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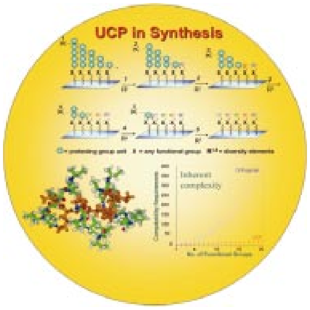
40/19
Pages 3487–3706

COVER PICTURE

The cover picture shows a new concept in protecting-group chemistry termed unichemo protection (UCP). This strategy only requires a single chemical process for all deprotection reactions. The UCP protecting groups are derived from a repetitive unit that permits their controlled and efficient step-wise removal. Functional-site selectivity is achieved by varying the degree of oligomerization at each site, and, after each deprotection cycle, only the newly liberated functional site is available for derivatization. The UCP strategy does not impose a restriction on the possible number of selectively protected sites in a molecule. The low-energy conformer of the pentalysine scaffold assembled with *N-sec*-butylglycyl protecting-group units is shown bottom left. By using the UCP approach the five protecting groups were sequentially removed and the exposed amino acid groups functionalized with five different organic acids. UCP facilitates an orthogonal process that is not dependent on a range of finely tuned and differently compatible processes. Moreover, since UCP is based on uniform deprotection reactions, the requirement of reaction compatibility with other parts of a molecule only increases linearly with the degree of polyfunctionalization (graph, bottom right). That is, after the initial requirement of parent-molecule stability is satisfied, only the sequential requirements towards each newly introduced group is an issue. In contrast, a quadratic increase in complexity with respect to the number of protected functional groups, even in the simplest cases, accompanies existing orthogonal protection strategies. More about the UCP strategy is reported by L. P. Miranda and M. Meldal on p. 3655ff.



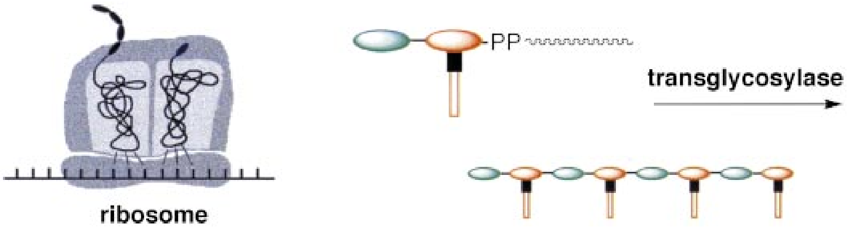
REVIEWS

Contents

The most important targets of antibiotics include the translation of RNA in bacterial ribosomes and the biosynthesis of the bacterial cell wall (see picture). As a result of the recent interest in antibiotic resistance, carbohydrate mimics have been considered as new inhibitors of these processes. Carbohydrate receptors as well as carbohydrate-modified enzymes have emerged as new targets.

T. K. Ritter, C.-H. Wong* .. 3508–3533

Carbohydrate-Based Antibiotics: A New Approach to Tackling the Problem of Resistance



Angew. Chem. **2001**, *113*, 3616–3641

Keywords: antibiotics · carbohydrates · enzyme inhibitors · peptidoglycans · RNA

What do the bent alkaline earth dihalides, the (distorted) trigonal-prismatic hexamethyltungsten or -molybdenum, and the “inverse Bent’s rule” structure of [$TiCl_2(CH_3)_2$] have in common? They all belong to the growing class of complexes with a formal d^0 electronic configuration of the metal center which defy the traditional structure models. This article provides a comprehensive review of both experimental and computational studies of such “non-VSEPR” d^0 systems. The bonding features that control the unusual structures are discussed in a unified framework, and the possible relevance for important catalytic or biological processes, as well as materials properties, is highlighted.

Angew. Chem. **2001**, *113*, 3642–3677

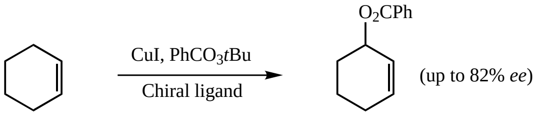
M. Kaupp* 3534–3565

“Non-VSEPR” Structures and Bonding in d^0 Systems

Keywords: bond theory · d^0 complexes · density functional calculations · transition metals · VSEPR model

MINIREVIEW

Chiral ligands such as oxazolines and prolines are important in the copper-catalyzed oxidative conversion of prostereogenic alkenes into enantiomerically pure allylic esters (see scheme). This contribution highlights some of the recent developments in this area using an asymmetric Kharasch–Sosnovsky reaction.



Angew. Chem. **2001**, *113*, 3679–3683

J. Eames,* M. Watkinson* . 3567–3571

Catalytic Allylic Oxidation of Alkenes Using an Asymmetric Kharasch–Sosnovsky Reaction

Keywords: alkenes · asymmetric catalysis · copper · enantioselectivity · oxidation

VIPs

The following communications are “Very Important Papers” in the opinion of two referees. They will be published shortly. Short summaries of these articles can be found on the *Angewandte Chemie* homepage at the address http://www.angewandte.com

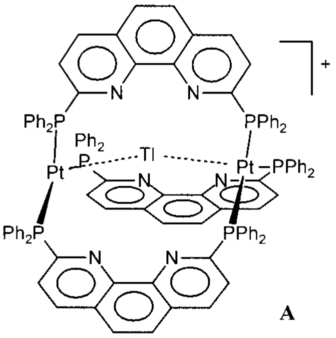
Experimental Detection of Tetraoxygen	F. Cacace,* G. de Petris, A. Troiani
[12.12]Paracyclophanedodecaynes $C_{36}H_8$ and $C_{36}Cl_8$: The Smallest Paracyclophynes and Their Transformation into the Carbon Cluster Ion C_{36}^-	Y. Tobe,* R. Furukawa, M. Sonoda, T. Wakabayashi
Fluorescence Quenching via Sequential Hydrogen, Electron, and Proton Transfer in the Proximity of a Conical Intersection	A. Sinicropi, R. Pogni*, R. Basosi, M. A. Robb, G. Gramlich, W. M. Nau,* M. Olivucci*
Side-Wall Functionalization of Carbon Nanotubes	M. Holzinger, O. Vostrowsky, A. Hirsch,* F. Hennrich, M. Kappes, R. Weiss, F. Jellen
Origin of Ferromagnetism in Cyano-Bridged Compounds Containing d^1 Octacyanometallates	L. F. Chibotaru,* V. S. Mironov, A. Ceulemans
Lewis Acid/Base-Stabilized Phosphanylalane and -gallane	U. Vogel, A. Y. Timshkin, M. Scheer*

HIGHLIGHT

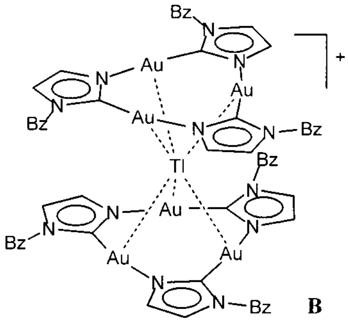
The assembly of a new class of metallocryptands **A** and "metallosandwiches" **B**, as well as studies on the bonding of Tl^+ with d^{10}-configured Group 10 and 11 complexes in solution and in the solid state have established relatively strong "metallophilic" interactions between d^{10} metal centers and thallium(I). These materials have interesting luminescence properties which differ markedly from those of the individual components. The stability of the $d^{10}-s^2$ aggregates contrasts with the weak attraction between s^2-metal centers proposed in the solid state for many thallium(I) compounds and which is frequently superceded by competing intra- and intermolecular interactions. Bz = benzyl.

L. H. Gade* 3573–3575

Encapsulated, Sandwiched, or Sticking Out: Closed-Shell Interactions of d^{10} Metal Centers with Thallium(I)



A



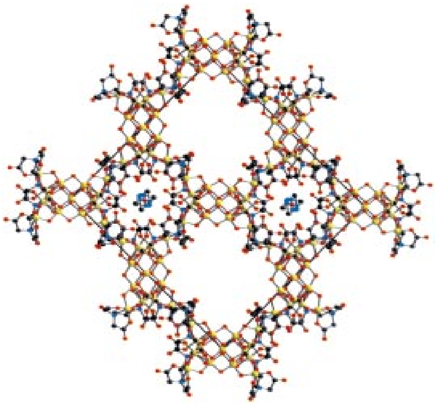
B

Angew. Chem. **2001**, *113*, 3685–3688

Keywords: cryptands · metal–metal interactions · thallium

COMMUNICATIONS

Separate areas of differing polarity in the structure of an inorganic cluster compound are favored by the introduction of organic ligands on the periphery of the aggregate. This has been demonstrated by the synthesis of compounds containing the title anion (see picture for an example).



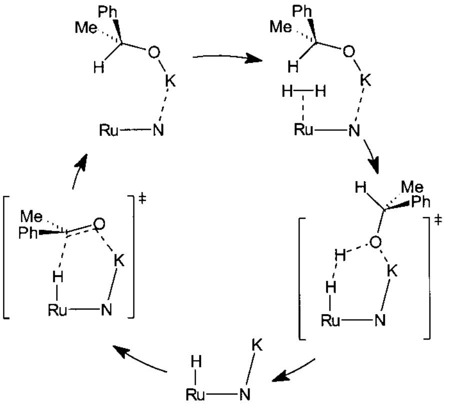
W. Schmitt, E. Baissa, A. Mandel, C. E. Anson, A. K. Powell* . 3578–3581

$[Al_{15}(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{14}\text{-}(hpdta)_4]^{3-}$—A New Al_{15} Aggregate Which Forms a Supramolecular Zeotype

Angew. Chem. **2001**, *113*, 3690–3693

Keywords: aluminum · cluster compounds · zeolite analogues

Alkali metal cations are indispensible cocatalysts for the high activity of Ru^{II} complexes with phosphane and amine ligands in the catalytic hydrogenation of ketones. The proposed mechanism (see scheme) is based on structural evidence as well as on the hydrogen-cleaving activity of other Ru^{II} complexes.



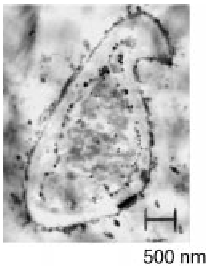
R. Hartmann, P. Chen* 3581–3585

Noyori's Hydrogenation Catalyst Needs a Lewis Acid Cocatalyst for High Activity

Angew. Chem. **2001**, *113*, 3693–3697

Keywords: asymmetric catalysis · homogeneous catalysis · hydrogenation · Lewis acids · ruthenium

Fungi make piles of gold! A green-chemistry route, based on the bioreduction of $AuCl_4^-$ ions by the fungus *Verticillium* sp., for the formation of gold nanoparticles is demonstrated. The TEM micrograph shows a single *Verticillium* cell after reaction with gold ions and entrapment of gold nanoparticles on the cell wall and cytoplasmic membrane.



Angew. Chem. **2001**, *113*, 3697–3701

P. Mukherjee, A. Ahmad, D. Mandal,
S. Senapati, S. R. Sainkar, M. I. Khan,
R. Ramani, R. Parischa,
P. V. Ajayakumar, M. Alam, M. Sastry,*
R. Kumar* 3585–3588

Bioreduction of $AuCl_4^-$ Ions by the Fungus, *Verticillium sp.* and Surface Trapping of the Gold Nanoparticles Formed

Keywords: bioinorganic chemistry · biosynthesis · gold · green chemistry · nanostructures

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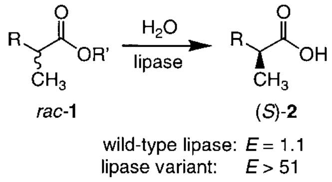
Recombinant methods work exceedingly well in the directed evolution of an enantioselective enzyme. For the kinetic resolution of the ester *rac*-**1** by a lipase [Eq. (a)] three steps were applied: 1) Generation of mutants by the error-prone polymerase chain reaction (epPCR), 2) identification of "hot spots" in the enzyme by epPCR and simplified combinatorial multiple-cassette mutagenesis (CMCM), and 3) extension of the process of CMCM to cover a defined region of protein sequence space. From lass then 40000 enzyme varients generated, one was found which catalyzes the reaction with almost 50-times higher enantioselectivity than the wild-type enzyme.



(a)

Angew. Chem. **2001**, *113*, 3701–3703

M. T. Reetz,* S. Wilensek, D. Zha,
K.-E. Jaeger 3589–3591

Directed Evolution of an Enantioselective Enzyme through Combinatorial Multiple-Cassette Mutagenesis

Keywords: asymmetric catalysis · combinatorial chemistry · directed evolution · enzyme catalysis · lipases

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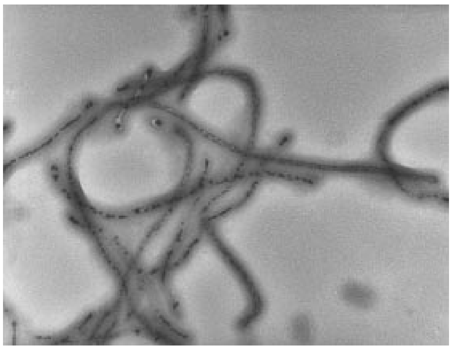
Impregnating the cores of triblock-copolymer nanotubes with Fe_2O_3 renders them superparamagnetic. The resultant polymer/Fe_2O_3 hybrid nanofibers (see TEM image) have interesting properties in magnetic fields. The nanofibers align themselves in the magnetic-field direction, and mixtures of the nanofibers and nanotubes undergo phase separation.



Angew. Chem. **2001**, *113*, 3705–3708

X. Yan, G. Liu,* F. Liu, B. Z. Tang,
H. Peng, A. B. Pakhomov,
C. Y. Wong 3593–3596

Superparamagnetic Triblock Copolymer/Fe_2O_3 Hybrid Nanofibers

Keywords: copolymerization · magnetic properties · nanostructures · self-assembly · thin films

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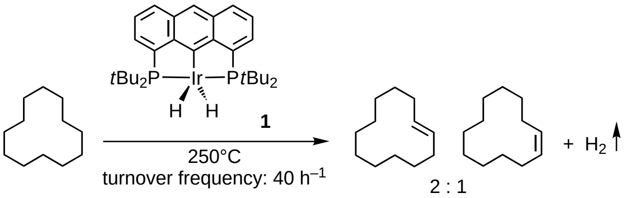
Thermostability is "conditio sine qua non" (a necessity) if organometallic compounds are used in the homogeneous catalysis of endothermic processes such as the dehydrogenation of alkanes to alkenes and hydrogen (see scheme). This thermostability and other requirements for such a catalyst are fulfilled by the anthraphos iridium(III)dihydride complex **1**.



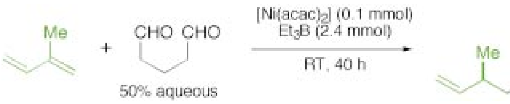
Angew. Chem. **2001**, *113*, 3708–3712

M. W. Haenel,* S. Oevers,
K. Angermund, W. C. Kaska,* H.-J. Fan,
M. B. Hall* 3596–3600

Thermally Stable Homogeneous Catalysts for Alkane Dehydrogenation

Keywords: C–H activation · dehydrogenation · density functional calculations · homogeneous catalysis · iridium · molecular modeling

Bishomoallyl alcohols are obtained with excellent 1,2- and 1,3-asymmetric induction from reactions of unsymmetrical dienes with glutaraldehyde (50% aqueous) or cyclic hemiacetals at room temperature [see for example, Eq. (1)]. These homoallylations of aldehydes in the presence of water are promoted by the catalytic system $[Ni(acac)_2]/Et_3B$ (acac = acetylacetone).



(1)

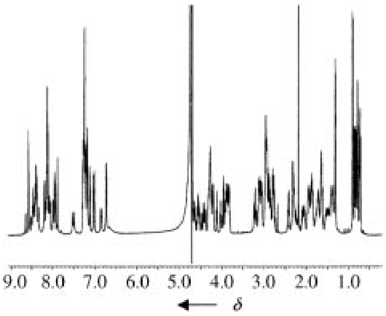
Angew. Chem. **2001**, *113*, 3712–3714

M. Kimura, A. Ezoe, S. Tanaka,
Y. Tamaru* 3600–3602

Nickel-Catalyzed Homoallylation of Aldehydes in the Presence of Water and Alcohols

Keywords: aldehydes · allylation · boron · dienes · nickel

Unlabeled samples of the β-amyloid peptide(1–28) fibrils typical of Alzheimer's disease could be used to obtain well-resolved one- and two-dimensional ^1H NMR spectra (see picture). The technique applied was high-resolution magic-angle spinning on a 600 MHz NMR spectrometer. The results are in agreement with a parallel, in-register arrangement of the β-amyloid peptide in the fibril.



Angew. Chem. **2001**, *113*, 3715–3717

E. Mikros,* D. Benaki, E. Humpfer,
M. Spraul, S. Loukas,
C. I. Stassinopoulou,
M. Pelecanou* 3603–3605

High-Resolution NMR Spectroscopy of the β-Amyloid(1–28) Fibril Typical for Alzheimer's Disease

Keywords: amyloid fibrils · NMR spectroscopy · structure elucidation

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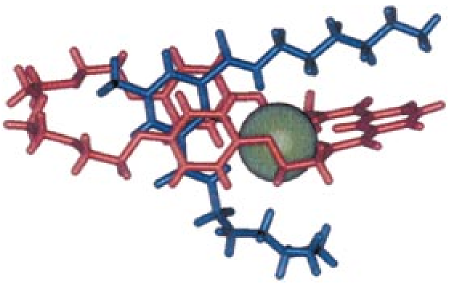
First- and second-sphere coordination of a chloride anion templates the formation of a [2]pseudorotaxane (see picture) in which a pyridinium diamide threads through the annulus of a macrocyclic isophthalamide wheel. The formation of the pseudorotaxane depends on the nature of the anion involved: the use of a larger anion destabilizes the entire recognition motif.



Angew. Chem. **2001**, *113*, 3718–3721

J. A. Wisner, P. D. Beer,*
M. G. B. Drew 3606–3609

A Demonstration of Anion Template and Selectivity in Pseudorotaxane Formation

Keywords: amides · anions · rotaxanes · self-assembly · supramolecular chemistry

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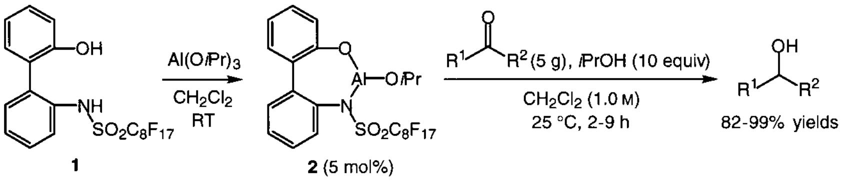
Simple mixing of Al(O*i*Pr)$_3$ with the requisite ligand 1 in CH_2Cl_2 at room temperature smoothly generates the new, powerful aluminum catalyst **2**, which efficiently catalyzes Meerwein–Ponndorf–Verley (MPV) reduction of various carbonyl substrates under mild conditions (see scheme). Scale-up experiments highlight the potential of the new MPV reduction procedure for practical use.



Angew. Chem. **2001**, *113*, 3722–3724

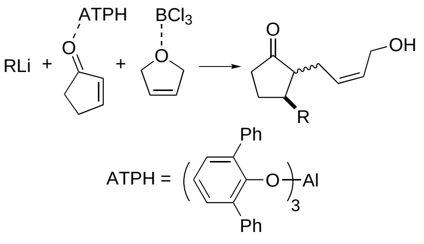
T. Ooi, H. Ichikawa,
K. Maruoka* 3610–3612

Practical Approach to the Meerwein–Ponndorf–Verley Reduction of Carbonyl Substrates with New Aluminum Catalysts

Keywords: aluminum · homogeneous catalysis · ketones · reduction

A one-pot three-component coupling involving organolithium reagents, ATPH · cyclopentenone complex, and dihydrofuran · BCl_3 complex (see scheme) gives moderate to good yields of the products with selective formation of either the 2,3-*cis* or 2,3-*trans* isomer, depending on the nature of the lithium reagent.

Angew. Chem. **2001**, *113*, 3725–3729



S. Saito, S. Yamazaki,
H. Yamamoto* 3613–3617

Novel Three-Component Coupling Using Aluminum Tris(2,6-diphenylphenoxide) (ATPH): The Same Synthetic Strategy Leads to *trans*- and *cis*-Jasmonates

Keywords: allylation · diastereoselectivity · enones · Michael addition · multicomponent reactions

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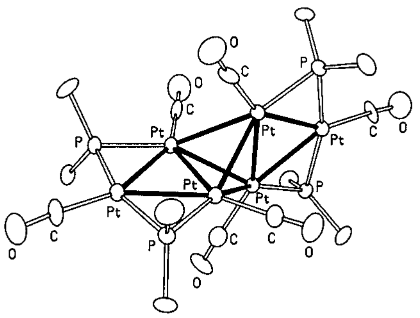
The unusual cluster $[Pt_6(CO)_6(\mu\text{-}PtBu_2)_4](CF_3SO_3)_2$ (**1**) has a tetrahedral Pt_4 core, two opposite edges of which are bridged by two other platinum atoms (see picture). Complex **1** is remarkably stable and can be regioselectively functionalized at the two apical sites. Its reaction with $NaBH_4$ affords the first platinum formyl complex: $[Pt_6(CO)_4(CHO)_2(\mu\text{-}PtBu_2)_4]$.

Angew. Chem. **2001**, *113*, 3729–3730



P. Leoni,* F. Marchetti, L. Marchetti,
M. Pasquali, S. Quaglierini .. 3617–3618

The First Platinum Formyl, a Member of a Series of Hexanuclear Clusters Exhibiting a Rare Structure

Keywords: carbonyl complexes · cluster compounds · formyl complexes · platinum · P ligands

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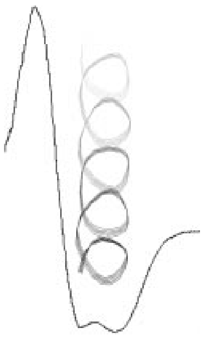
More helix than peptide? The helical polypeptides have distinctive circular dichroism (CD) spectra, as shown in the graphic. The recent experimental observation of a peptide with an intense CD spectrum, which suggests a helical content of greater than 100 % is therefore highly anomalous. We present calculations from first principles which could explain this unusual observation.

Angew. Chem. **2001**, *113*, 3731–3733



Z. Dang, J. D. Hirst* 3619–3621

Short Hydrogen Bonds, Circular Dichroism, and Over-Estimates of Peptide Helicity

Keywords: ab initio calculations · circular dichroism · helical structures · hydrogen bonds · peptides

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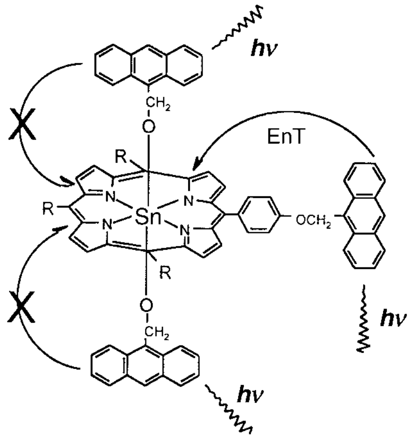
“Equatorial” energy transfer: Orientation control of intramolecular energy transfer (EnT) is found in the donor–acceptor system shown, light absorbed by the “peripheral” anthracene is efficiently transferred to the porphyrin, but that by the “axial” anthracene subunits is not.

Angew. Chem. **2001**, *113*, 3733–3736

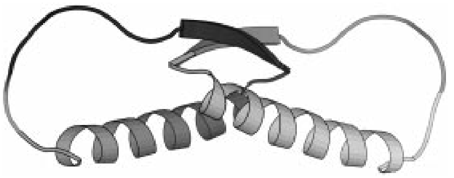


L. Giribabu, A. Ashok Kumar,
V. Neeraja, B. G. Maiya* ... 3621–3624

Orientation Dependence of Energy Transfer in an Anthracene–Porphyrin Donor–Acceptor System

Keywords: anthracene · donor–acceptor systems · energy transfer · fluorescence · porphyrinoids

In contrast to DNA, proteins with topologically linked backbone structures have not yet been observed in Nature. We have chemically synthesized a p53 protein catenane (see schematic representation) consisting of interlocking cyclic polypeptides to demonstrate that such structures are synthetically attainable and can significantly stabilize the folded conformation of a protein.



Angew. Chem. **2001**, *113*, 3737–3739

L. Z. Yan, P. E. Dawson* ... 3625–3627

Design and Synthesis of a Protein Catenane

Keywords: catenanes · chemoselectivity · protein design · protein engineering · solid-phase synthesis

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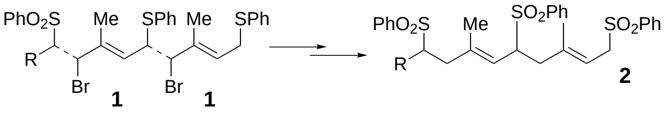
Successive elongation by a C_5 unit is possible when an allylic sulfone is coupled with 4-bromo-3-methyl-2-butenyl phenyl sulfide (**1**). The thiosulfone compound formed was then oxidized to the corresponding disulfone, which, upon coupling with another equivalent of **1** and oxidation, produced the trisulfone **2**, again elongated by a C_5 unit (see scheme). This process, which can be repeated again, is the basis for a highly efficient synthesis of carotenoids.



Angew. Chem. **2001**, *113*, 3739–3741

M. Ji, H. Choi, M. Park, M. Kee, Y. C. Jeong, S. Koo* 3627–3629

A Highly Efficient Chain-Extension Process in the Systematic Syntheses of Carotenoid Natural Products

Keywords: alkenes · carotenoids · sulfones · synthetic methods · total synthesis

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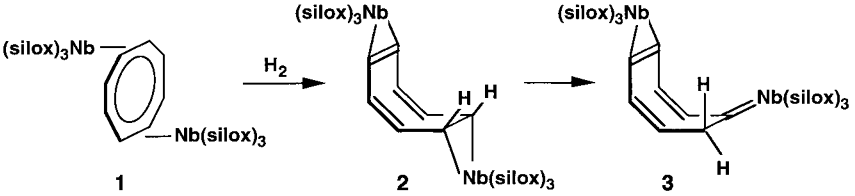
The resonance energy of COT^{2-} in [{(silox)$_3$Nb}$_2$(η-1,2;η-5,6-C_8H_8)] (**1**) is indirectly responsible for its dehydrogenation to **2**, but this olefin complex is thermodynamically *less* stable than the alkylidene **3**. silox = tBu$_3$SiO, COT = cyclooctatetraene.



Angew. Chem. **2001**, *113*, 3741–3744

A. S. Veige, P. T. Wolczanski,* E. B. Lobkovsky 3629–3632

Dehydrogenation of [{(silox)$_3$Nb}$_2$(η-1,2;η-5,6-C_8H_8)] (silox = tBu$_3$SiO) to [{(silox)$_3$Nb}$_2$(η-1,2;η-5,6-C_8H_6)] and Its Subsequent Alkene-to-Alkylidene Rearrangement

Keywords: alkylidene ligands · cyclooctatetraene · dehydrogenation · niobium · rearrangements

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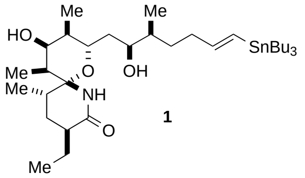
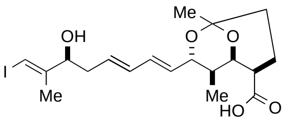
Crafting of the building blocks 1–3 allows the convergent conjoining of **2–3** in advance of macrolactonization. The subsequent linkup of the eastern sector with **1** by Stille coupling enabled the convenient stereocontrolled assembly of the immunosuppressive agent (−)-sanglifehrin A (Boc = *tert*-butoxycarbonyl).



1



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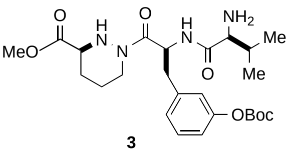

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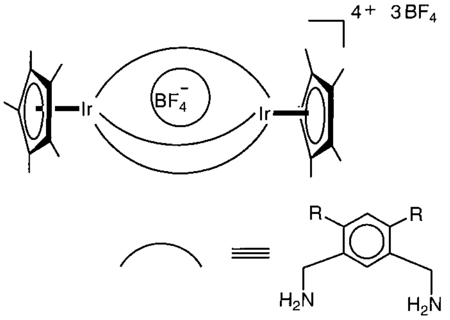
Angew. Chem. **2001**, *113*, 3744–3748

M. Duan, L. A. Paquette* 3632–3636

Enantioselective Total Synthesis of the Cyclophilin-Binding Immunosuppressive Agent Sanglifehrin A

Keywords: cyclizations · immunochemistry · macrolactonization · Stille coupling · total synthesis

Iridium and rhodium coordination chemistry has been used to self-assemble metallocryptands: Treatment of two equivalents of $[Cp^*M(solv)_3][BF_4]_2$ ($Cp^* = C_5(CH_3)_5$; M = Rh, Ir; solv = acetone) with three equivalents of the bidentate ligand 1,3-bis(aminomethyl)-2,5-dimethoxy-4,6-dimethylbenzene (L) afforded the first irido- and rhodiocryptands $[(Cp^*M)_2L_3][BF_4]_4$ in high yields (70–85 %). The use of less congested ligands increased the accessibility of the cavity of the metallocryptands and enabled the encapsulation of tetrafluoroborate ions (see scheme).



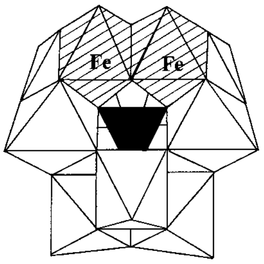
H. Amouri,* M. N. Rager, F. Cagnol, J. Vaissermann 3636–3638

Rational Design and X-ray Molecular Structure of the First Irido-Cryptand and Encapsulation of a Tetrafluoroborate Anion

Keywords: host–guest systems · iridium · rhodium · self-assembly · supramolecular chemistry

Angew. Chem. **2001**, *113*, 3748–3750

The diiron-substituted silicotungstate γ-$SiW_{10}\{Fe^{3+}(OH_2)\}_2O_{38}^{6-}$ (schematically shown) is an effective catalyst for the oxygenation of alkenes in homogeneous reaction media with 1 atm of molecular oxygen. For example, a selectivity for cyclooctene oxide of 98 % and a turnover number of 10000 were achieved in the epoxidation of cyclooctene. The catalyst is stable under the reaction conditions, and its ability to use molecular oxygen raises the prospect of using it in industrial epoxidation processes.



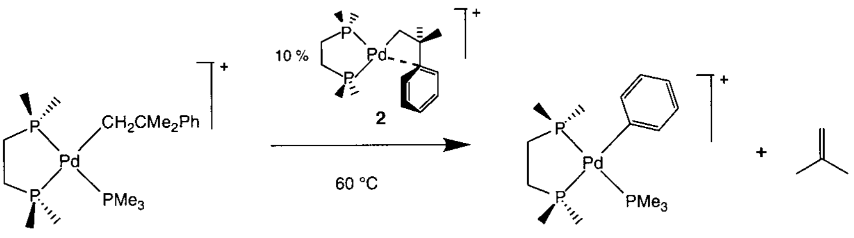
Y. Nishiyama, Y. Nakagawa, N. Mizuno* 3639–3641

High Turnover Numbers for the Catalytic Selective Epoxidation of Alkenes with 1 atm of Molecular Oxygen

Keywords: epoxidation · homogeneous catalysis · oxygenation · polyoxometalates

Angew. Chem. **2001**, *113*, 3751–3753

The extrusion of isobutene from the neophyl derivative **1** is catalyzed by the cationic palladium π-arene complex **2** in a process that involves the cleavage of the β C–C bond of the latter (see scheme). The inverse reactivity, that is olefin insertion, is observed when the reaction proceeds in the presence of ethylene.



1

3

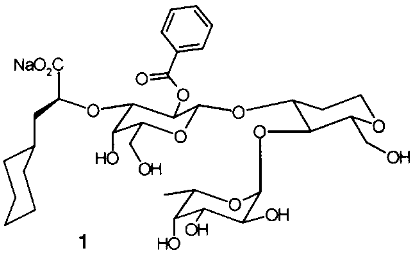
J. Cámpora,* E. Gutiérrez-Puebla, J. A. López, A. Monge, P. Palma,* D. del Río, E. Carmona* ... 3641–3644

Cleavage of the C_{alkyl}–C_{aryl} Bond of $[Pd–CH_2CMe_2Ph]$ Complexes

Keywords: arene ligands · C–C activation · insertions · metallacycles · palladium

Angew. Chem. **2001**, *113*, 3753–3756

A mix of accident, serendipity, and rational design led to compound **1**, the most potent E-selectin inhibitor known to date. It was assembled in ten linear steps in an overall yield of >25 %. In a static assay it was 100-fold more potent than sialyl Lewis^X. In an even more relevant flow assay that mimics the dynamic in vivo conditions, **1** showed an IC_{50} of 1–2 µM, whereas sialyl Lewis^X did not inhibit at concentrations up to 1000 µM.



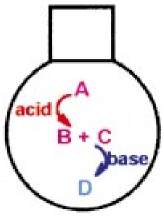
G. Thoma,* R. Bänteli, W. Jahnke, J. L. Magnani, J. T. Patton ... 3644–3647

A Readily Available, Highly Potent ESelectin Antagonist

Keywords: carbohydrates · inhibitors · medicinal chemistry · selectins · sialic acids

Angew. Chem. **2001**, *113*, 3756–3759

Here is a solution to a classical problem: How to put, in one pot, both an acid and a base without their mutual destruction? The sol–gel materials method offers an approach: acids or bases are entrapped within these materials, and then organic reaction sequences, which require these opposing reagents, are carried out simultaneously or consecutively in the same pot (see scheme).



Angew. Chem. **2001**, *113*, 3759–3761

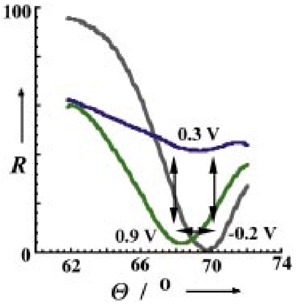
F. Gelman, J. Blum,*
D. Avnir* 3647–3649

Acids and Bases in One Pot while Avoiding Their Mutual Destruction

Keywords: Brønsted acids · Brønsted bases · heterogeneous catalysis · immobilization · multicomponent reactions · sol–gel processes

---

A prussian-blue thin film assembled on an Au electrode yields an optoelectronic three-state switching system for the photonic transduction of electrical signals, and a sensing device for the electrocatalyzed oxidation of NADH, using surface plasmon resonance (SPR) spectroscopy. The SPR spectra measured for the modified Au surface are shown for different potentials and the generation of the different redox states of the prussian-blue film: -0.2 V = fully reduced, 0.3 V = semi-oxidized, 0.9 V = fully oxidized.



Angew. Chem. **2001**, *113*, 3761–3764

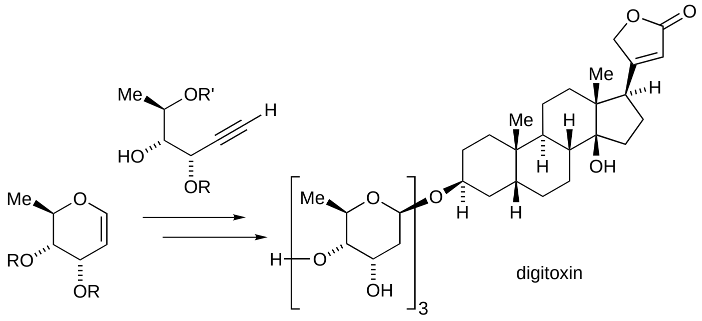
O. A. Raitman, E. Katz, I. Willner,*
V. I. Chegel, G. V. Popova ... 3649–3652

Photonic Transduction of a Three-State Electronic Memory and of Electrochemical Sensing of NADH by Using Surface Plasmon Resonance Spectroscopy

Keywords: electrochemistry · molecular switches · optoelectronics · prussian blue · sensors · surface plasmon resonance

---

Tungsten-catalyzed alkynol cycloisomerization and iterative acid-catalyzed stereoselective glycosylations form the basis of a revolutionary new strategy for oligosaccharide synthesis. The method has been successfully applied to a highly convergent synthesis of *Digitalis* 2-deoxyglycosides (see scheme).



Angew. Chem. **2001**, *113*, 3765–3767

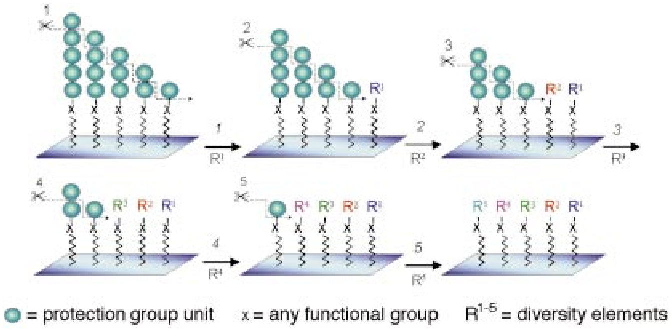
F. E. McDonald,*
K. S. Reddy 3653–3655

Convergent Synthesis of Digitoxin: Stereoselective Synthesis and Glycosylation of the Digoxin Trisaccharide Glycal

Keywords: cycloisomerization · glycosylation · homogeneous catalysis · oligosaccharides · tungsten

---

Modular cleavage of oligomer protecting groups is at the heart of the unichemo-protection (UCP) strategy (see scheme) that simplifies synthesis and facilitates construction of polyfunctional molecules.



Angew. Chem. **2001**, *113*, 3767–3769

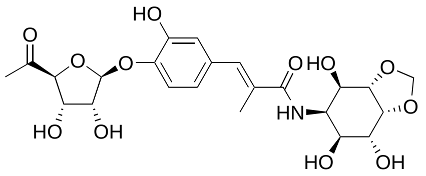
L. P. Miranda, M. Meldal* . 3655–3657

Unichemo Protection: A Concept for Chemical Synthesis

Keywords: combinatorial chemistry · protecting groups · solid-phase synthesis · synthetic methods

1433-7851/01/4019-3497 $ 17.50+.50/0

The power of Pd-catalyzed asymmetric allylic alkylation (AAA) reactions is clearly demonstrated by the efficient synthesis of the complex title compound **1**, an analogue of hygromycin A. The modular nature of the synthetic route is ideally suited to provide access to further analogues.



1

Angew. Chem. **2001**, *113*, 3770–3772

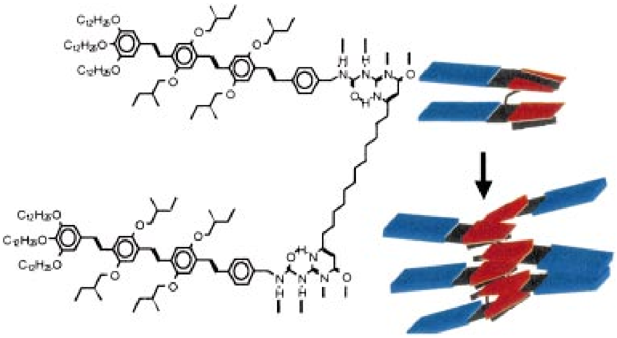
B. M. Trost,* O. Dirat, J. Dudash, Jr., E. J. Hembre 3658–3660

An Asymmetric Synthesis of C-2-*epi*-Hygromycin A

Keywords: asymmetric catalysis · asymmetric synthesis · natural products · palladium · total synthesis

---

A combination of the well-defined character of π-conjugated oligomers and the material properties of polymers is displayed by the supramolecular hydrogen-bonded π-conjugated architectures of the title compounds (see scheme). These compounds have been successfully used for the first time in electronic devices.



Angew. Chem. **2001**, *113*, 3772–3775

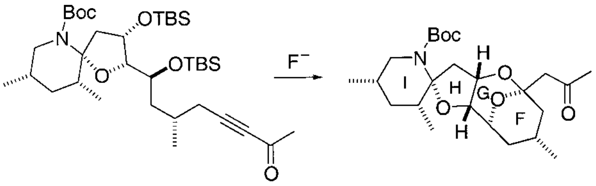
A. El-ghayoury, A. P. H. J. Schenning, P. A. van Hal, J. K. J. van Duren, R. A. J. Janssen,* E. W. Meijer* 3660–3663

Supramolecular Hydrogen-Bonded Oligo(*p*-phenylene vinylene) Polymers

Keywords: electronic devices · fullerenes · hydrogen bonds · polymers · supramolecular chemistry

---

A stereocontrolled synthesis of the C26–C40 domain of the azaspiracid shellfish toxins containing the intricate FGHI ring system has been achieved by the deployment of novel methods for heterocycle synthesis (see scheme). Boc = *tert*-butoxycarbonyl, TBS = *tert*-butyldimethylsilyl.



Angew. Chem. **2001**, *113*, 3775–3779

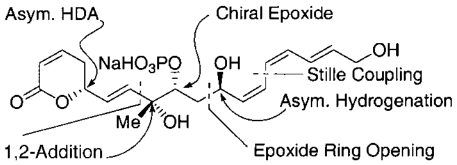
C. J. Forsyth,* J. Hao, J. Aiguade 3663–3667

Synthesis of the (+)-C26–C40 Domain of the Azaspiracids by a Novel Double Intramolecular Hetero-Michael Addition Strategy

Keywords: azaspiracid · natural products · synthetic methods · total synthesis

---

The most selective protein phosphatase inhibitor identified to date, fostriecin was synthesized in a highly convergent manner by a chiral building block approach (see picture). Three of the four stereocenters were introduced by using catalytic methods, including novel and practical applications of asymmetric hetero-Diels–Alder (HDA) and hydrolytic kinetic resolution reactions.



Angew. Chem. **2001**, *113*, 3779–3782

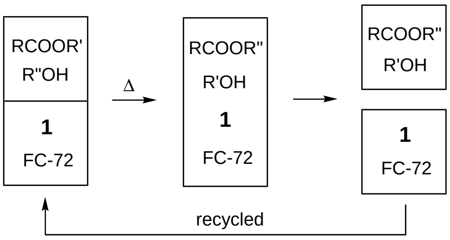
D. E. Chavez, E. N. Jacobsen* 3667–3670

Total Synthesis of Fostriecin (CI-920)

Keywords: antitumor agents · asymmetric catalysis · Diels–Alder reactions · epoxides · enzyme inhibitors · total synthesis

1433-7851/01/4019-3498 $ 17.50+.50/0

There is no need for the recovery of the catalyst in the fluorous biphasic transesterification catalyzed by $[\{Cl(C_6F_{13}CH_2CH_2)_2SnOSn(C_6F_{13}CH_2CH_2)_2Cl\}_2]$ (**1**; see scheme), which results in quantitative conversions and yields. An FC-72 solution of the dimeric fluoroalkyldistannoxane **1** can be recycled repeatedly without having to recover the neat catalyst.



Angew. Chem. **2001**, *113*, 3782–3784

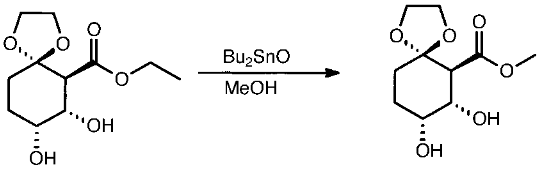
J. Xiang, S. Toyoshima, A. Orita,
J. Otera* 3670–3672

A Practical and Green Chemical Process: Fluoroalkyldistannoxane-Catalyzed Biphasic Transesterification

Keywords: fluorinated ligands · homogeneous catalysis · synthetic methods · tin · transesterification

---

An extraordinarily versatile transesterification of simple or highly functionalized esters of aliphatic and aromatic carboxylic acids in high yields is catalyzed by dibutyltin oxide [Eq. (1)]. The reaction is compatible with several functional groups, for example, acetals, ketals, aliphatic bromides, enol ethers, urethanes, as well as free hydroxy, phenolic, and amino groups, and even with water.



(1)

Angew. Chem. **2001**, *113*, 3784–3786

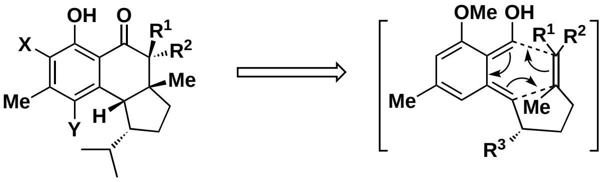
P. Baumhof, R. Mazitschek,
A. Giannis* 3672–3674

A Mild and Effective Method for the Transesterification of Carboxylic Acid Esters

Keywords: homogenous catalysis · synthetic methods · tin · transesterification

---

A streamlined and general method for the construction of benzannulated systems such as **I** involves the intramolecular Diels–Alder reaction of photochemically generated hydroxy-*o*-quinodimethanes, for example, **II**. The method was optimized to set the stage for the synthesis of the naturally occurring hamigerans.



I **II**

Angew. Chem. **2001**, *113*, 3787–3790

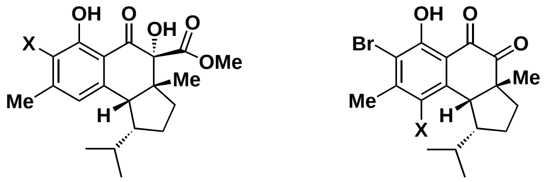
K. C. Nicolaou,* D. Gray,
J. Tae 3675–3678

Total Synthesis of Hamigerans: Part 1. Development of Synthetic Technology for the Construction of Benzannulated Polycyclic Systems by the Intramolecular Trapping of Photogenerated Hydroxy-*o*-quinodimethanes and Synthesis of Key Building Blocks

Keywords: cycloaddition · natural products · photochemistry · quinodimethanes · total synthesis

---

The synthesis of libraries of natural products is important for chemical biology studies. With this in mind, the intramolecular Diels–Alder reaction of photochemically generated hydroxy-*o*-quinodimethanes was used to produce the naturally occurring hamigerans **1**–**4** and several of their epimers.



1: X = H : debromohamigeran A **3: X = H : hamigeran B**
2: X = Br: hamigeran A **4: X = Br: 4-bromohamigeran B**

Angew. Chem. **2001**, *113*, 3791–3795

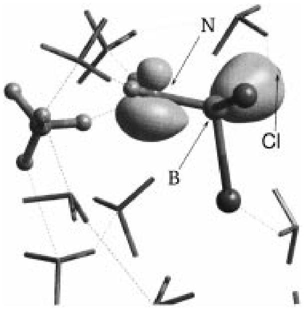
K. C. Nicolaou,* D. Gray,
J. Tae 3679–3683

Total Synthesis of Hamigerans: Part 2. Implementation of the Intramolecular Diels–Alder Trapping of Photochemically Generated Hydroxy-*o*-quinodimethanes; Strategy and Completion of the Synthesis

Keywords: cycloaddition · natural products · photochemistry · quinodimethanes · total synthesis

Contrary to the concerted two-step mechanism in the gas phase, the ammonolysis of boron trichloride in excess ammonia in the liquid phase follows an ionic three-step mechanism, according to a Car–Parrinello molecular dynamics investigation. The pair of electrons in the N–H bond becomes a lone electron pair on the N atom, whereas the electrons in the B–Cl bond leave the ionic intermediate together with the Cl atom (see picture).

Angew. Chem. **2001**, *113*, 3795 – 3797



S. Reinhardt, C. M. Marian,*
I. Frank .... 3683 – 3685

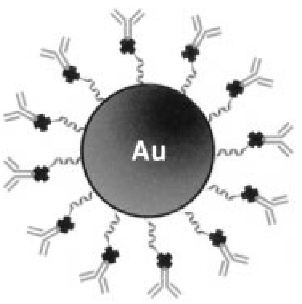
The Influence of Excess Ammonia on the Mechanism of the Reaction of Boron Trichloride with Ammonia—An ab initio Molecular Dynamics Study

Keywords: density functional calculations • molecular dynamics • reaction mechanisms • solvent effects • solvolysis

---

A supramolecular construction kit comprises DNA-functionalized gold nanoparticles, covalent DNA – streptavidin conjugates, and biotinylated antibodies and allows the generation of functional nanoparticle reagents (see schematic illustration). The combination of specific antibodies and DNA-stabilized colloidal gold is applicable for the detection of antigens attached to a chip.

Angew. Chem. **2001**, *113*, 3798 – 3801



C. M. Niemeyer,* B. Ceyhan 3685 – 3688

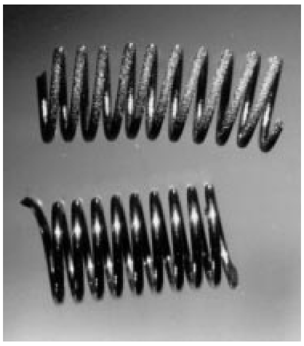
DNA-Directed Functionalization of Colloidal Gold with Proteins

Keywords: analytical methods • DNA • nanostructures • proteins • supramolecular chemistry

---

The macroscopic shape of the starting material is retained during the solid/gas reaction between iron and gaseous $SiCl_4$, which leads to the formation of iron silicide FeSi (as well as $FeCl_2$, which is gaseous under the reaction conditions (1000°C)): If, for example, an iron wire spiral (see bottom of picture) is used, the reaction product FeSi also retains this spiral form (top).

Angew. Chem. **2001**, *113*, 3801 – 3803



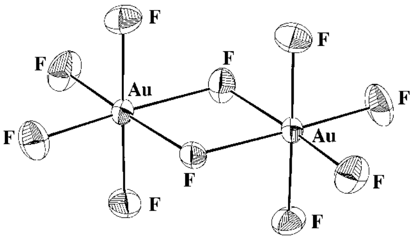
M. Binnewies,* A. Meyer,
M. Schütte .... 3688 – 3690

The Unusual Formation of Iron Silicide by Reaction of Iron with $SiCl_4$

Keywords: iron • silicon • solid-state reactions

The only pentafluoride with a dimeric structure is gold pentafluoride (see structure). According to calculations it has the highest fluoride-ion affinity and thus is the strongest Lewis acid known to date. It decomposes in HF under its own acidity to give AuF_3 and F_2.

Angew. Chem. **2001**, *113*, 3803 – 3805



I.-C. Hwang, K. Seppelt* ... 3690 – 3693

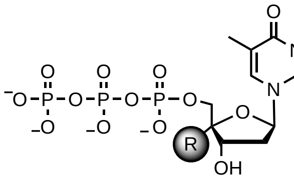
Gold Pentafluoride: Structure and Fluoride Ion Affinity

Keywords: ab initio calculations • fluorides • gold • superacidic systems

---

Do enzyme – sugar interactions contribute to DNA-polymerase fidelity? With the novel chemical probes **1** ($R = CH_3$, CH_2CH_3, $CH(CH_3)_2$, $CH_2CH(CH_3)_2$), which are used by a DNA polymerase more selectively than the natural counterpart ($R = H$), insights are obtained into the influence of enzyme – sugar interactions on the selectivity of the enzyme.

Angew. Chem. **2001**, *113*, 3806 – 3808

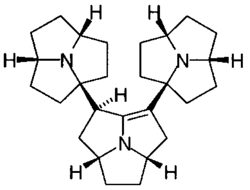

1

D. Summerer, A. Marx* .... 3693 – 3695

DNA Polymerase Selectivity: Sugar Interactions Monitored with High-Fidelity Nucleotides

Keywords: bioorganic chemistry • DNA polymerases • DNA recognition • DNA replication • nucleotides

A vicelike grip on a proton is exerted by the unusual nonacyclic product **1**, which forms spontaneously in a unique enamine trimerization that occurs when azatriquinenamine is heated in the presence of a proton source. pK_a measurements and computational modeling of the proton affinity substantiate the superbasic character of the trimer.



1

Angew. Chem. **2001**, *113*, 3809–3811

Keywords: ab initio calculations · enamines · polycycles · receptors · superbases

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* Author to whom correspondence should be addressed

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