

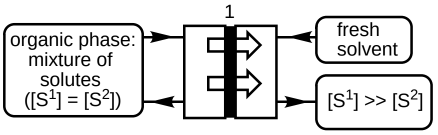
M. Mitsumi,* K. Kitamura, A. Morinaga,
Y. Ozawa, M. Kobayashi, K. Toriumi,*
Y. Iso, H. Kitagawa,
T. Mitani .... 2767 – 2771

Valence-Ordering Structures and Magnetic Behavior of Metallic MMX Chain Compounds

Keywords: conducting materials · electronic structure · magnetic properties · mixed-valent compounds · phase transition

---

Continuous separation of organic compounds is possible by selective transport through a supported liquid membrane, which contains the room-temperature ionic liquid 1-*n*-butyl-3-methylimidazolium hexafluorophosphate immobilized in the porous structure of a hydrophilic polyvinylidene fluoride membrane. A mixture (1:1 molar ratio) of the isomeric amines diisopropylamine (S^1) and triethylamine (S^2) was continuously fractionated over 14 days without any observable decrease in selectivity (see scheme).



1: selective transport through supported ionic liquid membrane

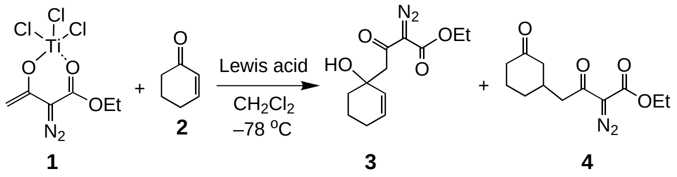
Angew. Chem. **2002**, *114*, 2895 – 2897

L. C. Branco, J. G. Crespo,
C. A. M. Afonso* .... 2771 – 2773

Highly Selective Transport of Organic Compounds by Using Supported Liquid Membranes Based on Ionic Liquids

Keywords: amines · ionic liquids · membranes · selective transport · separation processes

The selective generation of 1,2- and 1,4-addition products (**3** and **4**, respectively) in the addition of Ti^{IV} enolates **1** to α,β-unsaturated carbonyl compounds **2** can be almost completely controlled by the choice of Lewis acid. The high selectivity for 1,4 addition when the enones are activated by $TiCl_4$ or $SnCl_4$ is probably a result of the bridging chlorine atoms.



Angew. Chem. **2002**, *114*, 2897–2898

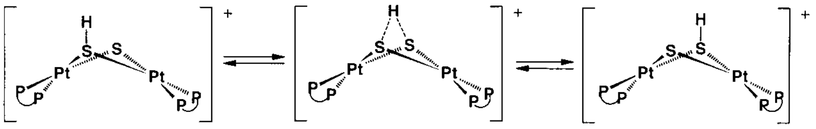
G. Deng, X. Tian, Z. Qu,
J. Wang* 2773–2776

Lewis Acid Controlled Regioselective 1,2 and 1,4 Reaction of α,β-Unsaturated Carbonyl Compounds with Ti^{IV} Enolates Derived from α-Diazo β-Keto Carbonyl Compounds

Keywords: addition · diazo compounds · enones · Lewis acids · Michael addition

---

Despite the weakness of S–H···S interactions and the fact that they have rarely been reported in transition-metal compounds, variable-temperature NMR data and theoretical calculations provide evidence for fast intramolecular proton exchange between the bridging sulfur atoms in the complexes $[Pt_2\{Ph_2P(CH_2)_nPPh_2\}_2(\mu\text{-}S)(\mu\text{-}SH)]ClO_4$ ($n = 2, 3$; see scheme).



Angew. Chem. **2002**, *114*, 2900–2902

G. Aullón, M. Capdevila, W. Clegg,
P. González-Duarte,* A. Lledós,*
R. Mas-Ballesté 2776–2778

First Evidence of Fast S–H···S Proton Transfer in a Transition Metal Complex

Keywords: hydrogen bonds · platinum · proton transfer · S ligands

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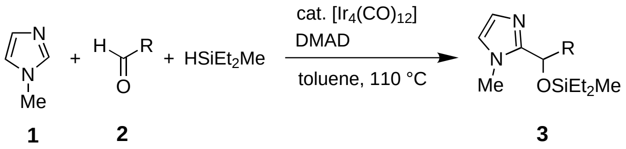
A significant increase in yield is observed when DMAD is added to the reaction of 1-methylimidazole (**1**) with aldehydes **2** and diethylmethylsilane in the presence of a catalytic amount of $[Ir_4(CO)_{12}]$ to produce 2-(1-diethylmethylsiloxyalkyl)-imidazoles **3**. DMAD = dimethyl acetylenedicarboxylate.



Angew. Chem. **2002**, *114*, 2903–2905

Y. Fukumoto, K. Sawada, M. Hagihara,
N. Chatani, S. Murai* 2779–2781

$[Ir_4(CO)_{12}]$-Catalyzed Coupling Reaction of Imidazoles with Aldehydes in the Presence of a Hydrosilane to Give 2-Substituted Imidazoles

Keywords: aldehydes · alkylation · imidazoles · iridium · silanes

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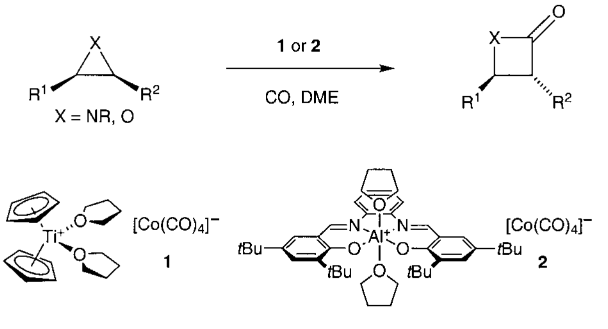
Efficient carbonyl insertion into C–O and C–N bonds using [Lewis acid]$^+[Co(CO)_4]^-$ complexes **1** and **2** gives regio- and stereoselective carbonylation of a variety of epoxides and aziridines to yield β-lactones and β-lactams, respectively. Both transformations are proposed to occur by the same mechanism, yielding products with inversion of configuration at the site of CO insertion.



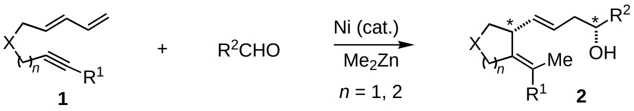
Angew. Chem. **2002**, *114*, 2905–2908

V. Mahadevan, Y. D. Y. L. Getzler,
G. W. Coates* 2781–2784

[Lewis Acid]$^+[Co(CO)_4]^-$ Complexes: A Versatile Class of Catalysts for Carbonylative Ring Expansion of Epoxides and Aziridines

Keywords: carbonylation · cobalt · lactams · lactones · ring-opening polymerization

A four-component reaction: A nickel catalyst promotes the conjugate addition of Me$_2$Zn and a carbonyl compound to 1,ω-dienynes **1** at the terminal positions of the alkyne and the diene moieties, respectively; the through-space interactions of the alkyne and diene groups ensure C–C coupling at the internal positions. The products **2** are obtained in good yields and with excellent 1,5-diastereoselectivity and stereoselectivity about the exocyclic double bond.



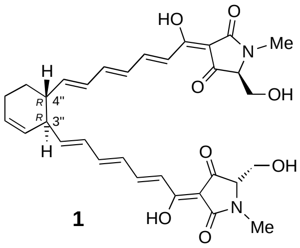
Angew. Chem. **2002**, *114*, 2908–2910

A. Ezoe, M. Kimura,* T. Inoue, M. Mori, Y. Tamaru* 2784–2786

Remarkably High 1,5-Diastereoselectivity in a Nickel-Catalyzed Conjugate Addition of Me$_2$Zn and Carbonyl Compounds to 1,ω-Dienynes with Through-Space Coupling

Keywords: aldehydes • alkynes • dienes • ketones • nickel • zinc

Only through total synthesis could the absolute configuration of the 3″*R*,4″*R* ring junction of the polyenoltetramic acid polycephalin C (**1**) be unambiguously established. Key features of the synthesis include a double Swern oxidation, double Stille coupling, and a double Takai olefination.



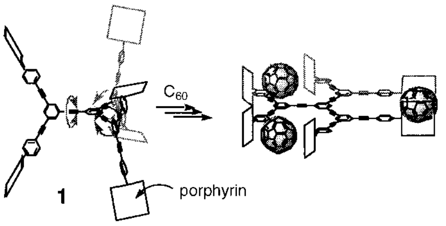
Angew. Chem. **2002**, *114*, 2910–2914

D. A. Longbottom, A. J. Morrison, D. J. Dixon, S. V. Ley* 2786–2790

Total Synthesis of Polycephalin C and Determination of the Absolute Configurations at the 3″,4″ Ring Junction

Keywords: alkenes • lactams • natural products • total synthesis

Treble clefts: The dendritic porphyrin receptor **1** has three fullerene-binding clefts, each of which consists of two face-to-face-oriented porphyrins. [60]Fullerene guests bind to each subunit, successively suppressing the rotational freedom ("domino" effect) and the guest-binding proceeds according to positive homotropic allosterism. As expected, the binding constant achieved in this system is large.



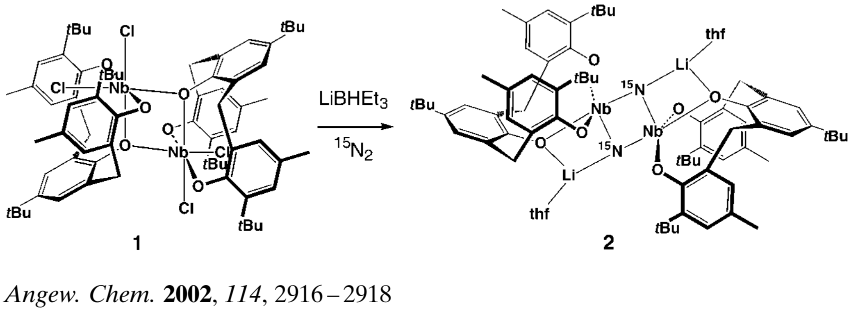
Angew. Chem. **2002**, *114*, 2914–2916

M. Ayabe, A. Ikeda, Y. Kubo, M. Takeuchi, S. Shinkai* 2790–2792

A Dendritic Porphyrin Receptor for C$_{60}$ Which Features a Profound Positive Allosteric Effect

Keywords: allosterism • fullerenes • host–guest systems • porphyrinoids • zinc

Nitrogen splits: The reaction of the linked aryloxide–niobium complex **1** with a hydride reagent under 1 atm of N$_2$ gave the nitride-bridging dimer **2**. The origin of the nitride ligands has been confirmed to be N$_2$ by repeating the experiment under an atmosphere of ^{15}N$_2$.



Angew. Chem. **2002**, *114*, 2916–2918

H. Kawaguchi,* T. Matsuo .. 2792–2794

Dinitrogen-Bond Cleavage in a Niobium Complex Supported by a Tridentate Aryloxide Ligand

Keywords: hydrides • niobium • nitrides • nitrogen fixation • O ligands

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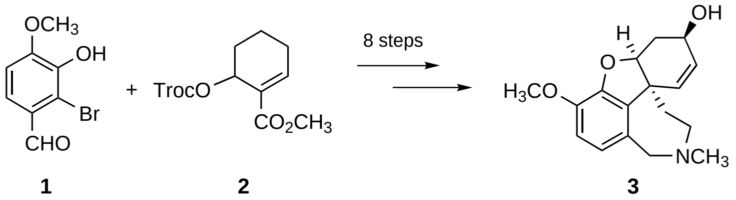
An effective sequence: Palladium-catalyzed asymmetric allylic alkylation, Heck cyclization, and diastereoselective allylic oxidation were used in the total synthesis of (−)-galanthamine (**3**) in 14.8% overall yield (from **1** and **2**, Troc = 2,2,2-trichloroethoxycarbonyl) and with 96% *ee*. This improved procedure provides the shortest and most efficient nonbiomimetic synthesis of the acetylcholinesterase inhibitor.



Angew. Chem. **2002**, *114*, 2919–2921

B. M. Trost,* W. Tang 2795–2797

An Efficient Enantioselective Synthesis of (−)-Galanthamine

Keywords: alkylation · allylic compounds · asymmetric synthesis · natural products · palladium

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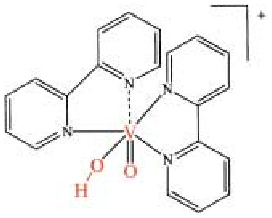
HYSCORE with a vanadium core: Examples of monomeric metal compounds containing the *cis*-$[M(=O)(OH)]^{n+}$ unit, namely the $V^{IV}O^{2+}$ complexes $[V^{IV}O(OH)(bipy)_2]BF_4$ (**1**; see picture) and $[V^{IV}O(OH)(phen)_2]BF_4 \cdot H_2O$ ($\mathbf{2} \cdot H_2O$), were isolated and structurally characterized. The continuous wave EPR and 2D ESEEM (HYSCORE; hyperfine sublevel correlation) spectroscopy parameters obtained for **1** and $\mathbf{2} \cdot H_2O$ provide spectroscopic signatures that enable the assignment of the *cis*-$[V^{IV}O(OH)]^+$ center in biomolecules.



Angew. Chem. **2002**, *114*, 2921–2925

E. J. Tolis, M. J. Manos, A. J. Tasiopoulos, C. P. Raptopoulou, A. Terzis, M. P. Sigalas,* Y. Deligiannakis,* T. A. Kabanos* 2797–2801

Monomeric Compounds Containing the *cis*-$[V(=O)(OH)]^+$ Core

Keywords: bioinorganic chemistry · density functional calculations · EPR spectroscopy · ESEEM spectroscopy · hydroxy ligands · vanadium

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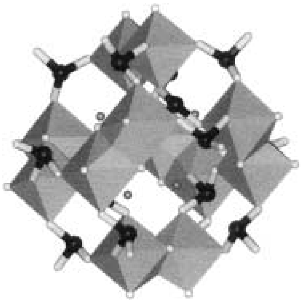
An unexplored family of polyoxometalates has evolved through the synthesis and structural characterization of the first examples of Mo^V sulfite heteropolyanions. The dodecanuclear molybdenum(v) sulfite exhibits a unique structural motif among polyoxometalates (see picture; gray polyhedra represent Mo^VO_6 octahedral units, black, white, and gray balls are sulfur, oxygen, and nitrogen atoms, respectively).



Angew. Chem. **2002**, *114*, 2925–2929

M. J. Manos, J. D. Woollins, A. M. Z. Slawin,* T. A. Kabanos* 2801–2805

Polyoxomolybdenum(v) Sulfite Complexes: Synthesis, Structural, and Physical Studies

Keywords: cluster compounds · molybdenum · polyoxometalates · sulfite

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Big rings and nanocleavage: Whereas a variety of molybdenum oxide based nanoobjects can be obtained by self-assembly concomitant with a variety of modifications of a parent cluster system under alterable boundary conditions, drastic changes—comparable to a molecular-scissors-type activity—can even cause splitting of the parent cluster to (large) fragments which subsequently can be linked in fascinating ways even with the option of generating giant cluster collectives (see picture $\{Mo_2^*\} \equiv \{Mo_2^{VI/V}O_7(H_2O)\}^{3-}$).

Angew. Chem. **2002**, *114*, 2929–2932

L. Cronin, C. Beugholt, E. Krickemeyer, M. Schmidtmann, H. Bögge, P. Kögerler, T. K. K. Luong, A. Müller* 2805–2808

“Molecular Symmetry Breakers” Generating Metal-Oxide-Based Nanoobject Fragments as Synthons for Complex Structures: $[\{Mo_{128}Eu_4O_{388}H_{10}(H_2O)_{81}\}_2]^{20-}$, a Giant-Cluster Dimer

Keywords: cluster compounds · europium · molybdenum · nanochemistry · polyoxometalates · symmetry breaking

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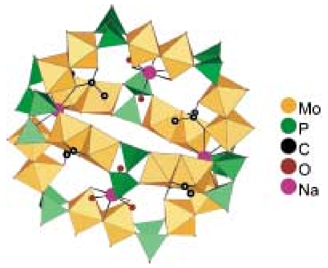
Interconnecting rings: The first pyrophosphate/Mo^V complex $Na_{24}\{Na_4(H_2O)_6\subset[(Mo_2O_4)_{10}(P_2O_7)_{10}(CH_3COO)_8(H_2O)_4]\}\cdot 97\,H_2O$ is synthesized in mild conditions, and has been characterized by X-ray diffraction (see polyhedral representation) and ^{31}P NMR spectroscopy. This molecular compound is formed of two nearly perpendicular interconnected wheels, an unprecedented topology for an inorganic compound.

Angew. Chem. **2002**, *114*, 2932–2934



C. du Peloux, P. Mialane, A. Dolbecq, J. Marrot, F. Sécheresse* 2808–2810

Mo^V/Pyrophosphate Polyoxometalate: An Inorganic Cryptate

Keywords: cryptands • host–guest systems • molybdenum • phosphates • polyoxometalates • sodium

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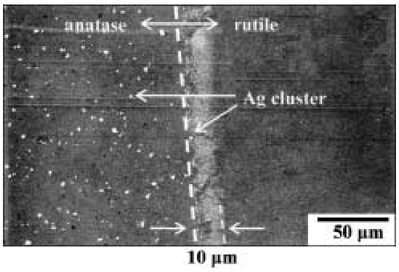
Coupling of anatase and rutile TiO_2 in a bilayer form significantly increases photocatalytic activity relative to the individual components. Reducing the dimensions of the junction to the charge-separation distance is of importance in increasing this activity. The interfacial electron transfer from anatase to rutile (< 10 µm) was revealed by labeling and visualizing the reduction sites by deposition of Ag nanoparticles (see picture).

Angew. Chem. **2002**, *114*, 2935–2937



T. Kawahara, Y. Konishi, H. Tada,* N. Tohge, J. Nishii, S. Ito 2811–2813

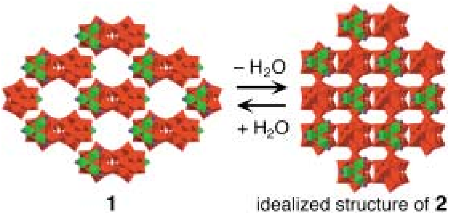
A Patterned TiO_2(Anatase)/TiO_2(Rutile) Bilayer-Type Photocatalyst: Effect of the Anatase/Rutile Junction on the Photocatalytic Activity

Keywords: heterogeneous catalysis • semiconductors • sol–gel processes • thin films

---

Molecular sieving to take your breath away: The breathing ionic crystal **1** is synthesized by the complexation of Keggin-type $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ (red) polyoxometalate with a macro cation $[Cr_3O(OOCH)_6(H_2O)_3]^+$ (green and white). The water of crystallization is easily removed from **1** by evacuation to form a guest-free phase **2**. Compound **2** reversibly adsorbs small alcohols and nitriles as well as water, while longer-chain alcohols and nitriles were excluded, which shows the novel molecular sieving of small hydrophilic molecules by **2**.

Angew. Chem. **2002**, *114*, 2938–2941



S. Uchida, M. Hashimoto, N. Mizuno* 2814–2817

A Breathing Ionic Crystal Displaying Selective Binding of Small Alcohols and Nitriles: $K_3[Cr_3O(OOCH)_6(H_2O)_3]$-$[\alpha\text{-}SiW_{12}O_{40}]\cdot 16\,H_2O$

Keywords: alcohols • hydrophilicity • microporous materials • nitriles • polyoxometalates

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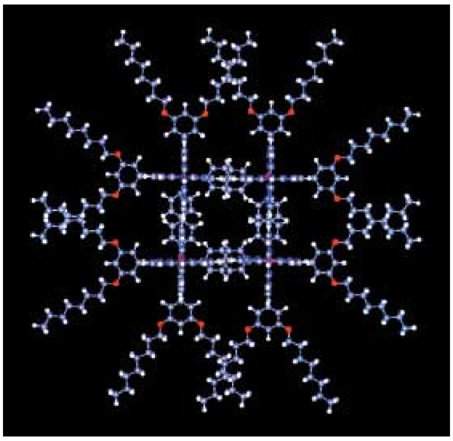
Box clever: A very stable box-shaped cyclic tetramer (see picture) was formed from *meso*-pyridyl substituted *meso*–*meso*-linked zinc(II) diporphyrin, in which the porphyrin subunits are held in a rigorous perpendicular orientation.

Angew. Chem. **2002**, *114*, 2941–2945

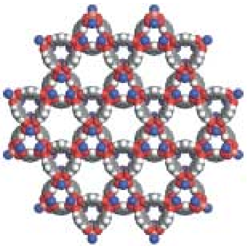


A. Tsuda, T. Nakamura, S. Sakamoto, K. Yamaguchi, A. Osuka* .. 2817–2821

A Self-Assembled Porphyrin Box from *meso*–*meso*-Linked Bis{5-*p*-pyridyl-15-(3,5-di-octyloxyphenyl)porphyrinato zinc(II)}

Keywords: chirality • porphyrinoids • self-assembly • zinc

Self-assembly of triangular nanoscale secondary building units affords a Kagomé lattice (see picture) that exhibits room-temperature magnetic hysteresis. This phenomenon is caused by spin frustration imparted by the triangular lattice topology, which is exemplified by direct comparison to a network having the same composition, but different topology.



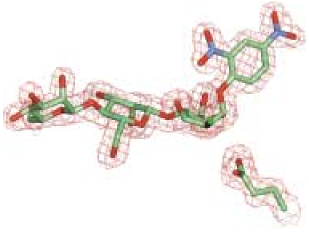
B. Moulton, J. Lu, R. Hajndl, S. Hariharan, M. J. Zaworotko* 2821–2824

Crystal Engineering of a Nanoscale Kagomé Lattice

Keywords: crystal engineering • Kagomé lattice • magnetic properties • nanostructures • self-assembly

Angew. Chem. **2002**, *114*, 2945–2948

The conformational reaction pathway for β-mannosidases proposed here is distinct from that of glucosidases and cellulases. The proposal is based on substrate distortions along the reaction pathway of a β-mannosidase (see picture) that were revealed by X-ray crystallography and are close in conformational space to known β-mannosidase inhibitors.



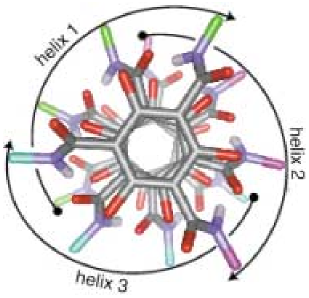
V. M.-A. Ducros, D. L. Zechel, G. N. Murshudov, H. J. Gilbert, L. Szabó, D. Stoll, S. G. Withers, G. J. Davies* 2824–2827

Substrate Distortion by a β-Mannanase: Snapshots of the Michaelis and Covalent-Intermediate Complexes Suggest a $B_{2,5}$ Conformation for the Transition State

Keywords: enzyme catalysis • glycosylation • inhibitors • mannosidases • X-ray diffraction

Angew. Chem. **2002**, *114*, 2948–2951

Chiral side chains installed into the stacks of overcrowded arenes enforce helical conformations (see picture). The assembly process can be directed with electric fields as a result of a dipole moment parallel to the stacking direction. In concentrated solutions, superhelices emerge that reflect circularly polarized light.



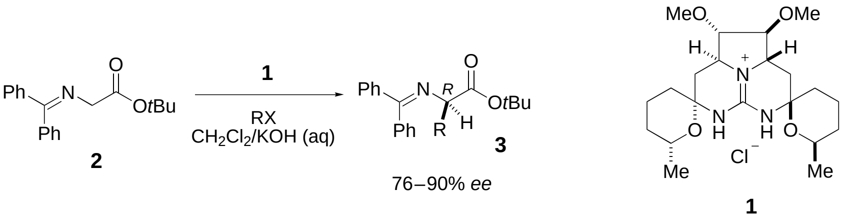
M. L. Bushey, A. Hwang, P. W. Stephens, C. Nuckolls* 2828–2831

The Consequences of Chirality in Crowded Arenes—Macromolecular Helicity, Hierarchical Ordering, and Directed Assembly

Keywords: helical structures • hydrogen bonds • molecular recognition • polar order • self-assembly

Angew. Chem. **2002**, *114*, 2952–2955

The enantioselective alkylation of the Schiff base 2 was carried out in the presence of a novel phase-transfer catalyst, the guanidine-containing pentacyclic compound **1**. The product **3** was obtained with enantiomeric excesses of 76–90 % (see scheme).



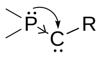
T. Kita, A. Georgieva, Y. Hashimoto, T. Nakata, K. Nagasawa* ... 2832–2834

C_2-Symmetric Chiral Pentacyclic Guanidine: A Phase-Transfer Catalyst for the Asymmetric Alkylation of *tert*-Butyl Glycinate Schiff Base

Keywords: alkylation • asymmetric synthesis • phase-transfer catalysis • synthetic methods

Angew. Chem. **2002**, *114*, 2956–2958

An electronic spectator in stable carbenes: A weak π-donor substituent such as a phosphanyl group brings enough stabilization to singlet phosphanyl(mesityl)carbenes prepared by photolysis of diazo precursors that the mesityl group remains an electronic spectator. The carbenes are sufficiently stable to allow characterization of the phosphanyl(*tert*-butyl)- and even phosphanyl(methyl)carbenes (see picture) by NMR spectroscopy (mesityl = 2,4,6-trimethylphenyl).



R = mesityl, *tert*-butyl, methyl

E. Despagnet, H. Gornitzka, A. B. Rozhenko, W. W. Schoeller, D. Bourissou, G. Bertrand* 2835–2837

Stable Non-Push–Pull Phosphanylcarbenes: NMR Spectroscopic Characterization of a Methylcarbene

Keywords: carbenes • phosphorus • reactive intermediates • substituent effects

Angew. Chem. **2002**, *114*, 2959–2961

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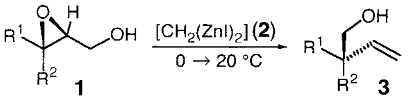
Retention of the configuration is observed in the pinacol-type rearrangement of 2,3-epoxy alcohols **1** in the presence of bis(iodozincio)methane (**2**). The 1,3-migration of the hydroxymethyl group affords an intermediate 2-hydroxyaldehyde, which is methylenated by **2** in situ to give homoallyl alcohol **3**.



Angew. Chem. **2002**, *114*, 2961 – 2964

S. Matsubara,* H. Yamamoto,
K. Oshima .... 2837 – 2840

Stereoselective Pinacol-Type Rearrangement of 2,3-Epoxy Alcohols with Retention of Configuration Mediated by Bis(iodozincio)methane

Keywords: asymmetric synthesis · Lewis acids · nucleophiles · rearrangement · zinc

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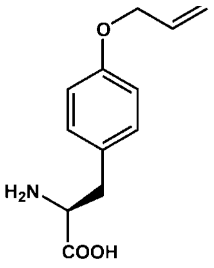
Synthetic anchor: An incorporated allyl group may act in this way to allow protein modification in a site-specific fashion. The nonnatural amino acid *O*-allyl-L-tyrosine (**1**) has been site-specifically incorporated into protein in *E. coli*. The yield of full-length mutant Z-domain protein is 5.6 mg L^{-1}, in comparison to 9.2 mg L^{-1} of native Z-domain protein. A high-resolution mass spectrum suggests the fidelity for the incorporation of **1** is better than 99.8 %.



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Angew. Chem. **2002**, *114*, 2964 – 2966

Z. Zhang, L. Wang, A. Brock,
P. G. Schultz* .... 2840 – 2842

The Selective Incorporation of Alkenes into Proteins in *Escherichia coli*

Keywords: allylic compounds · amino acids · biosynthesis · protein expression · protein modifications

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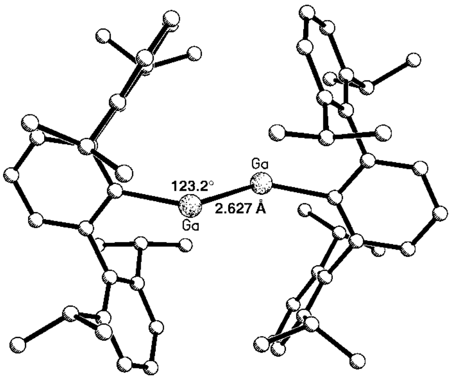
A Ga–Ga bond order considerably less than unity in the "digallene" Ar′GaGaAr′ (Ar′ = 2,6-Dipp$_2$C$_6$H$_3$, Dipp = 2,6-*i*Pr$_2$C$_6$H$_3$; see structure) is indicated by its structure and solution behavior.



Angew. Chem. **2002**, *114*, 2966 – 2968

N. J. Hardman, R. J. Wright,
A. D. Phillips, P. P. Power* .. 2842 – 2844

Synthesis and Characterization of the Neutral "Digallene" Ar′GaGaAr′ and Its Reduction to Na$_2$Ar′GaGaAr′ (Ar′ = 2,6-Dipp$_2$C$_6$H$_3$, Dipp = 2,6-*i*Pr$_2$C$_6$H$_3$)

Keywords: aryl substituents · gallium · metal-metal interactions · structure elucidation

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

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