



The following Communications have been judged by at least two referees to be "very important papers" and will be published online at www.angewandte.org soon:

N. Suzuki*, D. Hashizume, H. Koshino, T. Chihara

Transformation of 1-Zirconacyclopent-3-yne, a Five-Membered Cycloalkyne, into 1-Zirconacyclopent-3-ene and Formal 1-Zirconacyclopenta-2,3-dienes

S.-Y. Yu,* Q.-F. Sun, T. K.-M. Lee, E. C.-C. Cheng, Y.-Z. Li,*
V. W.-W. Yam*

Au₃₆ Crown: Macrocyclization Directed by Metal–Metal Bonding Interactions

A. Fürstner*, L. Morency

The Nature of the Reactive Intermediates in Gold-Catalyzed Cycloisomerization Reactions

G. Pasparakis, C. Alexander*

Sweet-Talking Double Hydrophilic Block Copolymer Vesicles

H.-Y. Kim, M.-K. Cho, D. Riedel, C. O. Fernandez, M. Zweckstetter*
Dissociation of Amyloid Fibrils of α -Synuclein in Supercooled Water

Inorganic Chemistry:

G. Férey Awarded _____ 4627

Organometallic Chemistry:

P. Knochel Honored _____ 4627

Practical Guide to Interpretive
Near-Infrared Spectroscopy

Jerry Workman, Jr., Lois Weyer

News

Materials Science:

Prize to T. Mallouk _____ 4627

Books

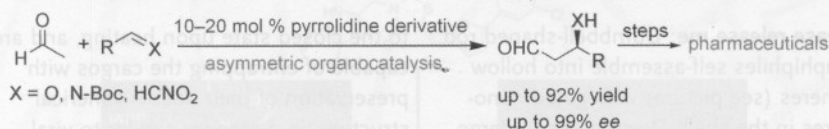
reviewed by R. Salzer _____ 4628

Highlights

Organocatalysis

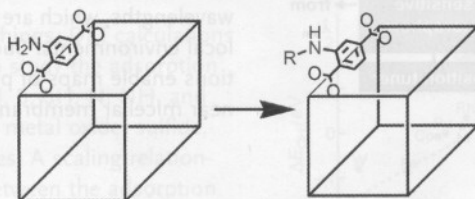
B. Alcaide,* P. Almendros* 4632–4634

Organocatalytic Reactions with
Acetaldehyde



Big step, small molecule: Although acetaldehyde is the simplest of enolizable carbonyl compounds, and low-molecular-weight enamine/iminium-ion organocatalysis is the more elegant and most economical way to introduce chirality into a molecule, the first reports of the direct

catalytic asymmetric reactions of acetaldehyde with electrophiles have just recently appeared (see scheme; Boc = *tert*-butoxycarbonyl). Elaboration of the obtained adducts provides precursors for the synthesis of pharmaceuticals.



MOF Tuning: Recent progress on post-synthetic covalent modification of MOF (metal–organic framework) materials has led to the discovery of exciting new porous

inorganic materials. These results involve transformation of the organic groups of MOFs without altering the three-dimensional structure.

Metal–Organic Frameworks

Y.-F. Song, L. Cronin* _____ 4635–4637

Postsynthetic Covalent Modification of
Metal–Organic Framework (MOF)
Materials

Reviews

Organocatalysis

A. Dondoni,* A. Massi* — 4638–4660

Asymmetric Organocatalysis: From Infancy to Adolescence



As Bernini's David, in the prime of adolescence, fought Goliath armed only with a sling and a stone, organocatalysis uses simple organic molecules to address some fundamental issues of organic synthesis. Important questions concern the chemical efficiency of such processes and the development of viable and simple routes to natural products and drug candidates.

Communications

Porous Nanostructures

J.-K. Kim, E. Lee, Y.-b. Lim, M. Lee* — 4662–4666

Supramolecular Capsules with Gated Pores from an Amphiphilic Rod Assembly



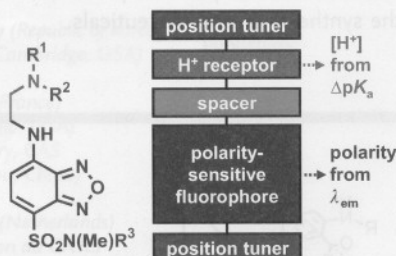
Please release me: Dumbbell-shaped rod amphiphiles self-assemble into hollow spheres (see picture) with gated nanopores in the shell. These pores undergo reversible transitions from the open state

to the closed state upon heating, and are capable of entrapping the cargos with preservation of their hollow spherical structure, in a manner similar to viral capsids.

Molecular Sensors

S. Uchiyama,* K. Iwai, A. P. de Silva* — 4667–4669

Multiplexing Sensory Molecules Map Protons Near Micellar Membranes



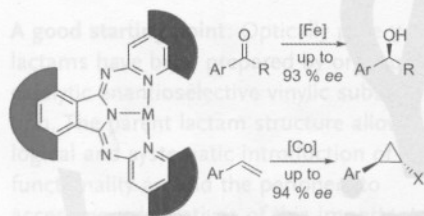
Hi-fi mapping: Multiplexing fluorescent sensors that simultaneously target proton concentration and polarity move to micellar nanospaces, self-regulate their positions, and report their pK_a values and wavelengths, which are controlled by their local environments. Such sensory functions enable maps of proton gradients near micellar membranes to be drawn.

For the USA and Canada:

ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200

Meacham Ave., Elmont, NY 11003. Periodicals postage paid at Jamaica, NY 11431. US POSTMASTER: send address changes to *Angewandte Chemie*, Wiley-VCH, 111 River Street, Hoboken, NJ 07030. Annual subscription price for institutions: US\$ 7225/6568 (valid for print and

electronic / print or electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.

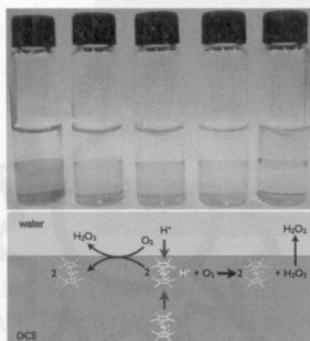


Protect your back: Chiral wedges (red, see scheme) at the wingtips of bis(2-pyridylimino)isoindole (bpi) pincer ligands with an appropriate protective hedge (green), to block the metal center from backside attack, in the backbone represent a new class of efficient 3d-metal catalysts. These catalysts gave excellent enantioselectivities in the iron-catalyzed hydrosilylation of arylketones and in the cobalt-catalyzed cyclopropanation of alkenes.

Asymmetric Catalysis

B. K. Langlotz, H. Wadepohl,
L. H. Gade* — 4670–4674

Chiral Bis(pyridylimino)isoindoles: A Highly Modular Class of Pincer Ligands for Enantioselective Catalysis

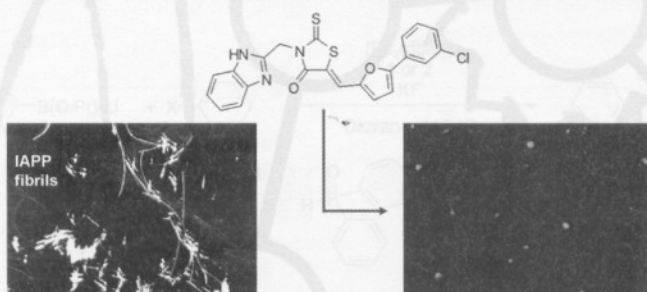


Hydrogen peroxide generation at a liquid|liquid interface occurs with a yield of 20% with respect to the concentration of reducing agent (decamethylferrocene). The liquid|liquid interface supplies electrons from the reducing agent and protons from the aqueous phase to drive the reduction of O_2 into H_2O_2 , which is extracted into the aqueous phase during the course of reaction (see picture; DCE = 1,2-dichloroethane).

Hydrogen Peroxide Production

B. Su, R. P. Nia, F. Li, M. Hojeij,
M. Prudent, C. Corminboeuf, Z. Samec,
H. H. Girault* — 4675–4678

H_2O_2 Generation by Decamethylferrocene at a Liquid|Liquid Interface



Small and effective: The pathological aggregation of amylin (IAPP), which leads to type II diabetes mellitus, is effectively inhibited by small-molecule rhodanine-

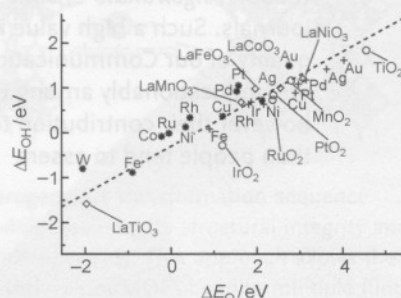
based inhibitors at nanomolar concentrations. The prevention of aggregation by treatment with the inhibitor is demonstrated by AFM (see image).

Small-Molecule Inhibitors

R. Mishra, B. Bulic, D. Sellin, S. Jha,
H. Waldmann, R. Winter* — 4679–4682

Small-Molecule Inhibitors of Islet Amyloid Polypeptide Fibril Formation

Getting on top of things: DFT calculations have been used to study the adsorption energies of O, OH, S, SH, N, NH, and NH_2 on transition metal oxide, sulfide, and nitride surfaces. A scaling relationship was found between the adsorption energies of the intermediates and the adsorption energies of the atoms which is independent of the metal and depends only on the number of H atoms in the molecule (see graph).

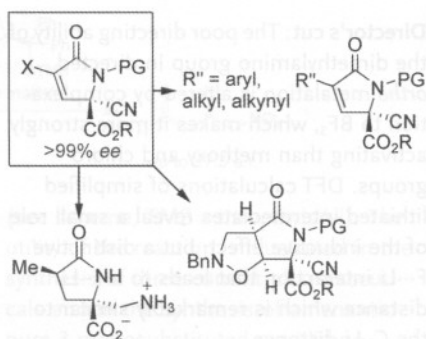


Surface Adsorption

E. M. Fernández, P. G. Moses,
A. Toftlund, H. A. Hansen, J. I. Martínez,
F. Abild-Pedersen, J. Kleis, B. Hinnemann,
J. Rossmeisl, T. Bligaard,
J. K. Nørskov* — 4683–4686

Scaling Relationships for Adsorption Energies on Transition Metal Oxide, Sulfide, and Nitride Surfaces

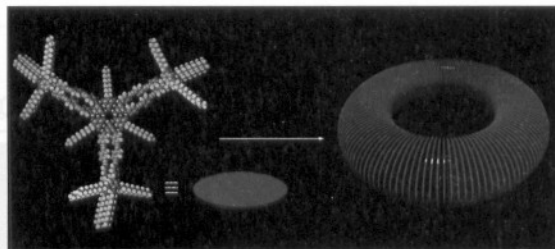
A good starting point: Optically pure γ -lactams have been prepared by organocatalytic enantioselective vinylic substitution. The parent lactam structure allows logical and systematic introduction of functionality around the periphery to access new derivatives of this important class of molecules. Bn = benzyl, PG = protecting group.



Asymmetric Synthesis

T. B. Poulsen, G. Dickmeiss, J. Overgaard, K. A. Jørgensen* 4687–4690

Organocatalytic Asymmetric Synthesis of Versatile γ -Lactams



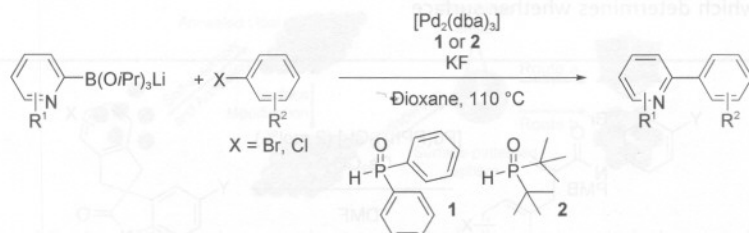
Nanodonuts! A hydrogen-bonded cyclic assembly (rosette, left) of a melamine featuring π -conjugated oligo(*p*-phenyleneethynylene) hierarchically self-organizes

with a cyanurate in decane under dilute conditions to form toroidal nanostructures (right) with a diameter of 40 nm.

Self-Assembly

S. Yagai,* S. Mahesh, Y. Kikkawa, K. Unoike, T. Karatsu, A. Kitamura, A. Ajayaghosh* 4691–4694

Toroidal Nanoobjects from Rosette Assemblies of Melamine-Linked Oligo(*p*-phenyleneethynylene)s and Cyanurates



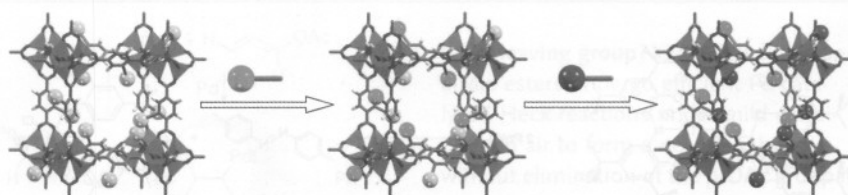
One of the most general systems for the cross-coupling of aryl and heteroaryl bromides and chlorides with 2-pyridyl-derived nucleophiles has been developed, for

which catalysts comprising $[\text{Pd}_2(\text{dba})_3]$ and either diaryl (1) or dialkyl phosphine oxide (2) supporting ligands were found to be ideal (see scheme).

Cross-Coupling Reactions

K. L. Billingsley, S. L. Buchwald* 4695–4698

A General and Efficient Method for the Suzuki–Miyaura Coupling of 2-Pyridyl Nucleophiles



More than a one-trick pony: Postsynthetic modification of metal–organic frameworks (MOFs) permits stepwise, “tandem” modification of the lattice. An MOF bearing reactive functional groups can be subjected to a controllable, het-

erogeneous transformation sequence while retaining its structural integrity and microporosity. This approach allows the synthesis of MOFs bearing multiple functional groups (represented in the scheme by green and pink spheres).

Metal–Organic Frameworks

Z. Wang, S. M. Cohen* 4699–4702

Tandem Modification of Metal–Organic Frameworks by a Postsynthetic Approach

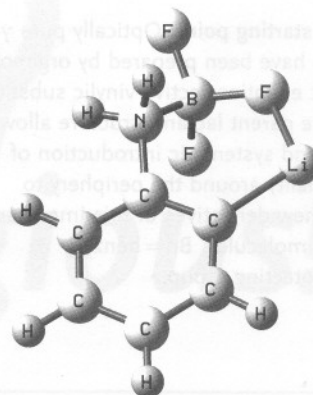
C–H Activation

S. V. Kessar,* P. Singh,* K. N. Singh,*
P. V. Bharatam,* A. K. Sharma, S. Lata,
A. Kaur ————— 4703–4706



A Study of BF₃-Promoted *ortho* Lithiation of Anilines and DFT Calculations on the Role of Fluorine–Lithium Interactions

Director's cut: The poor directing ability of the dimethylamino group in directed *ortho* metalation is altered by complexation to BF₃, which makes it more strongly activating than methoxy and chloro groups. DFT calculations of simplified lithiated intermediates reveal a small role of the inductive effect, but a distinctive F...Li interaction that leads to a F–Li distance which is remarkably similar to the C–Li distance.

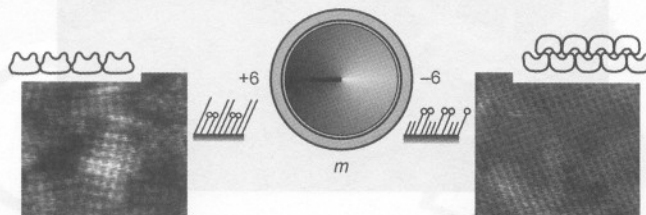


Protein Crystals

S. Moreno-Flores, A. Kasry, H.-J. Butt,
C. Vavilala, M. Schmittle, D. Pum,
U. B. Sleytr,
J. L. Toca-Herrera* ————— 4707–4710



From Native to Non-Native Two-Dimensional Protein Lattices through Underlying Hydrophilic/Hydrophobic Nanoprotrusions



Tuning to the terminals: Controlled tuning of protein–substrate interactions induces a transition from native to non-native protein crystals (see AFM images) as—depending on *m*, the chain-length difference, which determines whether surface

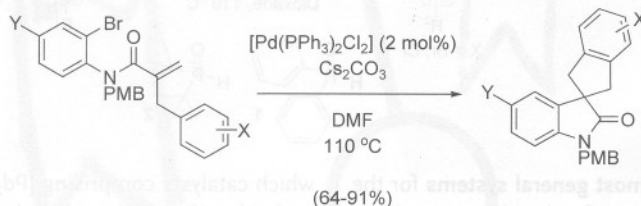
protrusions are hydroxy or methyl functionalized—the underlying non-ion-mediated interactions are gradually transformed from mainly associative (H-bonding) to hydrophobic.

Synthetic Methods

R. T. Ruck,* M. A. Huffman, M. M. Kim,
M. Shevlin, W. V. Kandur,
I. W. Davies ————— 4711–4714



Palladium-Catalyzed Tandem Heck Reaction/C–H Functionalization—Preparation of Spiro-Indane-Oxindoles



Tied up nicely: A novel tandem reaction involving an intramolecular Heck reaction with subsequent functionalization of an

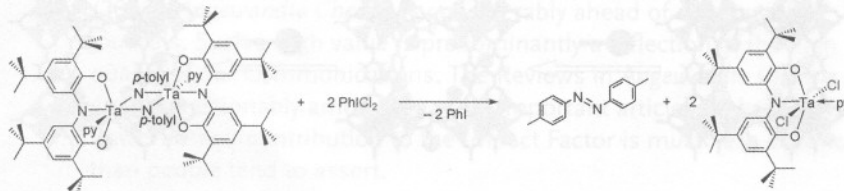
unactivated C–H bond to generate spiro-fused indane-oxindoles is described (see scheme; PMB = *p*-methoxybenzyl).

Redox-Active Ligands

R. A. Zarkesh, J. W. Ziller,
A. F. Heyduk* ————— 4715–4718

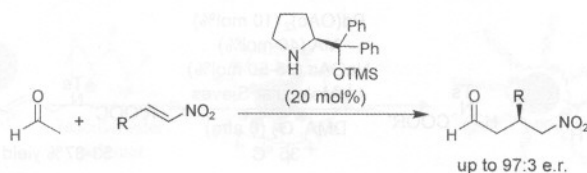


Four-Electron Oxidative Formation of Aryl Diazenes Using a Tantalum Redox-Active Ligand Complex



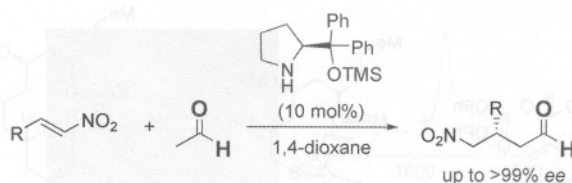
The active ingredient: The bis(μ-imido)tantalum dimer [(ONO^{red})Ta(μ-*N-p*-tolyl)(py)]₂ releases the aryl diazene (*p*-tolyl)N=N(*p*-tolyl) upon four-electron oxidation with PhICl₂ (see scheme;

py = pyridine). Studies suggest that the redox-active [ONO^{red}]^{3–} ligands act to collect single-electron oxidation equivalents for the multielectron reaction.



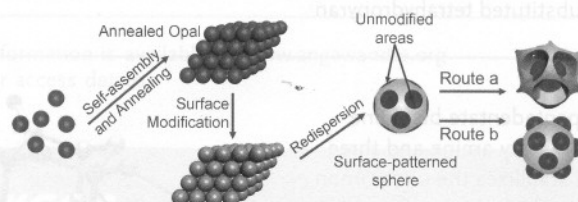
Acetaldehyde, now a big contender: A silyl prolinol derivative was found to catalyze the first Michael addition of acetaldehyde with both aromatic and aliphatic nitroolefins in excellent enantioselectivities

(see scheme, TMS = trimethylsilyl). The utility of the reaction is illustrated in the synthesis of three current pharmaceuticals and in the synthesis of an enantiopure 3-monosubstituted pyrrolidine.



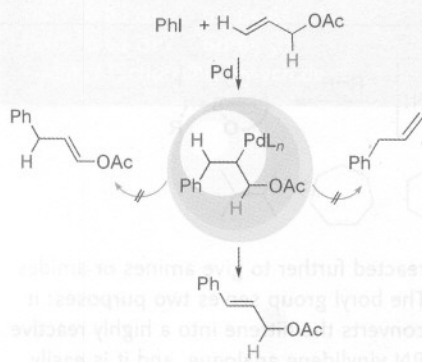
An acetaldehyde breakthrough: The catalytic asymmetric Michael addition reaction of acetaldehyde and various nitroalkenes in the presence of a chiral diphenylprolinol silyl ether organocatalyst is de-

scribed (see scheme; TMS = trimethylsilyl). The desired 1,4-addition products, α -unsubstituted γ -nitro aldehydes, were obtained in good yields with excellent enantioselectivities.



One seed for two: Microspheres with patterned surfaces were obtained by modifying the surface of microspheres of a self-assembled colloidal crystal and redispersion of the colloidal crystal into

individual particles. With these surface-patterned spheres as seeds, two types of nonspherical particles were fabricated by the seeded particle growth method.



What leaving group? Organic halides and allylic esters undergo efficient Pd-catalyzed Heck reactions under mild conditions in air to form a new C–C bond without elimination of the β -OAc group in the intermediate palladium complex. Instead a highly regioselective β -H elimination takes place to provide substituted derivatives of allylic alcohols (see scheme).

Organocatalysis

P. García-García, A. Ladépêche, R. Halder, B. List* 4719–4721

Catalytic Asymmetric Michael Reactions of Acetaldehyde

Organocatalysis

Y. Hayashi,* T. Itoh, M. Ohkubo, H. Ishikawa 4722–4724

Asymmetric Michael Reaction of Acetaldehyde Catalyzed by Diphenylprolinol Silyl Ether

Surface Patterning

L. Wang, L. Xia, G. Li, S. Ravaine, X. S. Zhao* 4725–4728

Patterning the Surface of Colloidal Microspheres and Fabrication of Nonspherical Particles

Heck Reaction

D. Pan, A. Chen, Y. Su, W. Zhou, S. Li, W. Jia, J. Xiao, Q. Liu, L. Zhang, N. Jiao* 4729–4732

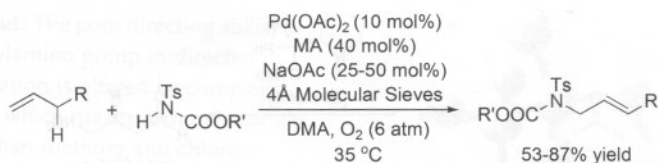
Ligand-Free Pd-Catalyzed Highly Selective Arylation of Allylic Esters with Retention of the Traditional Leaving Group

Aerobic Oxidation

G. Liu,* G. Yin, L. Wu — 4733–4736



Palladium-Catalyzed Intermolecular Aerobic Oxidative Amination of Terminal Alkenes: Efficient Synthesis of Linear Allylamine Derivatives



O₂-coupled allylic C–H amination: A first general palladium-mediated intermolecular aerobic oxidative allylic amination was developed to synthesize linear (*E*)-allyl-imides with high regioselectivity (see scheme; MA = maleic anhydride). The

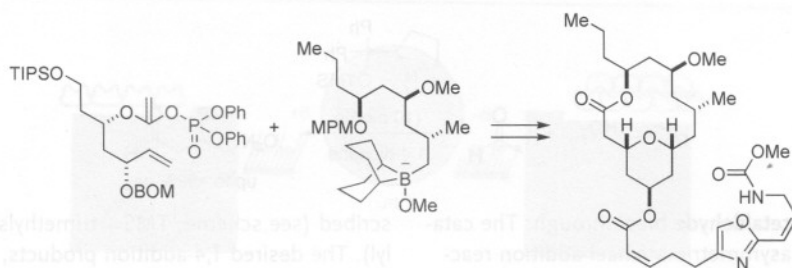
proposed mechanism involves an allylic C–H activation with subsequent nitrogen nucleophile substitution. The catalytic system allows efficient dioxygen-coupled turnover without additional cocatalysts.

Natural Products Synthesis

H. Fuwa,* S. Naito, T. Goto, M. Sasaki* — 4737–4739



Total Synthesis of (+)-Neopeltolide



Rapid elaboration: (+)-Neopeltolide, a novel marine metabolite with potent cytotoxicity against several cancer cell lines, was the target of an efficient total synthesis (see scheme). The construction of the 2,4,6-trisubstituted tetrahydropyran

substructure is based on a Suzuki–Miyaura coupling/ring-closing metathesis sequence. BOM = benzyloxymethyl, MPM = 4-methoxyphenylmethyl, TIPSO = triisopropylsilyl.

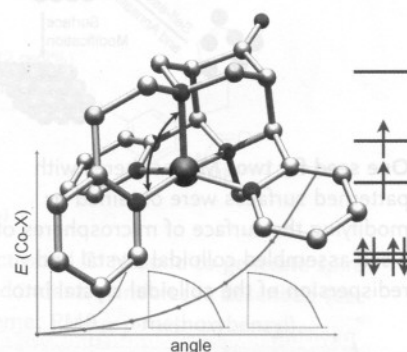
Chelating Ligands

P. Comba,* M. Kerscher, G. A. Lawrance, B. Martin, H. Wadepohl, S. Wunderlich — 4740–4743



Stable Five- and Six-Coordinate Cobalt(III) Complexes with a Pentadentate Bispidine Ligand

I am ligand: A pentadentate bispidine ligand with two tertiary amine and three pyridine donors stabilizes the uncommon intermediate-spin electronic configuration of Co^{III} (*S* = 1; see picture: C gray, N blue, O red, Co violet). Dissociation of the monodentate coligand yields a catalytically active pentacoordinate complex.

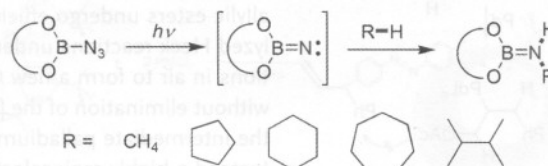


Alkane Activation

H. F. Bettinger,* M. Filthaus, H. Bornemann, I. M. Oppel — 4744–4747

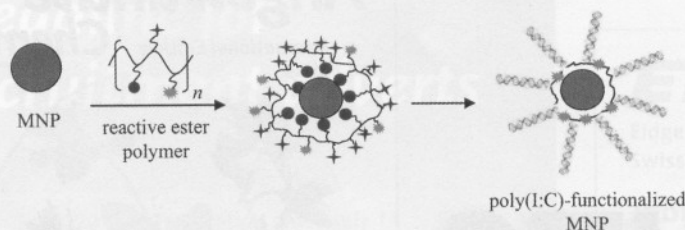


Metal-Free Conversion of Methane and Cycloalkanes to Amines and Amides by Employing a Borylnitrene



C–H insertion: Borylnitrenes, which are generated in situ by photolysis of azides, convert unactivated alkanes by intermolecular C–H insertion into aminoboranes (see scheme), which in turn can be

reacted further to give amines or amides. The boryl group serves two purposes: it converts the nitrene into a highly reactive BN vinylidene analogue, and it is easily cleaved from the product.



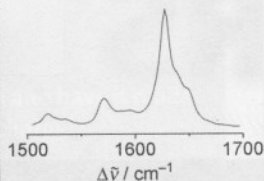
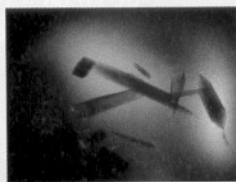
Specific cell recognition: Magnetic γ - Fe_2O_3 nanoparticles (MNPs) functionalized with a fluorescently labeled polymer and polyinosinic-polycytidylic acid [poly(I:C)] allow the specific visualization of the

TLR3 receptors on the the surface of Caki-1 cells. The expression of TLR3 on the Caki-1 cells was demonstrated independently by RT-PCR and immunostaining techniques.

Magnetic Nanoparticles

M. I. Shukoor, F. Natalio, N. Metz, N. Glube, M. N. Tahir, H. A. Therese, V. Ksenofontov, P. Theato, P. Langguth, J.-P. Boissel, H. C. Schröder, W. E. G. Müller, W. Tremel* **4748–4752**

dsRNA-Functionalized Multifunctional γ - Fe_2O_3 Nanocrystals: A Tool for Targeting Cell Surface Receptors



Crystals of the photoreceptor phytochrome were studied nondestructively by resonance Raman spectroscopy. The spectra of the chromophore-binding domains (CBD) of phytochrome from *Deinococcus radiodurans*, from which three-dimensional structures have been

determined, demonstrate the same chromophore structure in the parent Pr state as in solution. Unlike CBD, crystals of phytochrome from *Agrobacterium tumefaciens* including the CBD and the PHY domain can be photoconverted to a Meta-Rc-like state.

Photoreceptors

D. von Stetten, M. Günther, P. Scheerer, D. H. Murgida, M. A. Mroginski, N. Krauß, T. Lamparter, J. Zhang, D. M. Anstrom, R. D. Vierstra, K. T. Forest, P. Hildebrandt* **4753–4755**

Chromophore Heterogeneity and Photoconversion in Phytochrome Crystals and Solution Studied by Resonance Raman Spectroscopy

Supporting information is available on www.angewandte.org (see article for access details).

A video clip is available as Supporting Information on www.angewandte.org (see article for access details).

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