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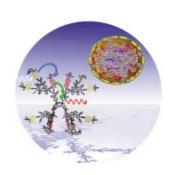
Deutscher Chemiker

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Pages 1809 - 1972

#### **COVER PICTURE**

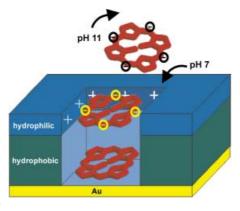
The cover picture shows the calculated energy-minimized 3D-structure of a polyphenylene dendrimer, which was prepared in a multistep synthesis. The nanoparticle carries three different types of chromophores, located in the center (terrylene), within the scaffold (perylene), and at the periphery (naphthalene). This multichromophoric triad absorbs over the whole range of the visible spectrum and shows, as shown in the picture, a stepwise vectorial energy transfer over a distance of 30 Å from the surface to the core. There is more about polyphenylene chromophores in the communication from Müllen et al. on p. 1904 ff.



**REVIEW** -Contents

Hydrogen-bond chains and stiff segments rigidify spherical lipid membranes in bulk water and molecular monolayers on carrier systems. Reactive components can be anchored within them at any desired separation on the Ångström scale. Reactive nanometer-sized hills and clefts are thus accessible and should be useful in the construction of complex reaction systems, including redox-active dyes (see picture).

Angew. Chem. 2002, 114, 1906-1931



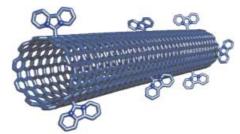
G. Li, W. Fudickar, M. Skupin, A. Klyszcz, C. Draeger, M. Lauer, J.-H. Fuhrhop\* ...... 1828–1852

Rigid Lipid Membranes and Nanometer Clefts: Motifs for the Creation of Molecular Landscapes

**Keywords:** membranes • molecular landscapes · nanostructures · self-assembly · synkinesis

Soluble carbon nanotubes can be obtained by chemical derivatization, such as functionalization of defects, covalent sidewall functionalization (see picture), and noncovalent formation of adducts with surfactants or polymers. This new nanochemistry not only provides a combination of the unprecedented materials properties of nanotubes with those of other compound classes, but also forms the basis for the processibility of these systems.

Angew. Chem. 2002, 114, 1933-1939



Functionalization of Single-Walled Carbon Nanotubes

**Keywords:** addition • carbon allotropes • electronic components . host-guest systems · nanotubes

## **HIGHLIGHTS**

Si bond-stretch isomers? Different Si-Si separations are proposed for the bond-stretch isomers of tetrasilabicyclobutane compounds. With 1, the existence of an isomer with a longer bond between the bridge-head Si atoms could be demonstrated. Thus the Si compound 1 has been obtained even before the corresponding carbon homologue. With regard to the great advances in the chemistry of small Si rings, other ring systems are discussed.

Angew. Chem. 2002, 114, 1941 – 1943

SiMe<sub>2</sub>tBu tBuMe<sub>2</sub>Si

R. Koch, M. Weidenbruch\* 1861 - 1863

A Spiropentasiladiene and Other Strained Silicon-Containing Rings

**Keywords:** bond-stretch isomers • silicon • small-ring systems • solid-state structures · spiro compounds

N. Kuhnert\* ...... 1863–1866

Microwave-Assisted Reactions in Organic Synthesis —Are There Any Nonthermal Microwave Effects?

**Keywords:** microwave chemistry • solid-phase synthesis · solvent effects · synthetic methods

"Definitely not" is the answer to the question posed in the title: New experiments, which allow a comparison between microwave reaction conditions and conventional reaction conditions for the first time, support this statement. However, it has not yet been clarified whether or not there are special microwave effects in the selectivity of chemical reactions.

Angew. Chem. 2002, 114, 1943-1946



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

Catalytic Activity and Poisoning of Specific Sites on Supported Metal **Nanoparticles** 

J. Hoffmann, V. Johánek, J. Hartmann, J. Libuda,\* H.-J. Freund

Understanding Zeolite Catalysis: Inverse Shape Selectivity Revised

M. Schenk, S. Calero, T. L. M. Maesen, L. L. van Benthem, M. G. Verbeek, B. Smit\*

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

L. C. Branco, J. G. Crespo, C. A. M. Afonso\*

Atom-Transfer Tandem Radical Cyclization Reactions Promoted by Lewis

D. Yang,\* S. Gu, H.-W. Zhao, N.-Y. Zhu

**Psychrophilic marine bacteria** can produce polyunsaturated fatty acids (PUFAs; see scheme). Until recently, PUFAs were known as important metabolites exclusively produced by eukaryotes with oxygen-dependent desaturases. Surprisingly, functional analysis of a PUFA biosynthetic gene cluster from *Shewanella* sp. strain SCRC2738 points towards a unique mixed pathway involving a polyketide synthase.

Angew. Chem. 2002, 114, 1947 - 1950

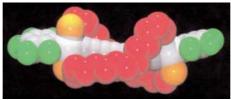
U. Kaulmann, C. Hertweck\* 1866-1869

Biosynthesis of Polyunsaturated Fatty Acids by Polyketide Synthases

**Keywords:** biosynthesis • biotechnology • fatty acids • marine bacteria • polyketides

#### COMMUNICATIONS

Neither bonding interactions between the strands nor covalent bonds to metal templates dispersed throughout the strands are needed for the molecules presented here to adopt double-helical structures (see picture). The molecules consist of



rigid  $(C \equiv C)_m$  chains that bridge two platinum atoms, which are in turn bridged by two diphosphane ligands of the formula  $Ar_2P(CH_2)_mPAr_2$ .

J. Stahl, J. C. Bohling, E. B. Bauer, T. B. Peters, W. Mohr, J. M. Martín-Alvarez, F. Hampel, J. A. Gladysz\* ................ 1871–1876

sp Carbon Chains Surrounded by sp<sup>3</sup> Carbon Double Helices: A Class of Molecules that are Accessible by Self-Assembly and Models for "Insulated" Molecular-Scale Devices

**Keywords:** Helical structures • Metathesis • Molecular devices • Platinum • Self-assembly

Angew. Chem. 2002, 114, 1951-1957

**The choice of enzyme is decisive**: for the enzyme-catalyzed addition of HCN to 4-substituted cyclohexanones **1**, highly selective biocatalysts are available that allow control to yield the *cis* or the *trans* addition product **2**. Modeling of the *S* enzyme-substrate complex reveals remarkable parallels with the Prelog/Ringold model of the LADH-catalyzed hydrogenation of cyclohexanones.

Angew. Chem. 2002, 114, 1957-1959

F. Effenberger,\* J. Roos, C. Kobler ......................... 1876–1879

cis – trans Selectivity of Enzyme-Catalyzed Additions to 4-Substituted Cyclohexanones—Correlation with the Prelog/Ringold Model of Enzymatic Hydrogenation

**Keywords:** cyanohydrins • enzyme catalysis • ketones • lyases • molecular modeling

**Hydroxy groups added consecutively**: the reaction of Ni<sup>II</sup> cyclotetrapeptide complexes **1** with oxygen affords selective and stepwise  $\alpha$ -C hydroxylation of the two ligand glycine units (formation of **2** and **3**). The mechanism of these reactions, which occur via Ni<sup>III</sup> intermediates, is related to the function of the coppercontaining enzyme peptidylglycine  $\alpha$ -hydroxylating monooxygenase (PHM).

Angew. Chem. 2002, 114, 1969-1972

K. Haas, H. Dialer, H. Piotrowski, J. Schapp, W. Beck\* ...... 1879–1881

Selective  $\alpha$ -Carbon Hydroxylation of Glycine in Nickel(II) – Cyclotetrapeptide Complexes by Oxygen

**Keywords:** amino acids • cyclopeptides • hydroxylation • nickel • N ligands

A nanostructured phase: this is how the Ga<sub>22</sub> unit in the  $[Ga_{12}(GaR)_{10}]^{2-}$  cluster (see picture), which exhibits a structure distinctly different from the one reported for other Ga22 units, can be interpreted. In this cluster 11 Ga atoms (black spheres) are grouped around a central Ga atom, this Ga<sub>12</sub> core is then stabilized by ten GaR units.



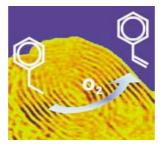
A. Schnepf,\* G. Stösser, H. Schnöckel\* ...... 1882 – 1884

 $[Ga_{22}\{N(SiMe_3)_2\}_{10}]^{2-}$ : A Metalloid Cluster Compound with a Variation of the Ga22 Framework

**Keywords:** cluster compounds • gallium • metal-metal interactions · subvalent compounds

Angew. Chem. 2002, 114, 1959-1962

The microstructure is appealing: Onion-like carbon forms are used for the first time in the field of catalysis and thus open new routes for the potential applications of nonplanar carbon materials. An example is given with the oxidative dehydrogenation of ethylbenzene to styrene (see scheme).



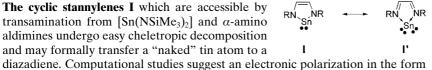
N. Keller, N. I. Maksimova, V. V. Roddatis, M. Schur, G. Mestl,\* Y. V. Butenko, V. L. Kuznetsov, R. Schlögl\* ...... 1885 – 1888

The Catalytic Use of Onion-Like Carbon Materials for Styrene Synthesis by Oxidative Dehydrogenation of Ethylbenzene

**Keywords:** carbon allotropes • dehydrogenation · heterogeneous catalysis · surface chemistry

Angew. Chem. 2002, 114, 1962-1966

The cyclic stannylenes I which are accessible by transamination from  $[Sn(NSiMe_3)_2]$  and  $\alpha$ -amino aldimines undergo easy cheletropic decomposition and may formally transfer a "naked" tin atom to a



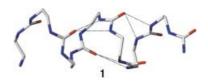
T. Gans-Eichler, D. Gudat,\* M. Nieger ...... 1888 – 1891

Tin Analogues of "Arduengo Carbenes": Synthesis of  $1,3,2\lambda^2$ -Diazastannoles and Transfer of Sn Atoms between a  $1,3,2\lambda^2$ -Diazastannole and a Diazadiene

Angew. Chem. 2002, 114, 1966-1969

**Keywords:** carbene homologues • cheletropic reaction · cycloaddition · oxidative addition • tin

Closely related to the  $(P)2.6_{14}$  helix of  $\gamma$ -peptides: Heptamer 1 bearing side chains of Ala, Val, and Tyr adopts a stable 2.5-helical secondary structure in solution that is characterized by a pitch of approximately



5.1 Å and by the simultaneous presence of 12- and 14-membered hydrogenbonded rings. Thus N,N'-linked oligoureas belong to the growing family of nonnatural non-peptide oligomers with defined and predictable secondary structure.

of the chelated atom canonical structure  $\mathbf{I}'$  as the reason for this behavior.

Angew. Chem. 2002, 114, 1973-1975

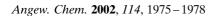
V. Semetey, D. Rognan, C. Hemmerlin, R. Graff, J.-P. Briand, M. Marraud, 

Stable Helical Secondary Structure in Short-Chain N,N'-Linked Oligoureas Bearing Proteinogenic Side Chains

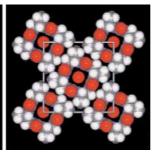
**Keywords:** molecular modeling • NMR spectroscopy · oligoureas · peptidomimetics · structure elucidation



Square-shaped hydrogen-bonded polar nanotubes are formed when the  $C_4$ -symmetrical all-S cyclotetraurea bearing side chains of alanine self-assembles in the solid state (see picture). The four urea fragments in the macrocyle present an all-trans planar conformation with an unidirectional alignment of all the carbonyl groups. The anisotropy is further maintained in the crystal as neighboring tubes are all arranged in the same direction.







V. Semetey, C. Didierjean, J.-P. Briand, A. Aubry, G. Guichard\* .... 1895 – 1898

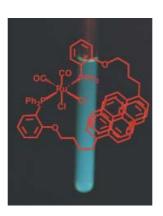
Self-Assembling Organic Nanotubes from Enantiopure Cyclo-N,N'-Linked Oligoureas: Design, Synthesis, and Crystal Structure

**Keywords:** macrocycles • nanotubes • peptidomimetics · self-assembly · solid-state structures



From weak blue to intense blue-green: this change in emission results when [RuCl<sub>2</sub>(POC4Pvr-P<sub>2</sub>O)<sub>2</sub>] reacts with carbon monoxide. The reason is the formation of the dicarbonyl complex shown (see picture), in which CO has replaced the labile coordinating site of the hemilabile ligand POC4-Pyr. The increased flexibility in the tethered pyrenyl groups allows the formation of inter- and intramolecular excimers in this complex. POC4Pyr = 4-{2-(diphenylphosphanyl)phenoxy}butylpyrene.

Angew. Chem. 2002, 114, 1978-1980



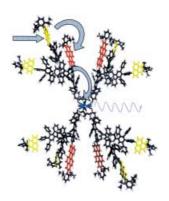
C. W. Rogers, M. O. Wolf\* 1898 - 1900

Drastic Luminescence Response to Carbon Monoxide from a Ru<sup>II</sup> Complex Containing a Hemilabile Phosphane Pyrene Ether

**Keywords:** fluorescence • hemilabile ligands · ruthenium · sensors

Dendritic multichromophores based on a rigid polyphenylene scaffold contain up to three different types of rylene chromophores incorporated at the focal point, the scaffold, and the periphery of the dendrimer. An energy gradient between the periphery and the core is thus generated and allows an efficient transfer of excitation energy (see picture).

Angew. Chem. 2002, 114, 1980-1984



T. Weil, E. Reuther, K. Müllen\* ...... 1900–1904

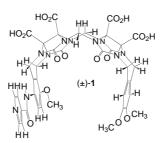
Shape-Persistent, Fluorescent Polyphenylene Dyads and a Triad for Efficient Vectorial Transduction of **Excitation Energy** 

**Keywords:** chromophores • dendrimers • dyes/pigments · energy transfer · light harvesting



Enantiomeric self-recognition is triggered by addition of [Pd(ONO<sub>2</sub>)-(en)] (2; en = 1,2-ethylenediamine) to a solution of  $(\pm)$ -1 in water, a process that results in a 2:2 aggregate  $(\mathbf{1}_2 \cdot \mathbf{2}_2)$  and  $(ent-\mathbf{1})_2 \cdot \mathbf{2}_2$  of welldefined geometry. The use of analytical ultracentrifugation as a tool for the elucidation of molecular weight and stoichiometry in synthetic self-assembly studies is highlighted.

Angew. Chem. 2002, 114, 1985-1987



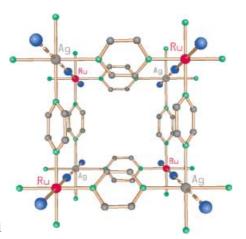
L. Isaacs,\* D. Witt .......... 1905-1907

Enantiomeric Self-Recognition of a Facial Amphiphile Triggered by  $[\{Pd(ONO_2)(en)\}_2]$ 

**Keywords:** amphiphiles • hydrophobic effect · palladium · pi interactions · glycoluril · self-assembly

Three structural motifs have been obtained by using the novel building block trans-[RuCl<sub>2</sub>(pyz)<sub>4</sub>] with different silver salts: A two-dimensional network with an unprecedented double-honeycomb topology, a three-dimensional array with the rutile (6,3) structure, and an interesting tetragonal network with both Ru and Ag in octahedral environments, which can be related to the rock-salt topology (see picture).

Angew. Chem. 2002, 114, 1987-1991

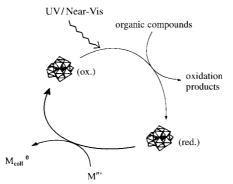


Crystal Engineering of Mixed-Metal Ru–Ag Coordination Networks by Using the *trans*-[RuCl<sub>2</sub>(pyz)<sub>4</sub>] (pyz = pyrazine) Building Block

**Keywords:** coordination polymers • N ligands • ruthenium • silver

Fine metal nanoparticles of Ag, Au, Pd, and Pt were obtained at room temperature, by simple mixing of the corresponding metal ions with reduced polyoxometalates (POMs) that serve both as photocatalysts and stabilizers, according to the cycle shown.

Angew. Chem. 2002, 114, 1991-1994



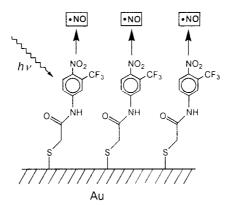
A. Troupis,\* A. Hiskia, E. Papaconstantinou\* ..... 1911–1914

Synthesis of Metal Nanoparticles by Using Polyoxometalates as Photocatalysts and Stabilizers

**Keywords:** homogeneous catalysis • nanostructures • photochemistry • polyoxometalates

Quantitative release of NO is exclusively controlled by light excitation in a self-assembled monolayer of an NO donor on a gold surface (see picture). The low excitation energy required, the absence of noxious side effects, the thermal stability under physiological conditions, and the ease of preparation are additional advantages offered by the monolayer-modified gold plate.

Angew. Chem. 2002, 114, 1994-1997



S. Sortino,\* S. Petralia, G. Compagnini, S. Conoci, G. Condorelli .... 1914–1917

Light-Controlled Nitric Oxide Generation from a Novel Self-Assembled Monolayer on a Gold Surface

**Keywords:** nitrogen oxides • photochemistry • monolayers



Samarium learns another trick: Complete stereospecific cyclopropanation of  $\alpha,\beta$ -unsaturated amides, in which the double bond is di-, tri-, or tetrasubstituted is promoted by Sm/CH<sub>2</sub>I<sub>2</sub> [Eq. (1)]. The reaction is high yielding and unaffected by the bulk of the substituents  $R^1-R^4$ .

complete stereospecificity

Angew. Chem. 2002, 114, 1997-1999

J. M. Concellón,\* H. Rodríguez-Solla, C. Gómez ...... 1917–1919

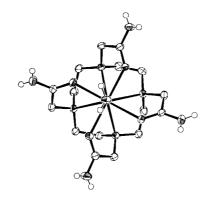
Complete Stereospecific Cyclopropanation of  $\alpha.\beta$ -Unsaturated Amides Promoted by Sm/CH<sub>2</sub>I<sub>2</sub>

**Keywords:** carbenoids • cyclopropanations • samarium • stereospecificity



Contrast agent for magnetic resonance imaging: The exchangeable amide protons in the Yb3+ complex of 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetamide (see crystal structure) act as efficient antennae for transfer of saturated spins to bulk water. Saturation of all eight protons in a 5 mm solution of this complex results in a 38% decrease in the signal intensity of bulk water. The compound thus has promise as a magnetization-transfer contrast agent for magnetic resonance imaging.

Angew. Chem. 2002, 114, 1999-2001

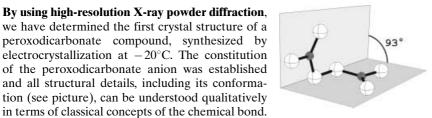


S. Zhang, L. Michaudet, S. Burgess, A. D. Sherry\* ...... 1919–1921

The Amide Protons of an Ytterbium(III) dota Tetraamide Complex Act as Efficient Antennae for Transfer of Magnetization to Bulk Water

**Keywords:** amides • imaging agents • lanthanides · macrocycles · NMR spectroscopy

#### By using high-resolution X-ray powder diffraction, we have determined the first crystal structure of a peroxodicarbonate compound, synthesized by electrocrystallization at $-20^{\circ}$ C. The constitution of the peroxodicarbonate anion was established and all structural details, including its conformation (see picture), can be understood qualitatively



R. E. Dinnebier, S. Vensky, P. W. Stephens, M. Jansen\* 1922 - 1924

Crystal Structure of  $K_2[C_2O_6]$ —First Proof of Existence and Constitution of a Peroxodicarbonate Ion

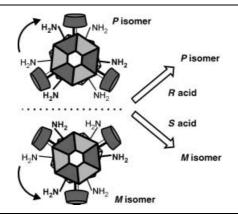
**Keywords:** electrocrystallization • peroxodicarbonate · solid-state structures · structure eluciation · X-ray powder diffraction

Angew. Chem. 2002, 114, 2002-2004



Stereospecific recognition of substrate molecules for certain chiral carboxylic acids is achieved by a noncovalent receptor system based on acid-base interactions of amino groups in the host system with the carboxylic acids. Enantioselectivity in the binding process is caused by secondary interactions with a chiral platform that preorganizes the amino functionalities (see scheme).

Angew. Chem. 2002, 114, 2004-2009



T. Ishi-i, M. Crego-Calama, P. Timmerman,\* D. N. Reinhoudt,\* 

Self-Assembled Receptors for Enantioselective Recognition of Chiral Carboxylic Acids in a Highly Cooperative Manner

**Keywords:** acid – base complexation • chirality · host-guest systems · hydrogen bonds · noncovalent interactions · supramolecular chemistry

B. M. Trost,\* K. Dogra, I. Hachiya,

T. Emura, D. L. Hughes,\* S. Krska,

R. A. Reamer, M. Palucki, N. Yasuda, P. J. Reider ...... 1929 – 1932

Unusual coordination in the asymmetric allylic alkylation catalyzed by molybdenum (see scheme) was revealed by a study on several ligands, for example, 1. Unexpectedly, only the nitrogen atom of one picolinamide group coordinates to Mo, while the other amide group rigidifies the system. Based on the effectiveness of the bisdeprotonated ligand, the observed reaction can be rationalized and new ligands can be designed for asymmetric induction in allylic alkylations.

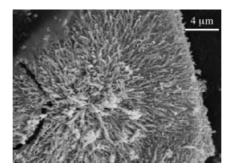
Designed Ligands as Probes for the Catalytic Binding Mode in Mo-Catalyzed Asymmetric Allylic Alkylation

**Keywords:** allylic compounds • asymmetric catalysis · ligand design · molybdenum · regioselectivity

Angew. Chem. 2002, 114, 2009-2012

A simple mixture of thiourea and  $AgNO_3$  in alkaline solution without any template or substrate, allowed to stand at room temperature, forms a unique self-supported pattern of  $Ag_2S$  nanorods. The picture shows a scanning electron micrograph of a typical product: a flake of polycrystalline  $Ag_2S$  with  $Ag_2S$  nanorods that radiate from a central point.

Angew. Chem. 2002, 114, 2012-2014



Q. Lu, F. Gao, D. Zhao\* .... 1932-1934

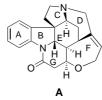
Creation of a Unique Self-Supported Pattern of Radially Aligned Semiconductor Ag<sub>2</sub>S Nanorods

**Keywords:** nanostructures • self-assembly • silver • sulfur



The power of palladium catalysts is shown in a total synthesis of (-)-strychnine (A). The construction of all the rings of this challenging molecule relied on  $Pd^0$ - or  $Pd^{II}$ -catalyzed reactions. The final step in this efficient synthesis involved the reduction of (+)-isostrychnine by a known method to form (-)-strychnine.

Angew. Chem. 2002, 114, 2014-2016



M. Nakanishi, M. Mori\* .... 1934–1936

Total Synthesis of (–)-Strychnine

**Keywords:** alkaloids • allylic compounds • Heck reaction • palladium • total synthesis

An efficient construction of the quinaldic acid macrocycle (see picture) of the antibiotic thiostrepton is based on state-of-the-art asymmetric synthesis. The 27-membered macrocycle includes a quinaldic acid moiety, a thiazole ring, and a dehydroalanine unit. The key steps in the convergent assembly included: a) amide bond formation, b) esterification, and c) macrolactamization.

Angew. Chem. 2002, 114, 2017-2020

K. C. Nicolaou,\* B. S. Safina, C. Funke, M. Zak, F. J. Zécri . . . . . . . . . . . . 1937 – 1940

Stereocontrolled Synthesis of the Quinaldic Acid Macrocyclic System of Thiostrepton

**Keywords:** antibiotics • asymmetric synthesis • macrocycles • natural products • total synthesis



**The key step** in the dimerization of the azadiene **1** is a hetero-Diels-Alder reaction. The product **2** constitutes the dehydropiperidine core of the antibiotic thiostrepton.

Angew. Chem. 2002, 114, 2021-2025

K. C. Nicolaou,\* M. Nevalainen, B. S. Safina, M. Zak, S. Bulat 1941–1945

A Biomimetically Inspired Synthesis of the Dehydropiperidine Domain of Thiostrepton

**Keywords:** antibiotics • asymmetric synthesis • cycloaddition • natural products • total synthesis



The window of reactivity is relatively narrow in the first Suzuki cross-coupling of alkyl chlorides with alkyl 9-borabicyclo[3.3.1]nonane (9-BBN) derivatives catalyzed by  $[Pd_2(dba)_3]$  [Eq. (1); dba = (E,E)-dibenzylideneacetone]: whereas good yields are obtained with the ligand tricyclohexylphosphane for ligands that are appreciably larger or smaller, essentially no coupling is observed. As the conditions are compatible with a variety of functional groups, this method introduces a new class of substrates into the family of potential partners in palladium-catalyzed cross-coupling reactions.

$$R_{alkyl} - CI = R - (9-BBN) = \begin{cases} 5\% & [Pd_2(dba)_3] \\ 20\% & ligand \\ \hline 1.1 & CsOH \cdot H_2O \\ dioxane, 90 \, ^{\circ}C \end{cases} R_{alkyl} - R$$
 (1)

Angew. Chem. 2002, 114, 2025 - 2027

A Method for Palladium-Catalyzed Cross-Couplings of Simple Alkyl Chlorides: Suzuki Reactions Catalyzed by [Pd<sub>2</sub>(dba)<sub>3</sub>]/PCy<sub>3</sub>

**Keywords:** alkyl chlorides • cross-coupling • homogeneous catalysis • palladium • P ligands



Changes of two orders of magnitude or more in the epoxidation to hydroxylation ratio of propene by the iron-oxo species 1, the primary active species of cytochrome P450 (see scheme) occur when the molecular species is subject to NH···S hydrogen bonding and electronic polarization as in the protein pocket.

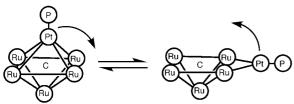
Angew. Chem. 2002, 114, 2027 - 2031

Hydrogen Bonding Modulates the Selectivity of Enzymatic Oxidation by P450: Chameleon Oxidant Behavior by Compound I

**Keywords:** density functional calculations • enzyme catalysis • epoxidation • hydroxylation • solvent effects



**Metal in motion**: The reaction of  $[Ru_5(CO)_{15}(\mu_5-C)]$  with  $[Pt(PtBu_3)_2]$  yields  $[Ru_5Pt(PtBu_3)(CO)_{15}(C)]$ . The product exists as two isomers, an open and a closed form, which interconvert rapidly on the NMR timescale by a process that resembles the diffusion of metal adatoms across a metal surface (see scheme; at  $20^{\circ}$ C the rate  $= 24\,000 \, \text{s}^{-1}$ ).



Angew. Chem. 2002, 114, 2031-2033

R. D. Adams,\* B. Captain, W. Fu, P. J. Pellechia, M. D. Smith 1951–1953

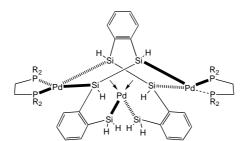
A Dynamic Rearrangement of a Metal Cluster in a Process that Closely Resembles the Hopping Mechanism of Adatom Diffusion on Metal Surfaces

**Keywords:** cluster compounds • platinum • rearrangements • ruthenium



 $Pd^{II}$  not  $Pd^{VI}$ : Electronic structure calculations indicate that the central palladium atom in the trinuclear Pd compound (see picture) is bonded to two SiH<sub>2</sub>R groups and two Si—Si  $\sigma$  bonds, consistent with an oxidation state of  $Pd^{II}$ , not  $Pd^{VI}$ , as might otherwise be inferred from the structural data.

Angew. Chem. 2002, 114, 2033-2036



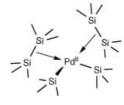
Electronic Structure and Bonding in Hexacoordinate Silyl – Palladium Complexes

**Keywords:** bond theory • density functional calculations • electronic structure • palladium • Si ligands



Side-bound Si–Si single bonds: A theoretical study indicates that in a recently reported compound, two Si–Si bonds are side-on coordinated to a square-planar  $Pd^{II}$  ion (see picture).

Angew. Chem. 2002, 114, 2036-2039



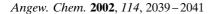


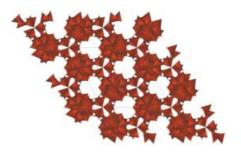
Hexakis(silyl)palladium(vi) or Palladium(II) with  $\eta^2$ -Disilane Ligands?

**Keywords:** agostic interactions • density functional calculations • electronic structure • palladium • Si ligands



Fine-tuning structures: A family of noncluster-based 3D open-framework indium chalcogenides are reported. The framework composition is highly flexible and controllable. Such a compositional diversity makes it feasible to tune structural, electronic, and optical properties. The structure shows a polyhedral view of 3D cross-linking in an In—Te compound.





A 3D Open-Framework Indium Telluride and Its Selenide and Sulfide Analogues

**Keywords:** chalcogens • indium • microporous materials • self-assembly

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### **CORRIGENDUM**

In the review by L. Que, Jr. and W. B. Tolman (Angew. Chem. Int. Ed. 2002, 41, 1114-1137) it was incorrectly stated that the Fe<sup>III</sup>Fe<sup>IV</sup> complex reported by Lee et al. in ref. [54] has a bis( $\mu$ -oxo)diiron structure. In fact, in ref. [54] it is made clear that from the experimental data for the complex the mode of ligation could not be specified. The authors apologize for this mistake.