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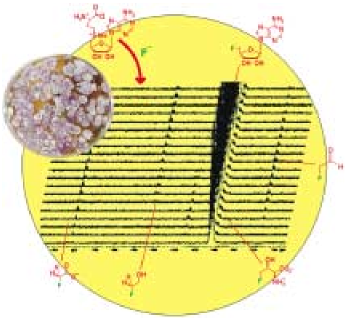
Pages 3723–3926

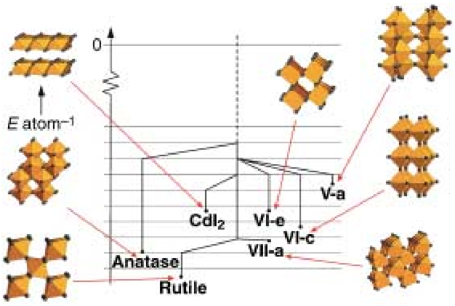
COVER PICTURE



The cover picture shows a series of ^{19}F NMR spectra taken every hour during the monitoring of a time-course experiment after addition of 5′-fluoro-5′-deoxyadenosine (5′-FDA) to a cell-free extract of *Streptomyces cattleya.* This bacterium has the unusual capacity to biosynthesise organofluorine compounds from inorganic fluoride. The ^{19}F NMR spectra illustrate that 5′-FDA is a true intermediate in the biosynthesis of fluoroacetate and 4-fluorothreonine. Other intermediates such as fluoroacetaldehyde are also observed for the first time. In a separate experiment, inorganic fluoride was converted into fluoroacetate, thus indicating that all of the enzymes involved in the fluoroacetate biosynthesis pathway are active in the cell-free extract. These experiments report the first cell-free biotransformations of inorganic fluoride into fluoroacetate, the most ubiquitous organic fluorine natural product, and pave the way for a biotechnological approach to organofluorine synthesis. Full details are described by O'Hagan and co-workers on p. 3913 ff.

REVIEW

Contents



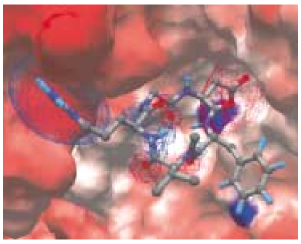
Hunter gatherers and not creators is how synthetic chemists could be described following a concept for the development of the (currently not yet feasible) goal-oriented synthesis of new solid-state compounds. The first step consists of the identification of realistic synthesis goals, which is achieved by the exploration of the energy landscape of the chemical system of interest using global optimization methods. Less developed are approaches for the second step, the rational design of feasible synthesis routes. Here, the crucial issues are the use of synthesis routes with extremely low activation and the control of nucleation processes. The picture shows the results of the theoretical exploration of the energy landscape of MgF_2 (structure candidates of low energy and the barrier structure depicted as a tree graph.)

Angew. Chem. **2002**, *114*, 3896–3917

Keywords: solid-state chemistry · solid-state reactions · structure prediction · synthesis planning

MINIREVIEW

A milestone in integrin research was the determination of the structure of the extracellular domain of $\alpha_v\beta_3$ integrin both in the free and complexed forms (an integrin complex with a cyclic RGD peptide is shown). Calculations on the interactions of the transmembrane α and β helices, NMR studies of the intracellular domain, and electron microsopic investigations provide a new insight into the mode of action of the integrin as well as a plausible model for signal transduction through the cell membrane.



Angew. Chem. **2002**, *114*, 3919–3927

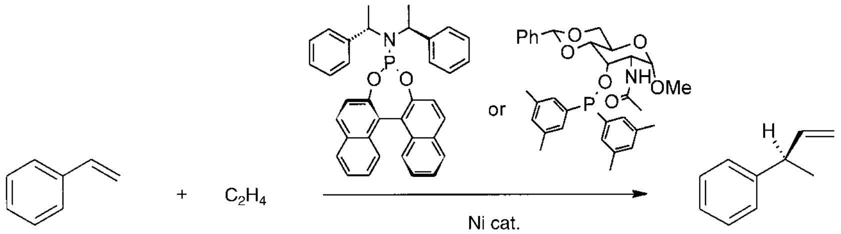
K.-E. Gottschalk,
H. Kessler* 3767–3774

The Structures of Integrins and Integrin–Ligand Complexes: Implications for Drug Design and Signal Transduction

Keywords: membrane proteins · molecular modeling · protein structures · signal transduction · structure–activity relationships

HIGHLIGHTS

At last the possibility of tailored catalyst design: Advances in the asymmetric hydrovinylation of olefins had not been made for a long time despite much effort, such that the interest in the reaction had dwindled. Recently, however, Leitner's and RajanBabu's research groups developed highly efficient, modular catalytic systems for this reaction (see scheme); thus, the prerequisite for further developments of this elegant reaction have finally been fulfilled.



Angew. Chem. **2002**, *114*, 3929–3932

L. J. Goossen* 3775–3778

Asymmetric Hydrovinylation: New Perspectives through Use of Modular Ligand Systems

Keywords: alkenes · asymmetric catalysis · dimerization · hydrovinylation · nickel

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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

A Synthesis Route to Enantiomerically Pure Jasmonoids — M. Ernst, G. Helmchen* ◆

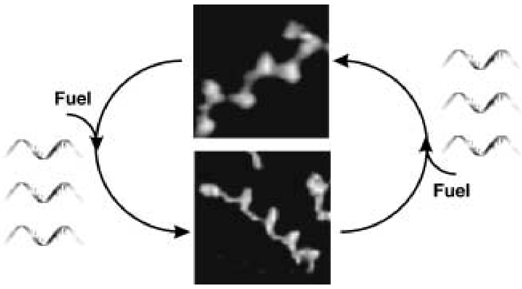
Pd^{II}-Catalyzed Cyclization of Alkynes with Aldehydes, Ketones, or Nitriles Initiated by the Acetoxypalladation of Alkynes — L. Zhao, X. Lu*

Experimental Observation and Confirmation of Icosahedral $W@Au_{12}$ and $Mo@Au_{12}$ Molecules — X. Li, B. Kiran, J. Li, H.-J. Zhai, L.-S. Wang*

Isoprenoid Biosynthesis through the Methylerythritol Phosphate Pathway: The (*E*)-4-Hydroxy-3-methylbut-2-enyl Diphosphate Synthase (GcpE) is a [4Fe–4S] Protein — M. Seemann, B. Tse Sum Bui, M. Wolff, D. Tritsch, N. Campos, A. Boronat, A. Marquet, M. Rohmer*

Tuning the Regioselectivity in the Palladium(II)-Catalyzed Isomerization of Alkylidenecyclopropyl Ketones: A Dramatic Salt Effect — S. Ma*, J. Zhang

Conformational changes of tailored DNA motifs, induced by chemical or physical means, can lead to nanomechanical motion, such as rotational movement, linear shrinking, and extension, and opening and closing of tweezer-shaped devices (see schematic illustration). The development of nanomotors based on nucleic acids might open up ways to fabricate molecular machines which are programmable to autonomously perform logical or mechanical tasks.



Angew. Chem. **2002**, *114*, 3933–3937

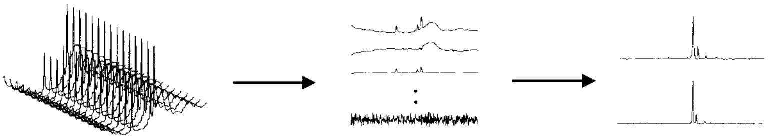
C. M. Niemeyer,* M. Adler . 3779–3783

Nanomechanical Devices Based on DNA

Keywords: DNA · molecular devices · nanostructures · supramolecular chemistry

COMMUNICATIONS

The pure-component spectra of $[HRh(CO)_4]$ and $[DRh(CO)_4]$ were obtained by investigating solutions of $[Rh_4(CO)_{12}]$ in *n*-hexane upon exposure to varying partial pressures of H_2/CO and D_2/CO. The in situ high-pressure FTIR spectra were measured and subjected to band-target entropy minimization (BTEM), an advanced signal processing technique (shown schematically).



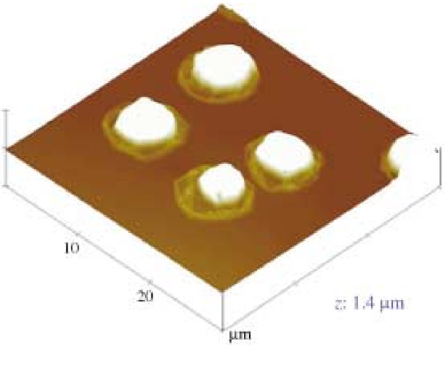
Angew. Chem. **2002**, *114*, 3940–3943

C. Li, E. Widjaja, W. Chew,
M. Garland* 3785–3789

Rhodium Tetracarbonyl Hydride:
The Elusive Metal Carbonyl Hydride

Keywords: carbonyl complexes · deuterium · hydrides · IR spectroscopy · rhodium

Water-soluble species can be deposited into preformed, multilayered polyelectrolyte capsules, templated onto melamine formaldehyde particles, with high integrity. Efficient encapsulation of albumin within capsules formed from a poly(styrene sulfonate)/poly(allylamine hydrochloride) composite was achieved at pH values below the isoelctric point of the protein through spontaneous deposition (see picture).



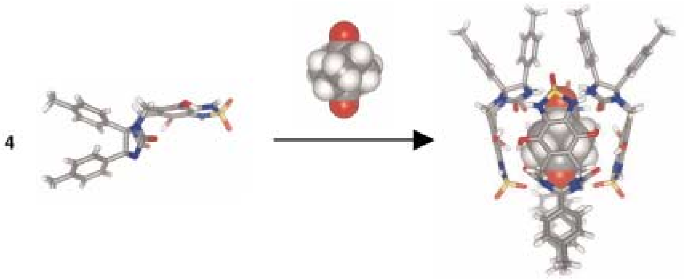
Angew. Chem. **2002**, *114*, 3943–3947

C. Gao,* E. Donath, H. Möhwald,
J. Shen 3789–3793

Spontaneous Deposition of Water-Soluble Substances into Microcapsules: Phenomenon, Mechanism, and Application

Keywords: capsules · colloids · layered compounds · polyelectrolytes · self-deposition

A tightly packed cavity that contains a guest molecule, 2,6-adamantanedione, is formed by a capsular hydrogen-bonded assembly (see figure). The crystal structure reveals an intricate network of hydrogen bonds, which specifically orients the ketone guest in the capsule cavity. The solid-state data complement the behavior of the assembly in the solution phase and provide a rationale for the guest-binding selectivity of the capsule.



Angew. Chem. **2002**, *114*, 3947–3950

D. W. Johnson, F. Hof, P. M. Iovine, C. Nuckolls, J. Rebek, Jr.* .. 3793–3796

Solid-State and Solution Studies of a Tetrameric Capsule and Its Guests

Keywords: host-guest systems · hydrogen bonds · molecular recognition · self-assembly · supramolecular chemistry

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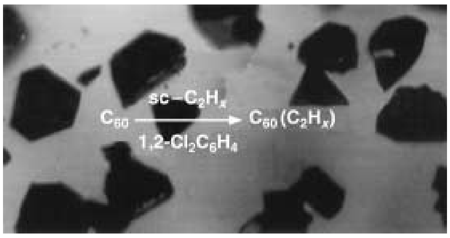
The intercalation of ethane and ethene into the octahedral interstitial sites of the C_{60} lattice can be achieved by antisolvent precipitation, using supercritical C_2H_4 and C_2H_6. This method of crystallization (see picture), which has yielded unprecedented intercalation compounds with hydrocarbons once thought too large to form such species, should be applicable to other gases, solvents, and fullerenes.



Angew. Chem. **2002**, *114*, 3950–3953

A. O'Neil, C. Wilson,* J. M. Webster, F. J. Allison, J. A. K. Howard, M. Poliakoff* 3796–3799

The Supercritical Fluid Antisolvent Synthesis of $C_{60}(C_2H_x)$ ($x = 4$ or 6): The Crystal Structures of Two Materials Which Were Thought Unlikely to Exist

Keywords: crystal growth · fullerenes · hydrocarbons · intercalations · supercritical fluids

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The pyridyltetrazolate ligand formed in situ from NaN_3 and 3-cyanopyridine in the presence of $ZnCl_2$ or $CdCl_2$ in water affords acentric (**1**) or chiral (**2**) coordination polymers, respectively. The corresponding reaction of $ZnCl_2$ with 4-cyanopyridine gives acentric **3** (not shown). Compounds **1**–**3** are second harmonic generation active.

(**1**: M = Zn, L = OH, $T = 160\,°C$, **2**: M = Cd, L = N_3, $T = 120\,°C$)

Angew. Chem. **2002**, *114*, 3954–3957

R.-G. Xiong,* X. Xue, H. Zhao, X.-Z. You, B. F. Abrahams,* Z. Xue 3800–3803

Novel, Acentric Metal–Organic Coordination Polymers from Hydrothermal Reactions Involving In Situ Ligand Synthesis

Keywords: cadmium · coordination polymers · hydrothermal synthesis · N ligands · nonlinear optics · zinc

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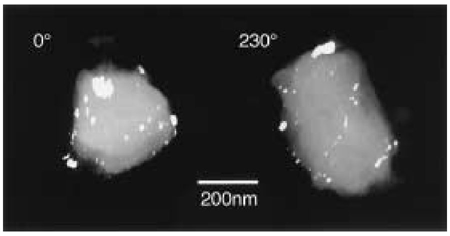
Images of supported nanoparticle catalysts have been recorded by scanning transmission electron microscopy (STEM), with a combination of high-angle annular dark-field (HAADF) imaging and back-scattered electron (BSE) imaging, which both utilize Rutherford-scattered electrons. The incoherent scattering process ensures that images are ideal for electron tomography and the reconstruction of 3D nanoparticle distributions (such as palladium on carbon, see picture).



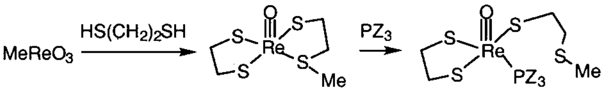
Angew. Chem. **2002**, *114*, 3958–3961

P. A. Midgley,* M. Weyland, J. M. Thomas,* P. L. Gai, E. D. Boyes 3804–3807

Probing the Spatial Distribution and Morphology of Supported Nanoparticles Using Rutherford-Scattered Electron Imaging

Keywords: back-scattering · electron microscopy · electron tomography · heterogeneous catalysis · nanoparticles

Methylation of a thiolate group, which has only been observed in vitamin B_{12} and its mimics, has been accomplished with $[MeReO_3]$ and $[MeReO(edt)PPh_3]$ (edt = 1,2-ethanedithiolato; see scheme). The proposed mechanism involves the formation of $[MeRe^{VII}O(edt)_2]$ through two stepwise condensation reactions; nucleophilic attack of a thiolate ligand on the methyl group leads to the product.



Angew. Chem. **2002**, *114*, 3961–3963

X. Shan, A. Ellern,
J. H. Espenson* 3807–3809

Methyl Transfer from Rhenium to Coordinated Thiolate Groups

Keywords: kinetics • methyl transfer • phosphane ligands • rhenium • S ligands

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A color change occurs when phosphate anions are added to an aqueous solution of H-bpmp (2,6-bis(bis(2-pyridylmethyl)aminomethyl)-4-methylphenol), zinc perchlorate, and pyrocatechol violet in a 1:2:1 molar ratio. The photograph shows the color of the mixture in the presence of no anions (far left), phosphate ions (yellow solution), and various other inorganic anions.

Angew. Chem. **2002**, *114*, 3963–3965

M. S. Han, D. H. Kim* 3809–3811

Naked-Eye Detection of Phosphate Ions in Water at Physiological pH: A Remarkably Selective and Easy-To-Assemble Colorimetric Phosphate-Sensing Probe

Keywords: anions • calorimetry • chromophores • phosphate • sensors

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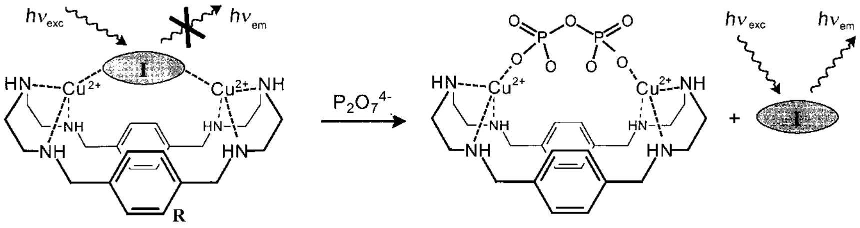
Displacement of the previously bound, and quenched, fluorescent indicator (**I**) by coordination of the pyrophosphate ion to the two Cu^{II} centers of the receptor **R** results in the generation of the natural fluorescence of the indicator, and thus signals pyrophosphate recognition (see scheme). Discrimination from interfering anions (HPO_4^{2-}, SO_4^{2-}, NO_3^-, Cl^-, NCO^-, N_3^-, acetate, benzoate) can be achieved by tuning the indicator affinity towards the receptor.



Angew. Chem. **2002**, *114*, 3965–3968

L. Fabbrizzi,* N. Marcotte, F. Stomeo,
A. Taglietti 3811–3814

Pyrophosphate Detection in Water by Fluorescence Competition Assays: Inducing Selectivity through the Choice of the Indicator

Keywords: fluorescent probes • molecular recognition • N ligands • pyrophosphate • sensors

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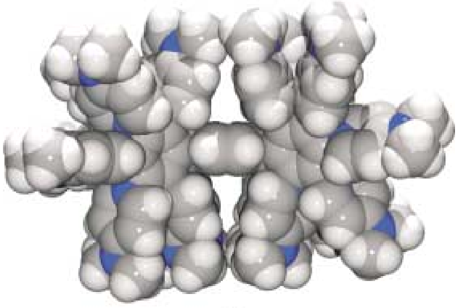
Cavities, indentations, and pockets aplenty! By means of self-activated silyl-assisted polyonio substitution (SASAPOS), *meso*-tetrakis(pentafluorophenyl)porphyrin can be nearly quantitatively converted into the twentyfold positively charged polycation **1**, within which 20 counterions are housed. The most drastic steric and electronic transformation of a porphyrin derivative to date has thus been achieved easily and efficiently.



1

Angew. Chem. **2002**, *114*, 3969–3971

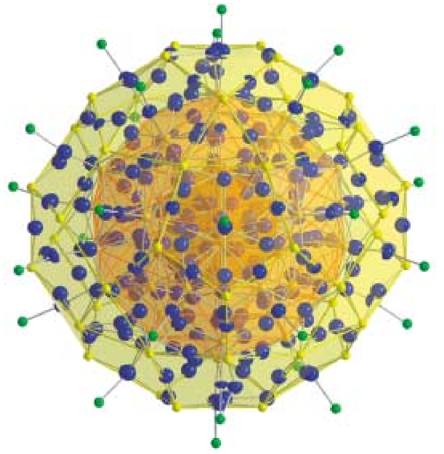
R. Weiss,* F. Pühlhofer, N. Jux,
K. Merz 3815–3817

SASAPOS, not Sisyphos: Highly Efficient 20-Step One-Pot Synthesis of a Discrete Organic–Inorganic Ion Cluster with a Porphyrin Core

Keywords: cluster compounds • electron transfer • electrostatic interactions • polycations • porphyrinoids

An almost spherical cluster with a diameter of about 2.5 nm is formed by Ag atoms (blue), S^{2-} ligands (yellow), and P atoms (green) of PnPr$_3$ ligands in [Ag$_{188}$S$_{94}$(PnPr$_3$)$_{30}$] (see picture). The phosphane ligands from the spherical Ag$_2$S cluster core point out like the spines of a hedgehog. The sulfur substructure is constructed from three almost spherical shells.

Angew. Chem. **2002**, *114*, 3972–3977



X.-J. Wang, T. Langetepe, C. Persau, B.-S. Kang, G. M. Sheldrick, D. Fenske* 3818–3822

Syntheses and Crystal Structures of the New Ag–S Clusters [Ag$_{70}$S$_{16}$(SPh)$_{34}$(PhCO$_2$)$_4$(triphos)$_4$] and [Ag$_{188}$S$_{94}$(PR$_3$)$_{30}$]

Keywords: cluster compounds · silver · structure elucidation · sulfur · X-ray diffraction

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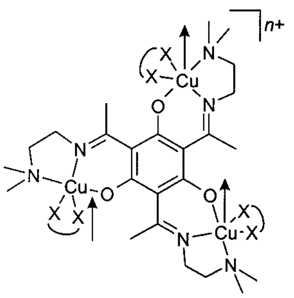
Trinuclear copper complexes have been obtained by using a 1,3,5-trihydroxybenzene ligand modified by attachment of pendant arms at the 2, 4, and 6 positions (see picture; X⌒X = bipyridine, 2-formylphenolate). The *m*-phenylene linkage results in ferromagnetic interactions through spin polarization in these complexes.

Angew. Chem. **2002**, *114*, 3984–3986



T. Glaser,* M. Gerenkamp, R. Fröhlich 3823–3825

Targeted Synthesis of Ferromagnetically Coupled Complexes with Modified 1,3,5-Trihydroxybenzene Ligands

Keywords: copper · ferromagnetic interactions · magnetic properties · N ligands · O ligands

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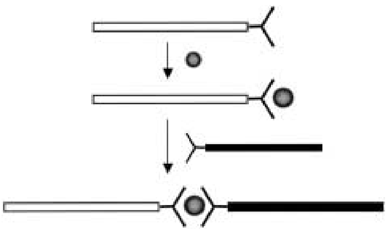
Metallo-supramolecular AB block copolymers are the first examples of macromolecular engineeering. A new concept for the formation of block copolymers by a supramolecular approach is presented. For this purpose the authors utilized an asymmetrical bis(terpyridine)–ruthenium complex as the supramolecular linkage between the two blocks (see figure).

Angew. Chem. **2002**, *114*, 3980–3984



B. G. G. Lohmeijer, U. S. Schubert* 3825–3829

Supramolecular Engineering with Macromolecules: An Alternative Concept for Block Copolymers

Keywords: metal complexes · polymers · supramolecular chemistry · terpyridine ligands

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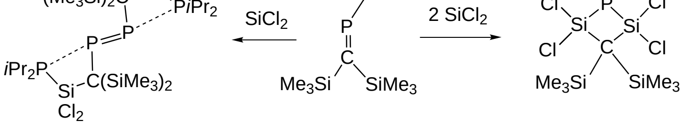
Silicon implants for double bonds: An unusual tetrasilylmethane derivative, the 2-phospha-1,3-disiletane **2** is formed through the spontaneous consecutive addition of two equivalents of SiCl$_2$ to the phosphaalkene **1**. Simultaneously the diphosphene **3** is also formed, which contains a central P=P bond and silylphosphane groups.



3 **1** **2**

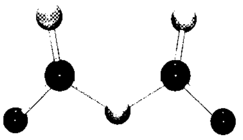
Angew. Chem. **2002**, *114*, 3977–3979

W.-W. du Mont,* T. Gust, E. Seppälä, C. Wismach, P. G. Jones, L. Ernst, J. Grunenberg, H. C. Marsmann 3829–3832

Unusual P=C Bond Cleavage by Double Dichlorosilylene Transfer from Trichlorosilyltrimethylgermane to *P*-Phosphanyl Phosphaalkenes

Keywords: cycloaddition · insertion · phosphaalkenes · phosphenes · silylenes

The missing link in the family of compounds FC(O)O$_x$C(O)F ($x = 0, 1, 2, 3$), the anhydride of fluoroformic acid (see picture), has been isolated in pure form and characterized. FC(O)OC(O)F is stable at room temperature for several days in a glass cell with a well conditioned surface.



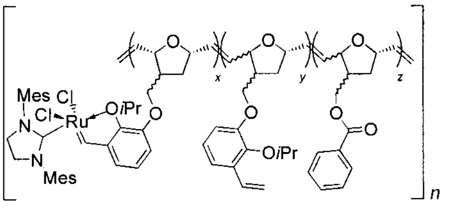
H. Pernice, H. Willner,* K. Bierbrauer, M. Burgos Paci, G. A. Argüello* 3832–3834

Fluoroformic Acid Anhydride, FC(O)OC(O)F

Keywords: ab initio calculations · anhydrides · fluorine · NMR spectroscopy · radical reactions

Angew. Chem. **2002**, *114*, 3987–3989

Sequential ring-opening-metathesis polymerization and cross-metathesis reactions allow a one-pot synthesis of the illustrated ruthenium catalyst. This conceptually novel polymer-bound catalyst shows excellent metathesis activity and recyclability.



$x{:}y{:}z = 1{:}9{:}30$

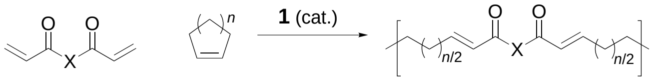
S. J. Connon, A. M. Dunne, S. Blechert* 3835–3838

A Self-Generating, Highly Active, and Recyclable Olefin-Metathesis Catalyst

Keywords: alkenes · homogeneous catalysis · metathesis · polymers · ruthenium

Angew. Chem. **2002**, *114*, 3989–3993

A variety of highly A,B-alternating copolymers are formed from diacrylates and cycloalkenes in the presence of [Cl$_2$(PCy$_3$)(H$_2$IMes)Ru=CHPh] (**1**). The high conversion and the high selectivity come from the thermodynamically favored formation of a C=C double bond between these monomers.



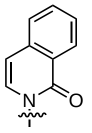
T.-L. Choi, I. M. Rutenberg, R. H. Grubbs* 3839–3841

Synthesis of A,B-Alternating Copolymers by Ring-Opening-Insertion-Metathesis Polymerization

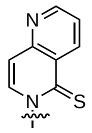
Keywords: copolymerization · cross-coupling · metathesis · ring-opening polymerization · ruthenium

Angew. Chem. **2002**, *114*, 3995–3997

More efficient and selective synthesis as well as more efficient extension by a DNA polymerase is achieved for unnatural base pairs upon heteroatom substitution. This has been demonstrated with modification of ICS (structure shown): Replacement of C6 with nitrogen and thio substitution at C10 provides the base SNICS, which forms stable self-pairs and can therefore be used for efficient unnatural base pair replication.



ICS



SNICS

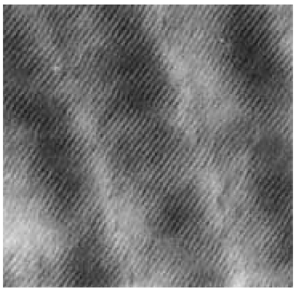
C. Yu, A. A. Henry, F. E. Romesberg,* P. G. Schultz* 3841–3844

Polymerase Recognition of Unnatural Base Pairs

Keywords: base pairs · DNA recognition · hydrophobic effect · nucleotides · substituent effects

Angew. Chem. **2002**, *114*, 3997–4000

Unusual lamellar mesostructures of metal oxides are obtained with silicone surfactants as templates. The authors present evidence for the unrestricted chain configuration of silicone surfactants being responsible for the formation of lamellae. The addition of a copolymer can create a hexagonal mesophase in the layered walls, thus leading to a hierarchically ordered mesophase (see TEM image).



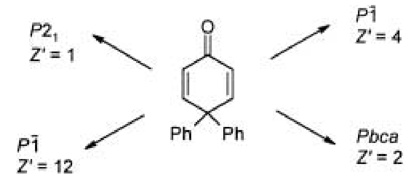
A.-W. Xu,* Y.-P. Cai, H.-X. Zhang, L.-Z. Zhang, J. C. Yu 3844–3848

Hierarchically Ordered Silica Mesophases Using Mixed Surfactant Systems as Templates

Keywords: lamellar structures · mesophases · silicon · surfactants

Angew. Chem. **2002**, *114*, 4000–4004

Small yet subtle conformational changes resulting from the correlated rotation of the geminal phenyl rings in the title compound lead to different crystal packing arrangements and thus different X-ray crystal structures (the four space groups are given in the picture). This provides the simultaneous occurence of conformational polymorphism, conformational isomorphism, and concomitant polymorphism for the same molecule.



Angew. Chem. **2002**, *114*, 4004 – 4007

V. S. S. Kumar, A. Addlagatta,
A. Nangia,* W. T. Robinson,*
C. K. Broder, R. Mondal, I. R. Evans,
J. A. K. Howard,*
F. H. Allen* .... 3848 – 3851

4,4-Diphenyl-2,5-cyclohexadienone: Four Polymorphs and Nineteen Crystallographically Independent Molecular Conformations

Keywords: conformation analysis · hydrogen bonds · polymorphism · structure elucidation · supramolecular chemistry

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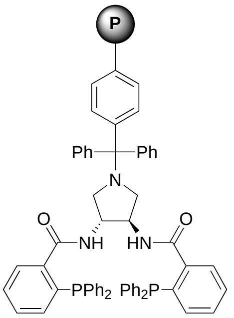
Easy recovery and reutilization of the catalyst in consecutive reactions: These are the advantages offered by a new class of polymer-bound Trost-type ligands (see Figure; ● is a polystyrene-based resin or JandaJEL). A complex is formed with $[\{(\eta^3\text{-}C_3H_5)PdCl\}_2]$ that catalyzes asymmetric allylic substitutions with excellent activity and enantioselectivity (up to 99 % *ee*).



Angew. Chem. **2002**, *114*, 4008 – 4010

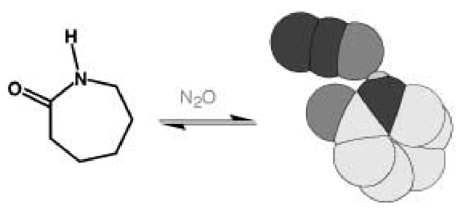
C. E. Song,* J. W. Yang, E. J. Roh,
S.-g. Lee, J. H. Ahn, H. Han* 3852 – 3854

Heterogeneous Pd-Catalyzed Asymmetric Allylic Substitution Using Resin-Supported Trost-Type Bisphosphane Ligands

Keywords: asymmetric catalysis · heterogeneous catalysis · palladium · P ligands · polymers

---

Is hydrogen bonding between N_2O and amides and peptides possible? Secondary *cis* amides and N_2O were found to interact in chloroform through hydrogen bonds and electrostatic interactions. In the absence of competing water molecules, such interactions may take place in hydrophobic enzyme pockets and in biological fluids, and may be responsible for a physiological activity of this gas.



Angew. Chem. **2002**, *114*, 4010 – 4013

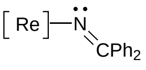
G. V. Zyryanov, E. M. Hampe,
D. M. Rudkevich* .... 3854 – 3857

Noncovalent Chemistry of Nitrous Oxide: Interactions with Secondary *cis* Amides in Solution

Keywords: amides · hydrogen bonds · molecular recognition · nitrogen oxides · noncovalent interactions

---

An enhanced reactivity towards isocyanates was found with compound **1** ($[Re] = [Re(CO)_3(bpy)]$) when compared with *N*-silylimines. A crystal structure determination established that **1** is a transition-metal *N*-metalloimine.


$[Re]{-}\ddot{N}{=}CPh_2$

1

d(Re–N)= 2.113(4) Å
Re-C-N= 133.9(4)°

Angew. Chem. **2002**, *114*, 4014 – 4016

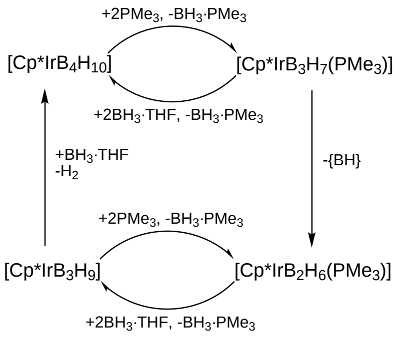
E. Hevia, J. Pérez,* V. Riera,
D. Miguel .... 3858 – 3860

Insertion and Cycloaddition Reactivity of a Transition-Metal *N*-Metalloimine

Keywords: cycloaddition · imines · insertion · isocyanates · rhenium

---

Reaction cycles of clusters: $[Cp^*IrB_3H_9]$ and $[Cp^*IrB_4H_{10}]$ react with PMe_3 to give cleavage products that undergo addition of borane to reconstruct the parent clusters. Overall, a new reaction cycle is formed, comprising two reversible and two irreversible steps, which involve the formation of new phosphane-substituted iridaboranes (see scheme).



Angew. Chem. **2002**, *114*, 4016 – 4018

R. Macías,* T. P. Fehlner,
A. M. Beatty .... 3860 – 3862

An Iridaborane Reaction Cycle Driven by PMe_3 and $BH_3 \cdot THF$: Synthesis and Characterization of $[Cp^*IrB_3H_7(PMe_3)]$ and $[Cp^*IrB_2H_6(PMe_3)]$

Keywords: boranes · cluster compounds · reaction cycles · transition metals

More pronounced twisting and divergence of the strands is seen for peptides containing type I′ turn nucleated β-hairpins. Superposition of the structure of the synthetic octapeptide Boc-Leu-Phe-Val-Aib-D-Ala-Leu-Phe-Val-OMe (black) with that of a peptide with the same strand residues but a type II′ turn nucleated β-hairpin (gray) illustrates the flattened nature of the latter. Aib = aminoisobutyric, Boc = *tert*-butoxycarbonyl.

Angew. Chem. **2002**, *114*, 4019–4021

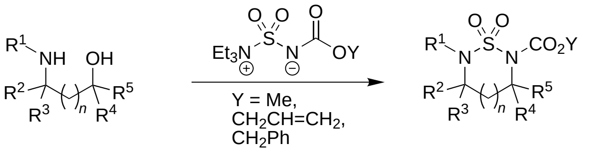
S. Aravinda, N. Shamala,* R. Rajkishore, H. N. Gopi, P. Balaram* 3863–3865

A Crystalline β-Hairpin Peptide Nucleated by a Type I′ Aib-D-Ala β-Turn: Evidence for Cross-Strand Aromatic Interactions

Keywords: amino acids · hydrogen bonds · peptides · protein folding · protein structures

---

A practical and high-yielding method for the efficient, one-step synthesis of diverse classes of *N,N′*-differentiated sulfamides has been developed from a wide range of amino alcohols and simple amines using Burgess-type reagents (see scheme). This method enables the possible differentiation of both sides of any cyclic sulfamide product.



Angew. Chem. **2002**, *114*, 4022–4026

K. C. Nicolaou,* D. A. Longbottom, S. A. Snyder, A. Z. Nalbanadian, X. Huang 3866–3870

A New Method for the Synthesis of Nonsymmetrical Sulfamides Using Burgess-Type Reagents

Keywords: amines · Burgess reagents · cyclization · sulfamides · synthetic methods

---

The reversible two-electron reduction of an acetonitrile ligand to the corresponding imine has been demonstrated for the first time with the title compound. Electrochemical reduction generates the Os^{III}–imino product [Eq. (a)], which can be isolated as the PF_6^- salt and used in further reactions for the reduction of organic carbonyl compounds. Ar = C_6H_5, 4-MeC_6H_4, 3,5-$Me_2C_6H_3$.

$$[(tpy)(Cl)(NSAr)Os^{III}{-}N{\equiv}CCH_3] + 2\,e^- + 2\,H^+ \rightarrow [(tpy)(Cl)(NSAr)Os^{III}{-}NH{=}CHCH_3] \qquad (a)$$

Angew. Chem. **2002**, *114*, 4026–4029

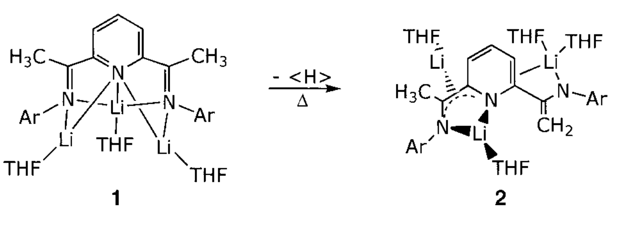
M. H. V. Huynh,* R. T. Baker, D. E. Morris, P. S. White, T. J. Meyer* 3870–3873

$[Os^{III}(tpy)(Cl)(NCCH_3)(NSAr)]$: Reversible Reduction of Acetonitrile by Os^{III}–Sulfilimido Complexes

Keywords: acetonitrile · imines · N ligands · osmium · reduction

---

Three electrons can be accepted into the antibonding orbitals of the α,α′-{2,6-(iPr)$_2$PhN=C(Me)}$_2$(C_5H_3N) ligand, so that reduction with [Li(naphthalenide)] yields the trianionic diamagnetic complex **2**. Treatment with Li metal, a stronger reducing agent, gives a mixture of **2** and paramagnetic complex **1**, which is thermally unstable and is converted into **2** on heating in toluene (see scheme).



1 **2**

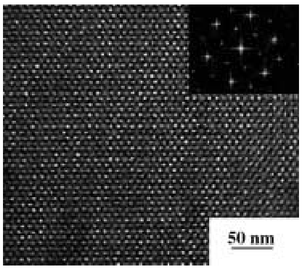
Angew. Chem. **2002**, *114*, 4029–4032

D. Enright, S. Gambarotta,* G. P. A. Yap, P. H. M. Budzelaar* 3873–3876

The Ability of the α,α′-Diiminopyridine Ligand System to Accept Negative Charge: Isolation of Paramagnetic and Diamagnetic Trianions

Keywords: density functional calculations · imino compounds · lithium · paramagnetism · radical ions

A triblock copolymer template and an organosiloxane or organic additive facilitated the first synthesis of large-pore (up to 9.5 nm) three-dimensional bicontinuous mesoporous silica with *Ia*3*d*-type symmetry at room temperature in acidic medium. The picture is a transmission electron micrograph showing the pores along [111] and the corresponding diffractogram (inset).



Angew. Chem. **2002**, *114*, 4032–4034

X. Liu, B. Tian, C. Yu, F. Gao, S. Xie, B. Tu, R. Che, L.-M. Peng, D. Zhao* 3876–3878

Room-Temperature Synthesis in Acidic Media of Large-Pore Three-Dimensional Bicontinuous Mesoporous Silica with *Ia*3*d* Symmetry

Keywords: mesoporous materials · silica · template synthesis · zeolite analogues

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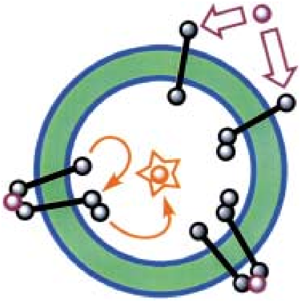
Talking through walls: A synthetic system has been developed for transducing a signal across a vesicular bilayer membrane. The external messenger (purple) does not cross the membrane itself, but instigates the release of a secondary messenger (red) on the interior of the vesicle.



Angew. Chem. **2002**, *114*, 4034–4037

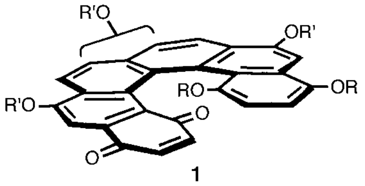
P. Barton, C. A. Hunter,* T. J. Potter, S. J. Webb, N. H. Williams* . 3878–3881

Transmembrane Signalling

Keywords: liposomes · membranes · signal transduction · supramolecular chemistry · vesicles

---

Oriented by an electric field (but not otherwise), a lyotropic nematic phase of helical discotic **1** in dodecane exhibits second-harmonic generation, the intensity of which is affected by the helicity of the irradiating circularly polarized light. The change reverses sign when the polarity of the orienting electric field reverses.



1

Angew. Chem. **2002**, *114*, 4038–4040

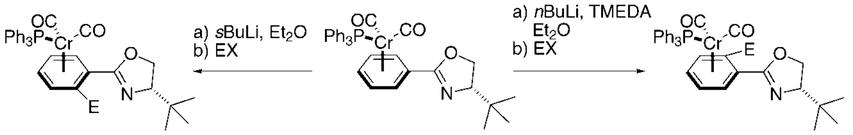
T. Verbiest,* S. Sioncke, A. Persoons, L. Vyklický, T. J. Katz 3882–3884

Electric-Field-Modulated Circular-Difference Effects in Second-Harmonic Generation from a Chiral Liquid Crystal

Keywords: chirality · circular dichroism · helical structures · liquid crystals · nonlinear optics

---

Incorporation of a triphenylphosphane ligand is the key to the direct lithiation of (η^6-2-phenyloxazoline)chromium(0) complexes. As diastereoselection can be modulated by the presence or absence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), both diastereomers of 1,2-disubstituted η^6-arene chromium(0) oxazoline complexes, which possess planar chiral moieties of opposite absolute configuration, can be prepared in useful chemical yields and high diastereoselectivities (10–50:1).



Angew. Chem. **2002**, *114*, 4040–4043

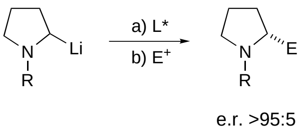
L. E. Overman,* C. E. Owen, G. G. Zipp 3884–3887

Diastereoselective Lithiation of (η^6-Arene)dicarbonyltriphenylphosphane Chromium(0) Oxazoline Complexes—Direct Preparation of Enantiopure Complexes Having Planar Chiral Fragments of Either Configuration

Keywords: arene complexes · chromium · lithiation · P ligands

---

Not restricted to allylic or benzylic derivatives: The dynamic resolution of chiral organolithium species in the presence of a chiral ligand, L*, followed by addition of an electrophile, E$^+$ (see scheme), has been shown to occur with excellent enantioselectivity at ambient temperature by using nonactivated 2-lithiopyrrolidines.



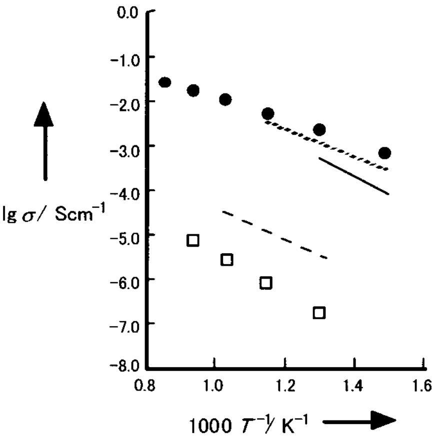
Angew. Chem. **2002**, *114*, 4043–4045

I. Coldham,* S. Dufour, T. F. N. Haxell, S. Howard, G. P. Vennall 3887–3889

Enantioselective Synthesis of Substituted Pyrrolidines by Dynamic Resolution

Keywords: amines · carbanions · dynamic resolution · enantioselectivity · lithiation

Calcium doping levels of up to 20% can be achieved for the $La_{1-x}Ca_xOCl_{1-x}$ solid solution series. At the highest doping levels ($x = 0.2$; see graph (●)), the conductivity of the solid solution is three orders of magnitude greater than that of undoped LaOCl (□). The potential for the design of new functional materials stems from their high thermal stability, relative density, and hardness, in addition to their insolublity in water.



Angew. Chem. **2002**, *114*, 4046–4048

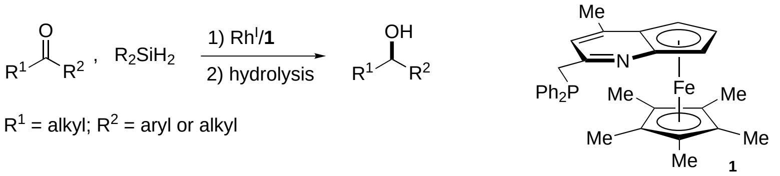
N. Imanaka,* K. Okamoto,
G.-y. Adachi 3890–3892

Water-Insoluble Lanthanum Oxychloride-Based Solid Electrolytes with Ultra-High Chloride Ion Conductivity

Keywords: conducting materials · electrochemistry · solid electrolytes · solid-state structures · X-ray diffraction

---

Comparable to or even better than the best enantioselectivities that can be obtained through asymmetric hydrogenation of dialkyl ketones are the *ee* values obtained in the catalytic asymmetric hydrosilylation of such ketones with the catalyst system Rh/**1** (see scheme). In terms of both scope and stereoselectivity, this method compares favorably with previously described catalysts for this process as the Rh/**1** system also furnishes consistently excellent *ee* values and yields with aryl alkyl ketones.



Angew. Chem. **2002**, *114*, 4048–4050

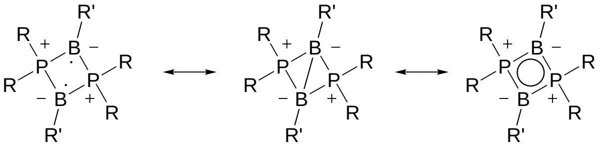
B. Tao, G. C. Fu* 3892–3894

Application of a New Family of P,N Ligands to the Highly Enantioselective Hydrosilylation of Aryl Alkyl and Dialkyl Ketones

Keywords: asymmetric catalysis · hydrosilylation · P,N ligands · reduction · rhodium

---

Substantial control over frontier orbital splittings in 1,3-diphospha-2,4-diboretanes can be achieved by variation of phosphorus substituents R, thereby enhancing diradical character (see scheme; e.g. $R = SiMe_3$, $R' = t$Bu).



Angew. Chem. **2002**, *114*, 4050–4052

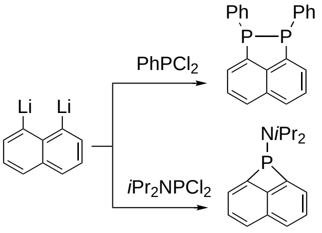
M. Seierstad, C. R. Kinsinger,
C. J. Cramer* 3894–3896

Design Optimization of 1,3-Diphospha-2,4-diboretane Diradicals

Keywords: density functional calculations · electronic structure · phosphorus heterocycles · radicals · singlet–triplet splitting

---

Strained rings and metal insertions: The product of the reaction between 1,8-dilithionaphthalene and $RPCl_2$ differs depending on the R group on the phosphorus atom. $PhPCl_2$ gave $(PhP)_2$-*peri*-bridged naphthalene, while $i\mathrm{Pr}_2\mathrm{NPCl}_2$ gave the $i\mathrm{Pr}_2$-bridged compound (see scheme). The reactivity of the new compounds with transition-metal complexes is also discussed.



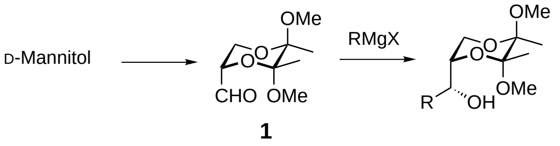
Angew. Chem. **2002**, *114*, 4052–4054

T. Mizuta,* T. Nakazono,
K. Miyoshi* 3897–3898

Naphtho[1,8-*b*,*c*]phosphete and 1,2-Diphosphaacenaphthene from the Reaction of 1,8-Dilithionaphthalene with $RPCl_2$

Keywords: heterocycles · metallacycles · P ligands · small ring systems · tungsten

Available on a large scale in both enantiomeric forms, the butanediacetal-protected aldehyde **1** is a stable glyceraldehyde derivative. The potential of **1** as a new chiral building block is illustrated by the highly stereoselective addition of Grignard reagents (see scheme).



Angew. Chem. **2002**, *114*, 4054–4057

P. Michel, S. V. Ley* 3898–3901

Butane-2,3-diacetals of Glyceraldehyde: A Stable Alternative to Glyceraldehyde Acetonide

Keywords: aldehydes · diacetals · diastereoselectivity · glyceraldehyde

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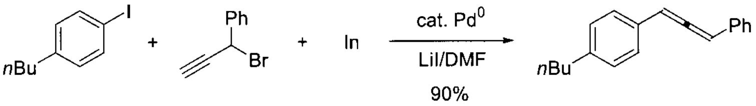
Versatile, convenient, mild: Allenylindium intermediates generated from the reaction of indium with propargyl bromides were employed as effective coupling partners in Pd-catalyzed cross-coupling reactions with a variety of electrophiles to produce allenes, polyallenes, and unsymmetrical bis(allenes) in excellent yields with complete regioselectivity and chemoselectivity (see scheme for one example).



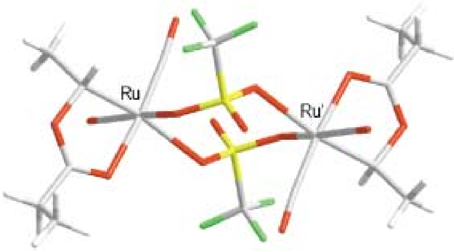
Angew. Chem. **2002**, *114*, 4057–4059

K. Lee, D. Seomoon,
P. H. Lee* 3901–3903

Highly Efficient Catalytic Synthesis of Substituted Allenes Using Indium

Keywords: allenes · cross-coupling · indium · palladium

The reaction of an ethene-coordinated Ru^{II} complex with carboxylic acids is catalytic and produces equimolar amounts of ethane and 1,1′-diesters. The intermediate of the catalytic cycle is the alkyl complex $[\mathrm{RuL}_n\{\mathrm{CHCH_3(OC(O)C_2H_5)}\}(\mathrm{CO})_2]^{(1-n)+}$ ($\mathrm{L} = \mathrm{RCOO^-}, \mathrm{CF_3SO_3^-}$), which was isolated in the dinuclear form.



Angew. Chem. **2002**, *114*, 4061–4063

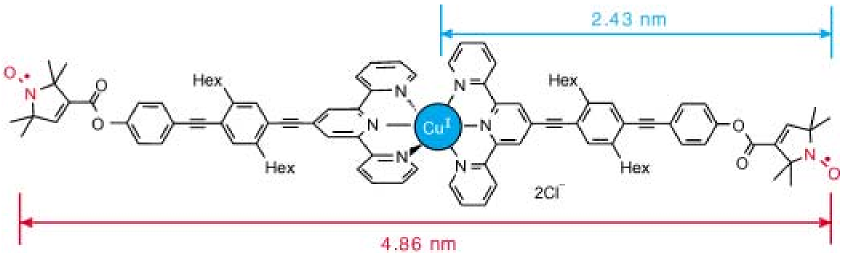
T. Funaioli,* F. Marchetti,
G. Fachinetti* 3905–3907

Ethane and Ethylidene Dicarboxylates from the Ruthenium(II)-Catalyzed "Disproportionative Addition" of Carboxylic Acids to Ethene

Keywords: alkenes · carboxylic acids · disproportionation · nucleophilic addition · ruthenium

---

Self-assembled supramolecular complexes that contain paramagnetic transition metal ions, such as that illustrated below, can be structurally characterized by the precise measurement of the separation between metal centers and spin labels. The technique, which employs double electron electron resonance (DEER), should also be applicable to metalloproteins.



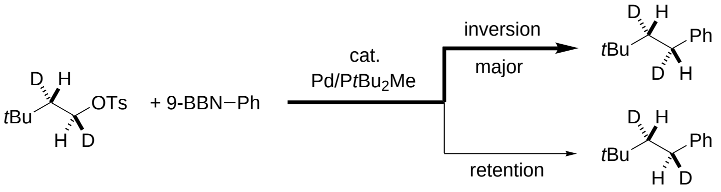
Angew. Chem. **2002**, *114*, 4063–4066

E. Narr, A. Godt,
G. Jeschke* 3907–3910

Selective Measurements of a Nitroxide–Nitroxide Separation of 5 nm and a Nitroxide–Copper Separation of 2.5 nm in a Terpyridine-Based Copper(II) Complex by Pulse EPR Spectroscopy

Keywords: copper · EPR spectroscopy · metalloproteins · structure elucidation · supramolecular chemistry

🏃 🖳 **A striking dependence of reactivity on phosphane structure** was observed in the first Suzuki-type cross-coupling process that is effective for functionalized alkyl tosylates. In this reaction, in which solely commercially available reagents are used, $\mathrm{P}t\mathrm{Bu}_2\mathrm{Me}$ is the ligand of choice. Through the use of deuterium-labeled compounds, it has been established that the coupling proceeds with predominant inversion of configuration at the carbon atom [Eq. (1), 9-BBN = 9-borabicyclo[3.3.1]nonane].



(1)

Angew. Chem. **2002**, *114*, 4066–4068

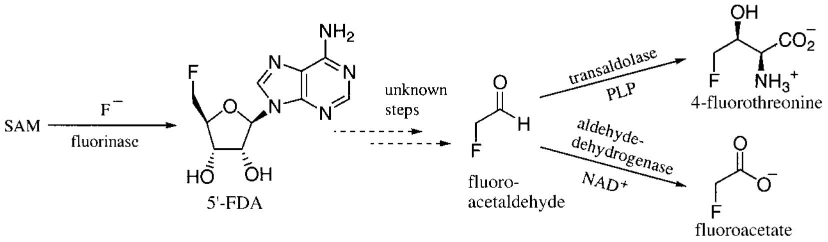
M. R. Netherton, G. C. Fu* . 3910–3912

Suzuki Cross-Couplings of Alkyl Tosylates that Possess β Hydrogen Atoms: Synthetic and Mechanistic Studies

Keywords: alkyl tosylates · C–C coupling · ligand effects · palladium · Suzuki reaction

---

🏃 🖳 **The biosynthesis of organofluorine compounds**, for example, fluoroacetate, was demonstrated from (*S*)-adenosyl-L-methionine (SAM) and fluoride ions in a cell-free extract of *Streptomyces cattleya*. Incubation of 5′-fluoro-5′-deoxyadenosine (5′-FDA), the first organofluorine product formed in the fluoroacetate pathway, with the cell-free extract resulted in the transient accumulation of fluoroacetaldehyde, thus confirming its role as an intermediate in the synthesis of fluorometabolites (see scheme).



Angew. Chem. **2002**, *114*, 4069–4071

C. Schaffrath, S. L. Cobb,
D. O'Hagan* 3913–3915

Cell-Free Biosynthesis of Fluoroacetate and 4-Fluorothreonine in *Streptomyces cattleya*

Keywords: biosynthesis · biotransformations · enzymes · fluorine

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

🏃 Accelerated publications

* Author to whom correspondence should be addressed

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CORRIGENDUM

In the Communication by **J.-M. Lehn and co-workers** in Issue 15, **2002**, pp. 2760–2764, references [4] and [5] were accidentally combined in the print version. The references should read:

[4] See, for instance,: a) C. Piguet, G. Bernardinelli, B. Bocquet, A. Quattropani, A. F. Williams, *J. Am. Chem. Soc.* **1992**, *114*, 7440; b) A. Marquis-Rigault, A. Dupont-Gervais, P. N. W. Baxter, A. Van Dorsselaer, J.-M. Lehn, *Inorg. Chem.* **1996**, *35*, 2307; c) A. Marquis-Rigault, A. Dupont-Gervais, A. Van Dorsselaer, J.-M. Lehn, *Chem. Eur. J.* **1996**, *2*, 1395; d) M. D. Levin, P. J. Stang, *J. Am. Chem. Soc.* **2000**, *122*, 7428.

[5] a) M. T. Youinou, N. Rahmouni, J. Fischer, J. A. Osborn, *Angew. Chem.* **1992**, *104*, 771; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 733; b) P. N. W. Baxter, J.-M. Lehn, B. O. Kneisel, D. Fenske, *Chem. Commun.* **1997**, 2231; c) G. S. Hanan, D. Volkmer, U. S. Schubert, J.-M. Lehn, G. Baum, D. Fenske, *Angew. Chem.* **1997**, *109*, 1929; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1842; d) D. M. Bassani, J.-M. Lehn, K. Fromm, D. Fenske, *Angew. Chem.* **1998**, *110*, 2534; *Angew. Chem. Int. Ed.* **1998**, *37*, 2364.

The editorial office apologizes for this mistake.