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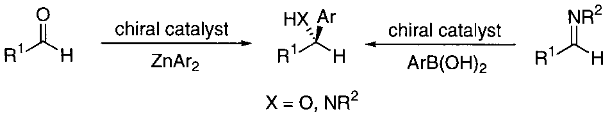
COVER PICTURE

The cover picture shows that chemical and biological knowledge need to be linked more to ensure that highly effective and target-specific drugs can be found more quickly. Additionally, the main and side effects must be controlled in the best interests of the individual patient. Despite the intensive use of high-throughput technologies in drug research, despite new insight in genomic and proteomic research and in structural biology, and despite the progress made in bio- and chemoinformatics, there is still a worldwide shortage of new and innovative drugs. The bottleneck in lead-structure generation lies in the preparation of new biologically relevant substances and therefore to a major extent in chemistry. The way medicinal chemists perceive their subject and its role in the natural sciences as well as in the value chain of drug research is crucial to counteract this shortage, as explained by Wess et al. on page 3341–3350.

REVIEWS

The asymmetric catalytic aryl transfer to prochiral substrates expands the scope of enantioselective C–C bond-forming reactions. Previously, variants of palladium-catalyzed cross-coupling reactions mostly allowed for asymmetric aryl transfer. In recent times, however, this picture has changed significantly. This overview demonstrates that not only are asymmetric cross-couplings available to the synthetic organic chemist today, but that there are various other transformations for the enantioselective introduction of aryl groups (see scheme).

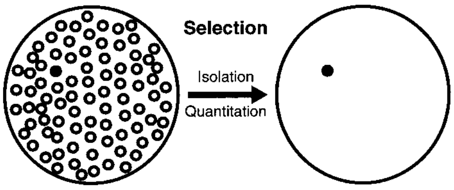


Angew. Chem. **2001**, *113*, 3382–3407

C. Bolm,* J. P. Hildebrand, K. Muñiz, N. Hermanns 3284–3308

Catalyzed Asymmetric Arylation Reactions

Keywords: arylation · asymmetric synthesis · homogeneous catalysis · transition metals



If you were to ask preparative chemists whether they would be interested in a method that rapidly and efficiently isolates a desired product from a reaction mixture, or analytical chemists whether they would use a technique for quantitative analysis that gives large, clear signals and practically no noise, the answers would likely be a resounding "Yes!". Genetic selection (see schematic representation) is an approach that is useful for biological chemists and can provide both advantages. This review is an overview of the use of selection systems in enzymology, structural analysis, and protein (re)design.

Angew. Chem. **2001**, *113*, 3408–3436

S. V. Taylor, P. Kast,
D. Hilvert* 3310–3335

Investigating and Engineering Enzymes by Genetic Selection

Keywords: directed evolution · enzyme catalysis · enzymes · genetic selection · protein design · protein structures

ESSAYS

The set of molecules assembled during a combinatorial experiment, is the antithesis of a library, says the author. Creating all combinations is a way of special significance for some, but is devoid of meaning for others—this debate has a venerable history. Playing with flowers and chocolates, his all too tardy gift to the talented concoctors of combinatorial pools, is a new, less pretentious, name.

Angew. Chem. **2001**, *113*, 3439–3443

R. Hoffmann* 3337–3340

Not a Library

Keywords: combinatorial chemistry

The sequencing of the human genome has led to a wealth of new pharmaceutical targets. However, medicinal chemistry has proved to be a bottleneck in the search for active drugs. This bottleneck can be overcome by chemical biology, which is crucial in the transition from a trial-and-error mentality to a predictive approach.

Angew. Chem. **2001**, *113*, 3443–3453

G. Wess,* M. Urmann,
B. Sickenberger 3341–3350

Medicinal Chemistry: Challenges and Opportunities

Keywords: chemical biology · combinatorial chemistry · drug research · medicinal chemistry

VIPs

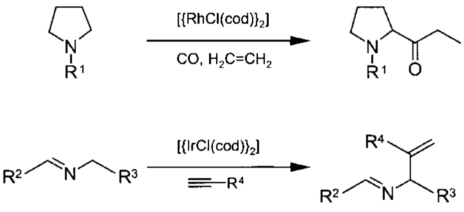
The following communications are "Very Important Papers" in the opinion of two referees. They will be published shortly (those marked with a diamond will be published in the next issue). Short summaries of these articles can be found on the *Angewandte Chemie* homepage at the address http://www.angewandte.com

High Turnover Numbers for Catalytic Selective Epoxidation of Alkenes with 1 atm Molecular Oxygen	Y. Nishiyama, Y. Nakagawa, N. Mizuno*	◆
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*	

HIGHLIGHTS

A very promising approach for the efficient synthesis of complex amines is provided by the transition metal catalyzed activation of sp^3 C–H bonds in the position α to a nitrogen atom. Two recent publications show that this approach can be realized impressively by the use of rhodium and iridium catalysts (see scheme; cod = 1,5-cyclooctadiene).

Angew. Chem. **2001**, *113*, 3455–3457



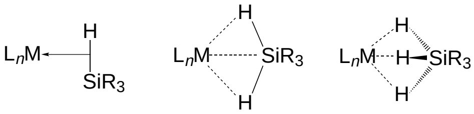
S. Doye* 3351–3353

Catalytic C–H Activation of sp^3 C–H Bonds in α-Position to a Nitrogen Atom—Two New Approaches

Keywords: carbonylation · C–H activation · homogeneous catalysis · iridium · rhodium

---

Dominated for two decades by agostic and σ complexes, the family of complexes with nonclassical interligand interactions is rapidly extending to include new types of compounds. Multicenter $(H)_2\cdots$Si and $(H)_3\cdots$Si interactions have recently been documented in transition metal silicon chemistry (see scheme).



Angew. Chem. **2001**, *113*, 3457–3459

G. I. Nikonov* 3353–3355

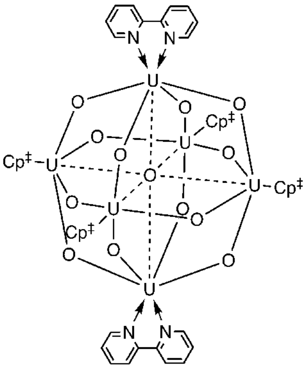
Going Beyond σ Complexation: Nonclassical Interligand Interactions of Silyl Groups with Two and More Hydrides

Keywords: bond theory · hydrido complexes · hypervalent compounds · nonclassical interactions · silicon

COMMUNICATIONS

Known for the Group 6 metals for over 100 years, the family of isopolyoxometalates has now been extended to include the first uranium derivative **1**, which contains a $[U_6O_{13}]$ core. In comparison to the well-studied transition metal analogues, the structural and electronic properties of **1** reflect the chemical attributes of the actinides. Cp‡ = 1,2,4-tBu$_3$C$_5$H$_2$.

Angew. Chem. **2001**, *113*, 3462–3465



1

P. B. Duval, C. J. Burns,* D. L. Clark,* D. E. Morris, B. L. Scott, J. D. Thompson, E. L. Werkema, L. Jia, R. A. Andersen 3358–3361

Synthesis and Structural Characterization of the First Uranium Cluster Containing an Isopolyoxometalate Core

Keywords: actinides · cluster compounds · polyoxometalates · uranium

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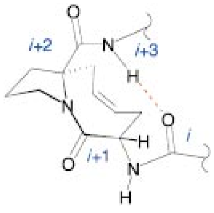
A fruitful combination of molecular dynamics based design and modern synthetic reactions led to a conformatively rigidized *cis*-peptidyl proline surrogate (see picture). NMR spectroscopic experiments clearly show the existance of type VIa β-turn properties that are of interest in drug discovery.

Angew. Chem. **2001**, *113*, 3465–3468

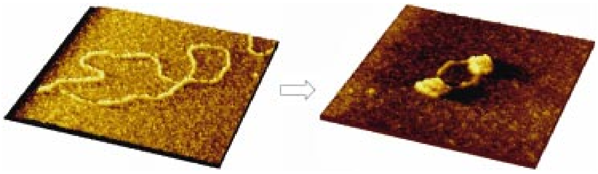


T. Hoffmann, H. Lanig,* R. Waibel, P. Gmeiner* 3361–3364

Rational Molecular Design and EPC Synthesis of a Type VI β-Turn Inducing Peptide Mimetic

Keywords: β-turns · metathesis · molecular dynamics · peptidomimetics · semiempirical calculations

DNA condensation by a fullerene vector has been imaged at the molecular level by atomic force microscopy (AFM); analysis of a mixture of plasmid DNA and DNA-binding fullerene with the aid of this carbonaceous vector provided the first information on the mechanism of transfection. The picture shows AFM images of pBR322 DNA in the absence of (left) and partially condensed by the fullerene (right).



Angew. Chem. **2001**, *113*, 3468 – 3471

H. Isobe, S. Sugiyama, K.-i. Fukui,
Y. Iwasawa, E. Nakamura* 3364 – 3367

Atomic Force Microscope Studies on Condensation of Plasmid DNA with Functionalized Fullerenes

Keywords: DNA recognition · fullerenes · polycations · scanning probe microscopy · transfection

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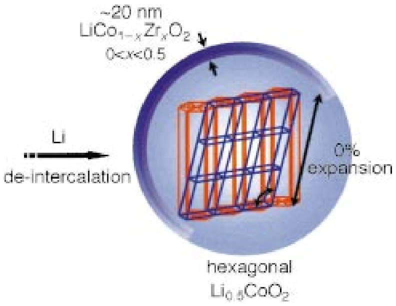
No strain, big gain: the possibility of producing more-efficient rechargeable lithium batteries is offered by a zero-strain $LiCoO_2$ cathode material produced by coating particles with thin films of high-fracture-toughness oxides. This method suppresses the changes in the lattice constant during electrochemical cycling and thereby suppresses phase transitions (see scheme). The order of capacity retention correlates with the fracture toughness of the coating thin-film oxides. The ZrO_2-coated sample does not show any noticeable capacity fading over 70 electrochemical cycles.



Angew. Chem. **2001**, *113*, 3471 – 3473

J. Cho, Y. J. Kim, T.-J. Kim,
B. Park* .... 3367 – 3369

Zero-Strain Intercalation Cathode for Rechargeable Li-Ion Cell

Keywords: electrochemistry · intercalation · lithium · thin films · zirconium

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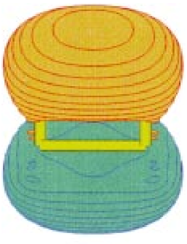
Mercury forms a wide range of alloys (amalgams), some of which are known from ancient times. Square-planar Hg_4^{6-} units are known to be particularly favorable building blocks in many amalgams. It is reported here that the unusual Hg_4^{6-} square is aromatic (the picture shows the HOMO – 1 ($1a_{2u}$) molecular orbital), analogous to the recently discovered all-metal Al_4^{2-} ion.



HOMO–1 ($1a_{2u}$)

Angew. Chem. **2001**, *113*, 3473 – 3476

A. E. Kuznetsov, J. D. Corbett,*
L.-S. Wang,* A. I. Boldyrev* 3369 – 3372

Aromatic Mercury Clusters in Ancient Amalgams

Keywords: ab initio calculations · amalgams · aromaticity · chemical bonding · cluster compounds

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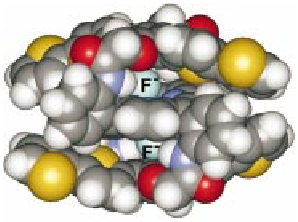
Fluoride fills cavities and insulates polymers: A doubly strapped porphyrin has been designed that is a highly specific receptor for fluoride ions (see picture, yellow: sulfur, red: oxygen, blue: nitrogen, and light blue: fluoride). The strap defines a small cavity about the porphyrin core, and fluoride ion was observed to bind with cooperative allosterism. Larger anions did not bind in the cavity or interfere with fluoride binding. The straps are composed of bis(dithienyl)phenyl groups that can be electropolymerized to give conducting polymers. Exposure of these polymers to fluoride ions results in a dramatic irreversible reduction in conductivity.



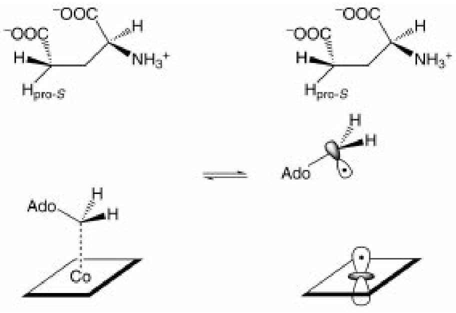
Angew. Chem. **2001**, *113*, 3476 – 3480

M. Takeuchi, T. Shioya,
T. M. Swager* .... 3372 – 3376

Allosteric Fluoride Anion Recognition by a Doubly Strapped Porphyrin

Keywords: conducting materials · fluoride ions · molecular recognition · polymers · porphyrinoids

Two alternate conformations of the adenosyl ligand of the cofactor are observed in the active site of the coenzyme B_{12} dependent enzyme glutamate mutase. This result shows ribose pseudorotation to be an elegant and safe mechanism for shuttling the "hot" methylene radical between the cofactor and substrate (see scheme).



Angew. Chem. **2001**, *113*, 3481–3484

K. Gruber,* R. Reitzer,
C. Kratky 3377–3380

Radical Shuttling in a Protein: Ribose Pseudorotation Controls Alkyl-Radical Transfer in the Coenzyme B_{12} Dependent Enzyme Glutamate Mutase

Keywords: enzyme catalysis · metalloenzymes · protein structures · radical reactions · reaction mechanisms

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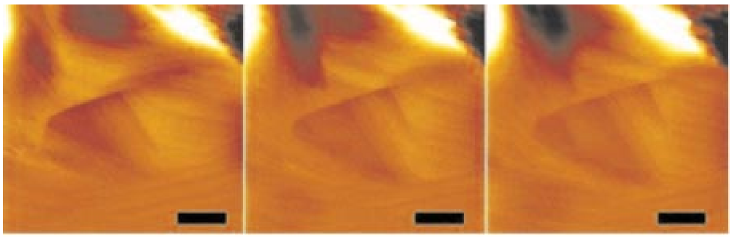
Etching edges: In situ measurement by atomic-force microscopy (AFM) is employed to investigate the dissolution of calcium phosphate crystals in the presence of different polymeric additives. The dissolution occurs in a way that is dependent on the pattern of functional groups on each polymer. The influence of poly(sodium)aspartate, polylysine, and serum albumins on the resulting crystal morphologies is discussed. The pictures show the dissolution of the (010) plane of brushit in the presence of polyaspartate (the bar = 1 μm).



Angew. Chem. **2001**, *113*, 3484–3488

A. Peytcheva,
M. Antonietti* 3380–3383

"Carving on the Nanoscale": Polymers for the Site-Specific Dissolution of Calcium Phosphate

Keywords: biomimetic synthesis · crystal engineering · molecular recognition · polymers

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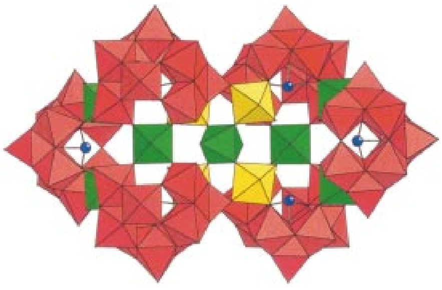
The largest tungstoarsenate(III) known to date is $[\mathrm{As}^{\mathrm{III}}_6\mathrm{W}_{65}\mathrm{O}_{217}(\mathrm{H}_2\mathrm{O})_7]^{26-}$ (**1**). This novel polyoxoanion is isolated as its potassium salt in aqueous, acidic medium in good yield. Structural characterization is based on single-crystal X-ray diffraction, ^{183}W NMR, FT-IR spectroscopy, and elemental analysis. The compact structure of **1** with an idealized C_{2h} symmetry (see picture) consists of four inner (β-$\mathrm{AsW_9O_{33}}$) and two outer (α-$\mathrm{AsW_9O_{33}}$) fragments (red) that are linked together by a total of eleven corner-sharing $\mathrm{WO_6}$ octahedra (green, yellow).



Angew. Chem. **2001**, *113*, 3488–3491

U. Kortz,* M. G. Savelieff, B. S. Bassil,
M. H. Dickman 3384–3386

A Large, Novel Polyoxotungstate: $[\mathrm{As}^{\mathrm{III}}_6\mathrm{W}_{65}\mathrm{O}_{217}(\mathrm{H}_2\mathrm{O})_7]^{26-}$

Keywords: arsenic · cluster compounds · polyoxometalates · self-assembly · tungsten

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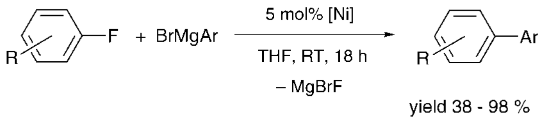
The activation of strong sp^2 C–F bonds in catalytic C–C cross-coupling reactions with aryl Grignard reagents under mild conditions is possible: A nickel complex bearing an N-heterocyclic carbene ligand was identified as the most active catalyst for this reaction [Eq. (1)]. With the selective activation of aromatic C–F bonds over C–H bonds present, cross-coupling chemistry employing aryl halides has finally overcome its most challenging hurdle with regard to catalyst activity.



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Angew. Chem. **2001**, *113*, 3500–3503

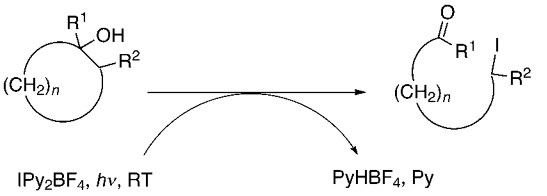
V. P. W. Böhm, C. W. K. Gstöttmayr,
T. Weskamp,
W. A. Herrmann* 3387–3389

Catalytic C–C Bond Formation through Selective Activation of C–F Bonds

Keywords: biaryls · carbene ligands · C–C coupling · C–F activation · homogeneous catalysis · nickel

1433-7851/01/4018-3271 $ 17.50+.50/0

Simply mix and switch on the light: This is all that is required to obtain ω-functionalized aldehydes and ketones from readily available cyclic alcohols and IPy$_2$BF$_4$. The unusual oxidation process is outlined in Equation (1). $R^1,R^2 = H, CH_3$; $n = 2, 3, 4, 10$; Py = pyridine.



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Angew. Chem. **2001**, *113*, 3491–3494

J. Barluenga,* F. González-Bobes,
S. R. Ananthoju, M. A. García-Martín,
J. M. González 3389–3392

Oxidative Opening of Cycloalkanols: An Efficient Entry to ω-Iodocarbonyl Compounds

Keywords: alcohols · cleavage reactions · iodine reagents · oxidation · radical reactions

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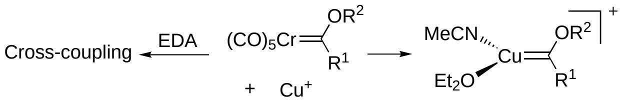
The chromium–copper interaction is evidenced for chromium–carbene complexes and Cu$^+$ in the CuBr-catalyzed cross-coupling reaction of ethyl diazoacetate (EDA) and Fischer alkoxycarbene–chromium complexes (see scheme). In contrast, with [Cu(MeCN)$_4$][PF$_6$] (0.5 equiv) instead of CuBr a carbene ligand exchange between a chiral alkenylchromium carbene complex ($R^1 = (E)$-CH=CH-2-furyl, $R^2 = (1R, 2S, 5R)$-menthyl) and this Cu compound occurs at room temperature. The resulting novel trigonal-planar copper(I)–carbene complex, which contains MeCN and Et$_2$O as the remaining ligands, has been isolated and structurally characterized by X-ray diffraction.



Angew. Chem. **2001**, *113*, 3495–3497

J. Barluenga,* L. A. López, O. Löber,
M. Tomás, S. García-Granda,
C. Alvarez-Rúa, J. Borge ... 3392–3394

Chromium–Copper Exchange of Fischer Carbene Complexes: X-Ray Crystal Structure of a [Cu{=CR^1(OR^2)}-(MeCN)(Et$_2$O)][PF$_6$] Complex

Keywords: carbene ligands · chromium · copper · cross-coupling · transmetalation

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AlMe$_3$ and ethanethiol can be used to cleave peptides directly and efficiently from a variety of commercial resins to give C-terminal thioesters. Successful synthesis of the 37 amino acid long BPTI$^{1-37}$-SEt, an activated fragment used to prepare bovine pancreatic trypsin inhibitor (BPTI; see formula) by native chemical ligation, shows that even thioesters of long peptides of complex composition are accessible using standard resins and 9-fluorenylmethoxycarbonyl (Fmoc) chemistry.

`RPDFCLEPPYTGPCKARIIRYFYNAKAGLCQTFVYGG↓CRAKRNNFKSAEDCMRTCGGA`

Angew. Chem. **2001**, *113*, 3503–3505

A. Sewing, D. Hilvert* 3395–3396

Fmoc-Compatible Solid-Phase Peptide Synthesis of Long C-Terminal Peptide Thioesters

Keywords: ligation · peptide fragment condensation · peptides · peptide thioester · solid-phase synthesis

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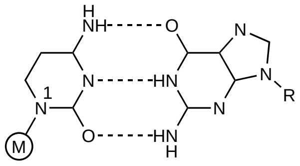
Stronger than the natural Watson–Crick base pairing is the association between N1-platinated cytosine and neutral, unplatinated guanine in DMSO. Nevertheless, in aqueous solution the Pt-containing associate **I** (M = Pt) is stable in a narrower pH range.



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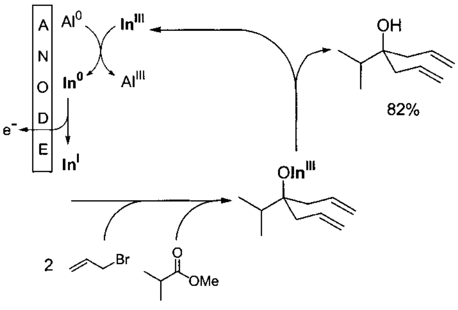
Angew. Chem. **2001**, *113*, 3497–3500

W. Brüning, R. K. O. Sigel, E. Freisinger,
B. Lippert* 3397–3399

Pt^{II} Binding to N1 of Cytosine: Strengthening the Watson–Crick Pair with Guanine and yet Confining Its pH Existence Range

Keywords: hydrogen bonds · nucleobases · platinum

It seems almost paradoxical that reactive low-valent indium(I) species can be generated at the anode through reduction of indium(III) salts under electrochemical conditions (see scheme). The resulting indium(I) species are highly effective catalysts for the allylation of different aldehydes, ketones, and esters on a preparative scale.



Angew. Chem. **2001**, *113*, 3514–3516

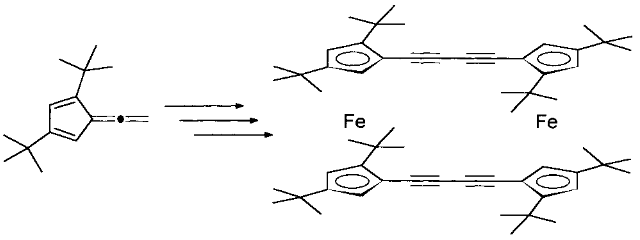
G. Hilt,* K. I. Smolko 3399–3402

Electrochemical Regeneration of Low-Valent Indium(I) Species as Catalysts for C–C Bond Formations

Keywords: allylation · aluminum · carbonyl compounds · electrochemistry · indium

1433-7851/01/4018-3272 $ 17.50+.50/0

Building butadiyne bridges: The kinetically stabilized 1,1′-diethynylferrocene, readily prepared from the pentafulvenoid allene **1**, can be transformed into the [4.4]ferrocenophane **2** by oxidative coupling. This compound exhibits a remarkably symmetrical structure in which the electrons are delocalized through the butadiyne bridges; in the crystalline state **2** exists in a helical-chiral conformation.



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Angew. Chem. **2001**, *113*, 3517–3520

K. H. H. Fabian, H.-J. Lindner,
N. Nimmerfroh, K. Hafner* 3402–3405

Synthesis and Properties of the First [4.4]Ferrocenophane-1,3,15,17-tetrayne

Keywords: alkyne complexes • alkynes • C–C coupling • cumulenes • cyclic voltammetry

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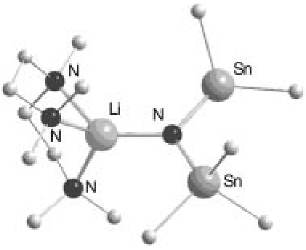
Monomers as well as dimers have been established for the structures of *N*-lithiostannylamines in the solid state as well as in solution (the picture shows the crystal structure of the monomer $[(Me_3Sn)_2NLi\{(Me_2NCH_2CH_2)_2NMe\}]$). These compounds, which were synthesized for the first time from stannylamines with *n*-butyllithium, are remarkably reactive in solution despite having extremely short Li–N and Sn–N bonds. The selective and successive cleavage of the Li–N and Sn–N bonds under mild conditions holds great promise for their synthetic application.



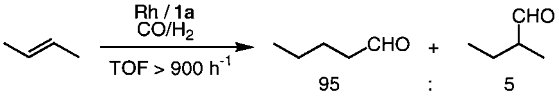
Angew. Chem. **2001**, *113*, 3511–3514

C. Neumann, T. Seifert, W. Storch,*
M. Vosteen,
B. Wrackmeyer* 3405–3407

New Building Blocks in Amide Chemistry—*N*-Lithiobis(trimethylstannyl)amine and *N*-Lithiotrimethylstannyl(trimethylsilyl)amine

Keywords: amides • lithium • tin

Readily accessible and highly efficient: Substituted 2,2′-bis(diphenylphosphanylmethyl)-1,1′-binaphthyl (NAPHOS) ligands **1** can be readily prepared from 2,2′-bis(dichlorophosphanylmethyl)-1,1′-binaphthyl. Especially ligands with electron-withdrawing aryl substituents (for example, $3,4,5\text{-}F_3C_6H_2$ (instead of Ph), **1a**) show a remarkable high activity and *n*:*i* selectivity in the rhodium-catalyzed hydroformylation of internal olefins (see scheme).



Angew. Chem. **2001**, *113*, 3505–3508

H. Klein, R. Jackstell, K.-D. Wiese,
C. Borgmann, M. Beller* .. 3408–3411

Highly Selective Catalyst Systems for the Hydroformylation of Internal Olefins to Linear Aldehydes

Keywords: homogeneous catalysis • hydroformylation • P ligands • rhodium

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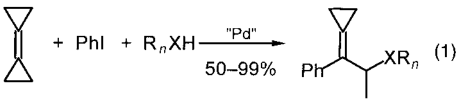
The primary carbopalladation intermediate resulting under Heck conditions from bicyclopropylidene and phenyl iodide in the presence of tris(*α*-furyl)phosphane rearranges to give a π-allylpalladium complex which is efficiently trapped by various nucleophiles R_nXH. This rearrangement leads to substituted methylenecyclopropanes in good to excellent yields (42–99%) [Eq. (1); X = C ($n = 3$), N ($n = 2$), O ($n = 1$)]. The intermediate 1,1-dimethyleneallylpalladium complex was isolated and fully characterized by an X-ray crystal-structure analysis.



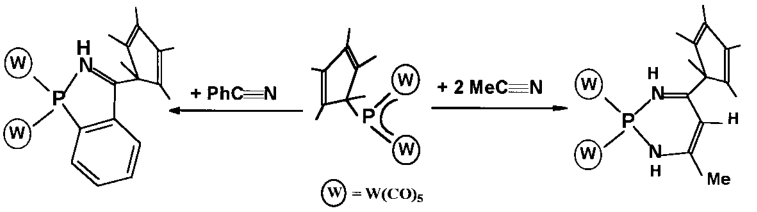
Angew. Chem. **2001**, *113*, 3509–3511

H. Nüske, M. Noltemeyer,
A. de Meijere* 3411–3413

Nucleophilic Trapping of π-Allylpalladium Intermediates Generated by Carbopalladation of Bicyclopropylidene: A Novel Three-Component Reaction

Keywords: domino reactions • Heck reaction • multicomponent reactions • palladium • small ring systems

Unexpectedly, nitriles are inserted at room temperature into the unstrained P–C bond of $[Cp^*P\{W(CO)_5\}_2]$. Depending on the nitrile used, dihydro-1,3,2-diazaphosphinine and benzo-1,2-azaphosphole derivatives, which are stablized by $[W(CO)_5]$ moieties, are formed (see scheme). The synthesis of the azaphosphole is accompanied by an additional C–H activation at room temperature and offers a novel and straightforward synthetic approach to this class of compounds.



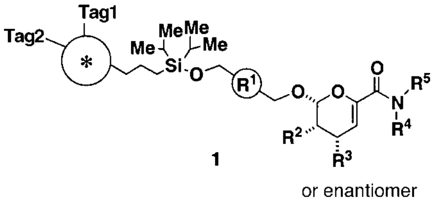
Angew. Chem. **2001**, *113*, 3520–3523

M. Schiffer, M. Scheer* 3413–3416

Insertion Reactions of Nitriles into the P–C Bond of $[(\eta^1\text{-}C_5Me_5)P\{W(CO)_5\}_2]$—A Novel Approach to Phosphorus-Containing Heterocycles

Keywords: insertion · phosphorus heterocycles · tungsten

Pathway development and library realization are reported for the generation of spatially segregated stock solutions of more than 4000 dihydropyrancarboxamides **1**. This is achieved by a diversity-oriented synthesis with use of enantioselective catalysis, high-capacity polystyrene macrobeads, encoding, and split-pool strategies.



Angew. Chem. **2001**, *113*, 3525–3529

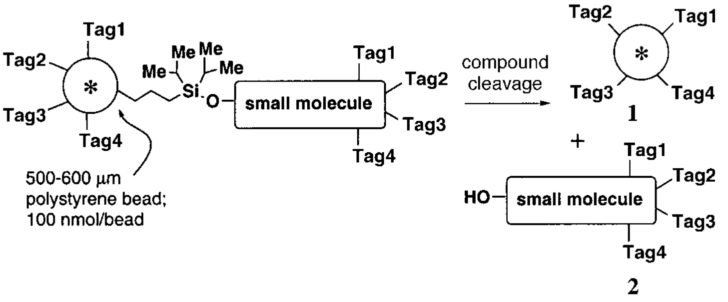
R. A. Stavenger,
S. L. Schreiber* 3417–3421

Asymmetric Catalysis in Diversity-Oriented Organic Synthesis: Enantioselective Synthesis of 4320 Encoded and Spatially Segregated Dihydropyrancarboxamides

Keywords: asymmetric catalysis · combinatorial chemistry · cycloaddition · enantioselectivity · solid-phase synthesis

---

Binary encoding with chloroaromatic diazoketone tags allows for efficient decoding from either beads (**1**) or stock solutions (**2**), which were derived from a "one-bead, one-stock-solution" chemical technology platform. This process is demonstrated in the partial decoding of a library of 4,320 dihydropyrancarboxamides.



Angew. Chem. **2001**, *113*, 3529–3533

H. E. Blackwell, L. Pérez,
S. L. Schreiber* 3421–3425

Decoding Products of Diversity Pathways from Stock Solutions Derived from Single Polymeric Macrobeads

Keywords: combinatorial chemistry · library encoding · polystyrene beads · solid-phase synthesis · structure elucidation

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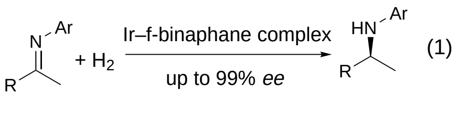
The key control factor in the hydrogenation of imines is the chiral ferrocene phosphane ligand f-binaphane. High yields and enantioselectivities were obtained in the Ir-catalyzed conversion of imines into amines [Eq. (1)].



Angew. Chem. **2001**, *113*, 3533–3536

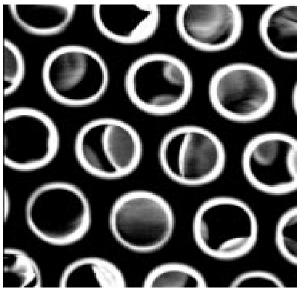
D. Xiao, X. Zhang* 3425–3428

Highly Enantioselective Hydrogenation of Acyclic Imines Catalyzed by Ir–f-Binaphane Complexes

Keywords: asymmetric catalysis · hydrogenation · imines · iridium · P ligands

Star pores! Star and block polymer architectures are made using living radical polymerization. Isoporous honeycomb films (see scanning electron microscope image) are cast under humid conditions from solutions of these macromolecules. The pore diameter is shown to be dependent not only on the casting conditions but on the specific molecular architecture and molecular weight of the polymers.

Angew. Chem. **2001**, *113*, 3536–3540



M. H. Stenzel-Rosenbaum, T. P. Davis,* A. G. Fane, V. Chen 3428–3432

Porous Polymer Films and Honeycomb Structures Made by the Self-Organization of Well-Defined Macromolecular Structures Created by Living Radical Polymerization Techniques

Keywords: membranes · polymers · radical reactions · self-assembly · styrene

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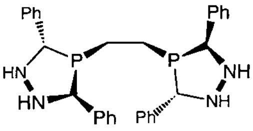
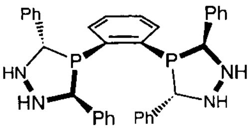
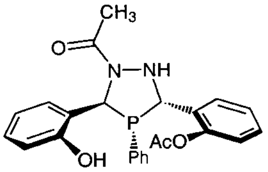
Effective ligands for transition metals: a diverse array of chiral five-membered phosphacycles, for example, **1**–**3**, can be synthesized in two steps starting from simple primary phosphanes, hydrazine, and aldehydes.



1



2



3

Angew. Chem. **2001**, *113*, 3540–3542

C. R. Landis,* W. Jin, J. S. Owen, T. P. Clark 3432–3434

Rapid Access to Diverse Arrays of Chiral 3,4-Diazaphospholanes

Keywords: cyclization · homogeneous catalysis · P ligands · phosphorus heterocycles

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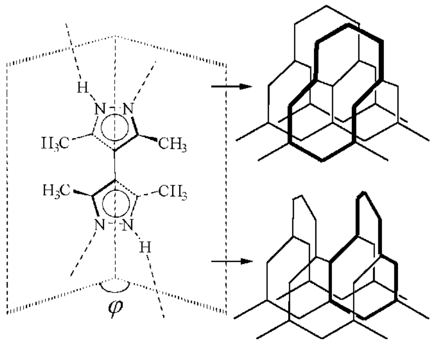
The inter-ring angle *φ* of 4,4′-bipyrazolyls, which can be controlled by varying the 3,3′- and 5,5′-substituents, determines their association into different three-dimensional arrays through interaction of their self-complementary hydrogen-bond donor and acceptor sites. Thus, for $\varphi \approx 90°$, a (10,3)-*b* net is formed (see picture, top), while for $\varphi \approx 60°$, the inherently chiral (10,3)-*c* net is obtained (see picture, bottom).

Angew. Chem. **2001**, *113*, 3543–3546



I. Boldog, E. B. Rusanov, A. N. Chernega, J. Sieler, K. V. Domasevitch* 3435–3438

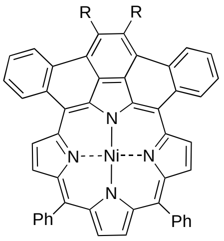
Acentric Extended Solids by Self-Assembly of 4,4′-Bipyrazolyls

Keywords: chirality · crystal engineering · hydrogen bonds · self-assembly · supramolecular chemistry

---

Bergman cyclization of 2,3-dialkynyl-*meso*-tetraphenylporphyrins and carbon–carbon bond formation (mediated by 1,4-diradicals) with the adjacent *meso*-phenyl rings lead to formation of an unprecedented multicarbocycle fused onto the porphyrin periphery. The highly π-extended parent molecules (**1**; R = Bu, H, Ph) are described and are named picenoporphyrins after their [5]phenacene structure.

Angew. Chem. **2001**, *113*, 3547–3549



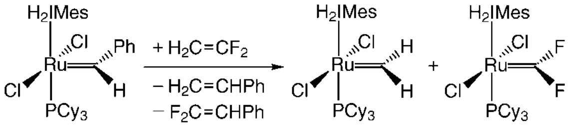
1

H. Aihara, L. Jaquinod, D. J. Nurco, K. M. Smith* 3439–3441

Multicarbocycle Formation Mediated by Arenoporphyrin 1,4-Diradicals: Synthesis of Picenoporphyrins

Keywords: C–C coupling · cyclization · diradicals · nickel · porphyrinoids

Unsaturated halocarbene complexes can be synthesized in the first example of olefin metathesis with a directly fluorinated substrate. The ruthenium catalyst **1** reacts with 1,1-difluoroethylene to yield the corresponding methylidene [Ru]$=$CH$_2$ (**2**) and difluorocarbene [Ru]$=$CF$_2$ complexes (**3**). H$_2$IMes $=$ 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene; Cy $=$ cyclohexyl.



1 **2** **3**

Angew. Chem. **2001**, *113*, 3549 – 3552

Keywords: carbene ligands · fluorinated ligands · homogeneous catalysis · metathesis · ruthenium

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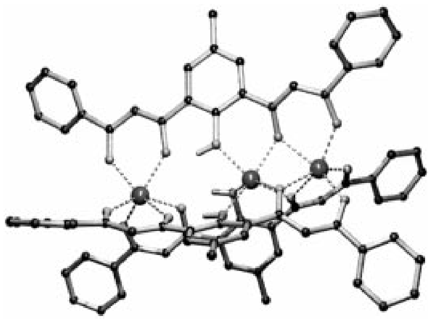
A new topology within the family of metallohelicates has been revealed by the crystal structure of the complex [Mn$_3$(HL)$_3$] (see picture). The novel oxygen-based pentadentate ligand H$_3$L reacts with Mn(OAc)$_2$ to produce this unique triple-stranded helicate with an unprecedented asymmetric arrangement of the metal ions along the molecular axis. This helicate displays intramolecular magnetic coupling.



Angew. Chem. **2001**, *113*, 3552 – 3554

Keywords: chirality · helical structures · magnetic properties · manganese · supramolecular chemistry

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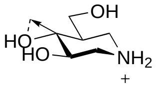
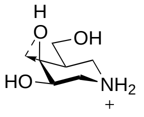
A new answer to a 100-year-old puzzle is presented here, namely, why are galactosides hydrolyzed faster than glucosides? This disparity was long attributed to facilitation by axial OH groups of a conformational change en route to the transition state. However, the results presented here indicate that differences in the electron-withdrawing effects (represented by arrows) of equatorial (**A**) and axial OH groups (**B**) are decisive.



A



B

Angew. Chem. **2001**, *113*, 3555 – 3557

Keywords: amines · basicity · glycosides · hydrolysis · kinetics

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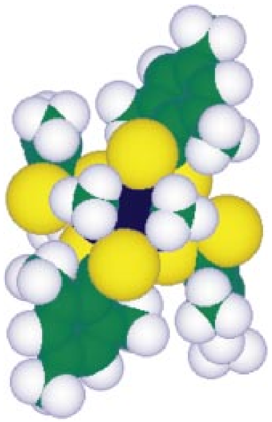
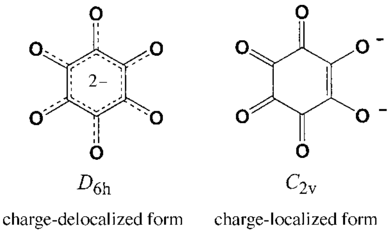
Intramolecular S–Si interactions occur between the silicon and the sulfur atoms in the disilane [Me(MesCS$_2$)$_2$Si]$_2$, in which each silicon atom bears two [2,4,6-trimethyl(thiobenzoyl)]thio ligands. This results in a coordination number of seven for both silicon atoms (the picture shows a space-filling representation of the structure). The hexacoordinate monosilane (MesCS$_2$)$_2$SiPh$_2$ was also synthesized. Mes $=$ mesityl $=$ 2,4,6-trimethylphenyl.



Angew. Chem. **2001**, *113*, 3558 – 3560

Keywords: hypervalent compounds · silanes · silicon · S ligands

The nonbenzenoid aromatic D_{6h} and enediolate C_{2v} valence tautomers of the relatively unstable rhodizonate dianion (see picture) have been generated in situ and stabilized by hydrogen bonding with (3-hydroxyphenyl)urea and 1,1′-ethylenediurea, respectively, in two novel crystalline inclusion compounds.



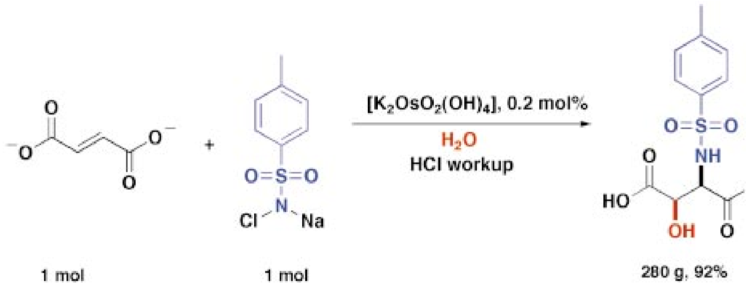
Angew. Chem. **2001**, *113*, 3561–3563

C.-K. Lam, T. C. W. Mak* .. 3453–3455

Generation and Stabilization of D_{6h} and C_{2v} Valence Tautomeric Structures of the Rhodizonate Dianion in Hydrogen-Bonded Host Lattices

Keywords: aromaticity · inclusion compounds · rhodizonate · tautomerism · urea

In water and in the absence of any ligands, salts of unsaturated carboxylic acids are readily and cleanly aminohydroxylated to provide vicinal hydroxyamino acid derivatives in high yields (see scheme).



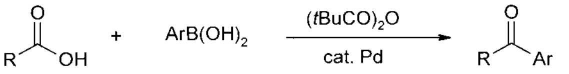
Angew. Chem. **2001**, *113*, 3563–3565

V. V. Fokin,*
K. B. Sharpless* 3455–3457

A Practical and Highly Efficient Aminohydroxylation of Unsaturated Carboxylic Acids

Keywords: amino acids · amino alcohols · homogeneous catalysis · osmium · oxidation

Mild and convenient: a palladium-catalyzed cross-coupling reaction between arylboronic acids and carboxylic anhydrides, which are generated in situ from the corresponding carboxylic acids, allows the efficient synthesis of a broad variety of functionalized aryl ketones [Eq. (1)].



$$\mathrm{RC(O)OH} + \mathrm{ArB(OH)_2} \xrightarrow[\text{cat. Pd}]{(t\mathrm{BuCO})_2\mathrm{O}} \mathrm{RC(O)Ar} \qquad (1)$$

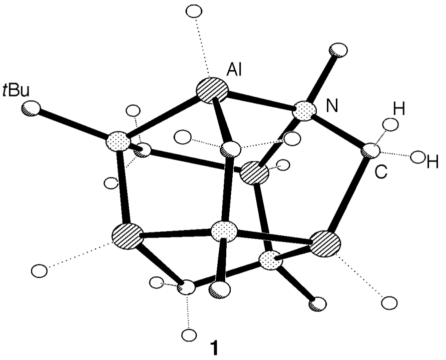
Angew. Chem. **2001**, *113*, 3566–3568

L. J. Goossen,* K. Ghosh .. 3458–3460

Palladium-Catalyzed Synthesis of Aryl Ketones from Boronic Acids and Carboxylic Acids or Anhydrides

Keywords: boronic acids · carboxylic acids · homogeneous catalysis · ketones · palladium

A significant difference in the arrangement of the atoms within the cage skeleton of the $Al_4C_4N_4$ polyhedron **1** was found in comparison with those of other known hexagonal-prismatic arrays of aluminum compounds containing a twelve-membered core. Compound **1** was prepared in good yield by the reaction of equivalent amounts of $H_3Al \cdot NMe_3$ and *tert*-butyl isocyanide in refluxing toluene.



1

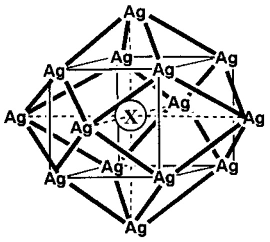
Angew. Chem. **2001**, *113*, 3569–3572

W. Zheng, A. Stasch, J. Prust,
H. W. Roesky,* F. Cimpoesu,
M. Noltemeyer,
H.-G. Schmidt 3461–3464

A Polyhedral Aluminum Compound with an $Al_4C_4N_4$ Framework

Keywords: ab initio calculations · aluminum · cage compounds · isocyanides

A templating anion is a must for the formation of the cage compounds $[Ag_{14}(C{\equiv}CtBu)_{12}X]OH$ (X = Cl, Br), in which a rhombic dodecahedron of silver atoms surrounds the central X atom (see picture). The silver atoms are held together by a combination of bridging alkynyl groups (not shown) and argentophilic Ag⋯Ag interactions. In the absence of the templating anion insoluble polymeric materials are obtained.



Angew. Chem. **2001**, *113*, 3572–3575

D. Rais, J. Yau, D. M. P. Mingos,*
R. Vilar,* A. J. P. White,
D. J. Williams 3464–3467

Anion-Templated Syntheses of Rhombohedral Silver–Alkynyl Cage Compounds

Keywords: alkynyl ligands · cage compounds · metal–metal interactions · silver · template synthesis

A supramolecular triangle results, instead of the expected square, from the reaction of a compact, ditopic 90° platinum(II) center and the most rigid, aromatic linear linker, pyrazine (see picture). This unexpected species is characterized both in solution and the solid state.

Angew. Chem. **2001**, *113*, 3575–3577

M. Schweiger, S. R. Seidel, A. M. Arif, P. J. Stang* 3467–3469

The Self-Assembly of an Unexpected, Unique Supramolecular Triangle Composed of Rigid Subunits

Keywords: N ligands · platinum · pyrazine · self-assembly · supramolecular chemistry

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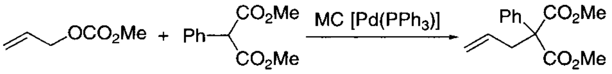
Buried alive! A triphenylphosphane palladium catalyst was immobilized onto/into a polymer by microencapsulation and the polymer-supported catalyst (MC[Pd(PPh$_3$)]) successfully used in several palladium-catalyzed reactions (one example is shown). The reactions proceeded in high yields, and the catalyst was recovered by filtration and reused. The air-sensitivity of the palladium complex is substantially suppressed by this immobilization.



Angew. Chem. **2001**, *113*, 3577–3579

R. Akiyama, S. Kobayashi* 3469–3471

Microencapsulated Palladium Catalysts: Allylic Substitution and Suzuki Coupling Using a Recoverable and Reusable Polymer-Supported Palladium Catalyst

Keywords: allylic compounds · homogeneous catalysis · palladium · supported catalysts · Suzuki coupling

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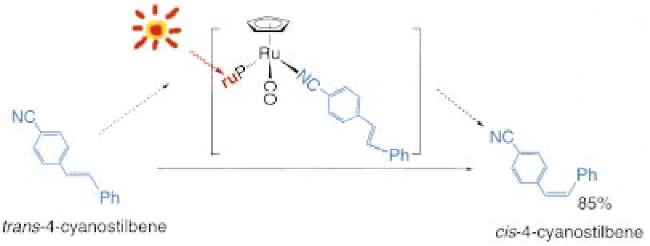
Intramolecular photosensitization by using the new visible-light-active *tert*-phosphane ligand (**ru**P) which changes a transition metal complex into a photoactive reaction center on coordination. The scheme shows the resulting intramolecular *trans*→*cis* photoconversion of a stilbene group.



Angew. Chem. **2001**, *113*, 3580–3582

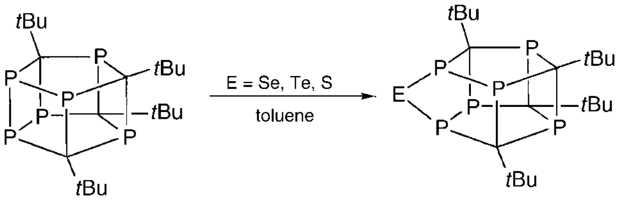
M. Osawa,* M. Hoshino, Y. Wakatsuki 3472–3474

A Light-Harvesting *tert*-Phosphane Ligand Bearing a Ruthenium(II) Polypyridyl Complex as Substituent

Keywords: energy transfer · light harvesting · P ligands · photoisomerization · ruthenium

---

Exclusive opening of the unique P–P bond with formation of **2** is observed when **1** is treated with carbene analogues [Eq. (1)]! This behavior is explicable by the release of strain resulting in a low-lying (20 kcal mol^{-1}) reactive singlet biradical. The HOMO and LUMO centred at the reactive sites and the thermodynamic stability of the products support this behavior.



(1)

1 **2**

Angew. Chem. **2001**, *113*, 3582–3585

M. M. Al-Ktaifani, D. P. Chapman, M. D. Francis, P. B. Hitchcock, J. F. Nixon,* L. Nyulászi* .. 3474–3477

The Hexaphosphapentaprismane P$_6$C$_4t$Bu$_4$: A “Jaws-Like” Cage Molecule That Bites!

Keywords: ab initio calculations · cage compounds · chalcogens · insertion · phosphorus heterocycles

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

* Author to whom correspondence should be addressed

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