

VIP

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"

A. Fürstner*, L. Morency
On the Nature of the Reactive Intermediates in Gold-Catalyzed
Cycloisomerization Reactions

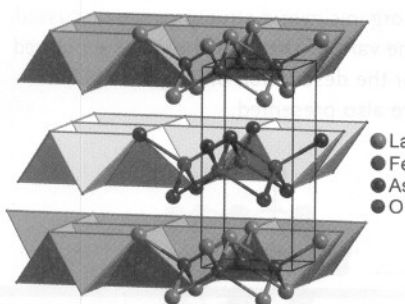
H.-Y. Kim, M.-K. Cho, D. Riedel, C. O. Fernandez, M. Zweckstetter*
Dissociation of Amyloid Fibrils of α -Synuclein in Supercooled
Water

Nanotechnology

Ben Rogers, Sumita Pennathur,
Jesse Adams

Books

reviewed by J. Bachmann, K. Nielsch 4778



Competition for the cuprates: A new family of high- T_c superconductors has been discovered. Iron pnictide oxides of the rare earth elements, such as $\text{LaFeAs}(\text{O}_{1-x}\text{F}_x)$ (see crystal structure), are superconducting at temperatures up to 55 K and have critical magnetic fields up to 60 T. This result heralds a new era for superconductivity research, 22 years after the discovery of the cuprates.

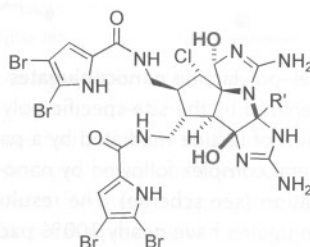
Highlights

Superconductivity

D. Johrendt,* R. Pöttgen* — 4782–4784

Pnictide Oxides: A New Class of High- T_c
Superconductors

Oxidation with a difference: The complexity of the oroidin alkaloid family of marine natural products is generated biosynthetically from one simple alkene precursor, but has left the synthetic community with problems. The first total synthesis of the tetracyclic axinellamines (see structure) was recently completed. Key to the success was the chemoselective oxidative functionalization of imidazolin(e) rings (green).



Alkaloids

H.-D. Arndt,* M. Riedrich — 4785–4788

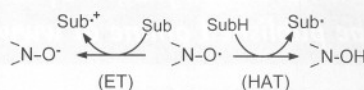
Synthesis of Marine Alkaloids from the
Oroidin Family

Minireviews

Synthetic Methods

C. Galli,* P. Gentili,
O. Lanzalunga — 4790–4796

Hydrogen Abstraction and Electron
Transfer with Aminoxy Radicals: Synthetic
and Mechanistic Issues



A two-pronged attack: Aminoxy radicals can react either by hydrogen atom transfer (HAT) or by electron-transfer (ET) mechanisms (see scheme). These different reaction pathways (mechanistic dichotomy) reflect a balance between the redox potential and the C–H bond energy of the substrate, but also depend on the reduction potential of the $R_2NO^\bullet$ species and the NO–H bond energy of the parent hydroxylamine.

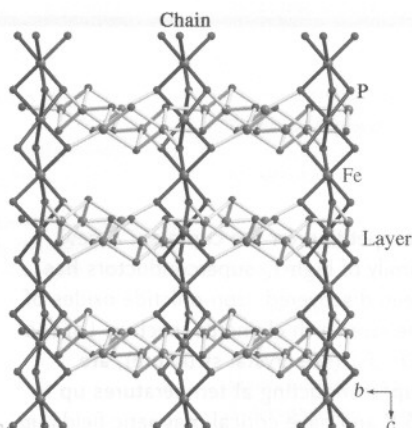
Reviews

Open-Framework Structures

S. Natarajan,* S. Mandal — 4798–4828



Open-Framework Structures of Transition-
Metal Compounds



Putting the frame in the picture: The synthesis, structure, and important properties of open framework transition metal compounds of silicates, germanates, phosphates, phosphites, arsenates, borates as well as of analogous organic–inorganic hybrid structures are discussed. The various theoretical models employed for the description of magnetic behavior are also presented.

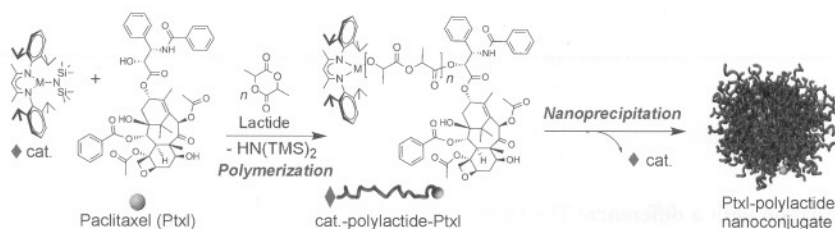
Communications

Drug Delivery

R. Tong, J. Cheng* — 4830–4834



Paclitaxel-Initiated, Controlled
Polymerization of Lactide for the
Formulation of Polymeric Nanoparticulate
Delivery Vehicles



Paclitaxel–poly(lactide) nanoconjugates were prepared by the site-specific polymerization of lactide mediated by a paclitaxel–metal complex followed by nanoprecipitation (see scheme). The resulting nanoconjugates have nearly 100% pacli-

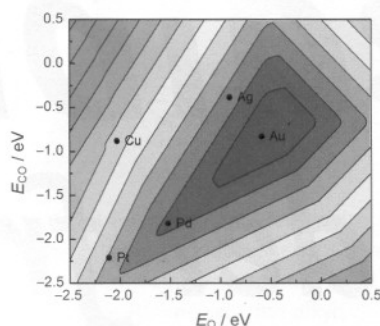
taxel incorporation efficiencies and pre-defined drug loadings, and are less than 100 nm in diameter. The drug burst release effect is completely eliminated with this drug delivery vehicle.

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national chemical society prices are available
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included. All prices are subject to local VAT/
sales tax.

Going for gold: Density functional calculations show how gold nanoparticles are more active catalysts for CO oxidation than other metal nanoparticles. The high catalytic activity of nanosized gold clusters at low temperature is found to be related to the ability of low-coordinate metal atoms to activate reactants.

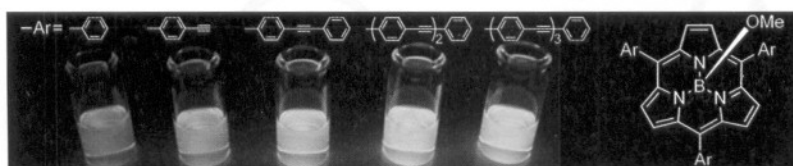


Gold Catalysis

VIP

H. Falsig, B. Hvolbæk, I. S. Kristensen, T. Jiang, T. Bligaard, C. H. Christensen, J. K. Nørskov* 4835–4839

Trends in the Catalytic CO Oxidation Activity of Nanoparticles



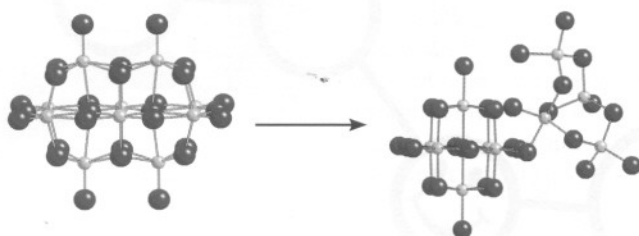
Go with the glow: A series of *meso*-oligo(1,4-phenyleneethynylene) substituted subporphyrins shows a significant amplification in absorption coefficient and fluorescence quantum yield as the chain length of the substituents increases

(see picture). Particularly, enhancement of the two-photon absorption properties along the series can be characterized by an octupolar effect rather than a conjugation effect.

Porphyrinoids

Y. Inokuma, S. Easwaramoorthi, S. Y. Jang, K. S. Kim, D. Kim,* A. Osuka* 4840–4843

Effective Expansion of the Subporphyrin Chromophore through Conjugation with *meso*-Oligo(1,4-phenyleneethynylene) Substituents: Octupolar Effect on Two-Photon Absorption



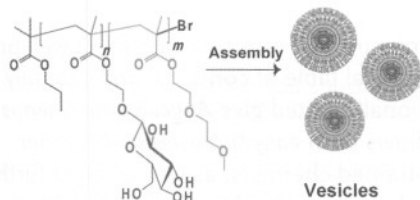
The nanometer-size title cluster is unique in that it reacts slowly enough in water that one can simultaneously observe steady-state oxygen-isotope exchanges

and dissociation pathways (see scheme; O red, Nb green), leading to conceptual advances in both geochemistry and polyoxometalate chemistry.

Polyoxometalates

E. M. Villa, C. A. Ohlin, E. Balogh, T. M. Anderson, M. D. Nyman, W. H. Casey* 4844–4846

Reaction Dynamics of the Decaniobate Ion $[H_xNb_{10}O_{28}]^{(6-x)-}$ in Water



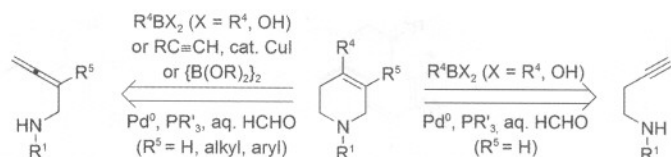
How sweet it is: Double hydrophilic block copolymers containing glucose functionalities form vesicles in aqueous solutions with sugar groups on their surface. Small vesicles form large aggregates with glucose-binding lectins or cells, whereas larger vesicles form discrete complexes. The “language” of association between cells and vesicles was demonstrated, and information transfer was shown by dye transport from vesicle to cell through glycopolymer links.

Vesicles

VIP

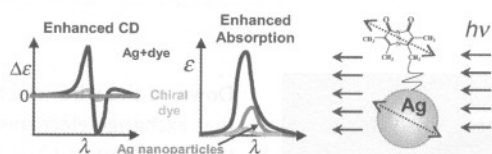
G. Pasparakis, C. Alexander* 4847–4850

Sweet Talking Double Hydrophilic Block Copolymer Vesicles



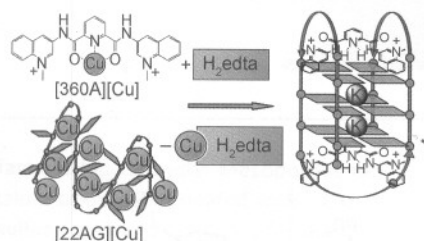
The biologically important title heterocyclic compounds can be synthesized by two methods based on the cyclization of alkynyl and allenyl iminium ions generated in situ in the presence of organometallic reagents (see scheme). Symme-

trical and unsymmetrical tetrahydropyridines with diverse substituents R^4 were prepared in a single step under mild conditions. $R^1 = n$ -, *sec*-, *tert*-alkyl; $R^4 =$ aryl, 1-alkenyl, alkyl, 1-alkynyl, B(pinacolato).

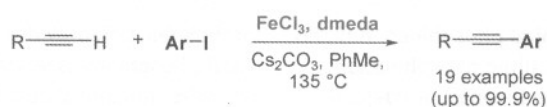


Colloidal Ag nanoparticles coated with L-glutathione attached to bimane chromophores were studied by absorption, circular dichroism (CD), and fluorescence spectroscopies. The absorption and CD

spectra were resonantly enhanced by Ag surface plasmons. The wavelength and particle-size dependence of the enhancement indicated that an electromagnetic "antenna" effect is in action.



Control by copper: Cu^{II} ions modulate the quadruplex affinity of the high-affinity ligand 360A and denature the folded quadruplex form of DNA 22AG to an unfolded form. So removal of copper through complexation enables the cycling of both 360A quadruplex affinity and quadruplex unfolding.



With an iron will: Terminal alkynes undergo reaction with aryl and heteroaryl iodides in the presence of an iron catalyst formed from FeCl_3 and *N,N'*-dimethylethylenediamine (dmeda, see scheme). The method displays a broad substrate

scope and is economical, environmentally friendly, and experimentally simple. A "one-pot" Sonogashira/intramolecular hydroalkoxylation has also been achieved by this method.



To C-OMe and go: The title reaction, involving cleavage of a C-OMe bond, is demonstrated for the coupling of aryl methyl ethers on fused aromatic systems, such as naphthalene and phenanthrene,

as well as anisoles containing electron-withdrawing groups with a wide range of boronic esters. cod=cycloocta-1,5-diene, Cy=cyclohexyl.

Multicomponent Synthesis

H. Tsukamoto,* Y. Kondo — 4851–4854

Palladium(0)-Catalyzed Alkynyl and Allenyl Iminium Ion Cyclizations Leading to 1,4-Disubstituted 1,2,3,6-Tetrahydropyridines

Nanoparticle Antennae

I. Lieberman, G. Shemer, T. Fried, E. M. Kosower, G. Markovich* — 4855–4857

Plasmon-Resonance-Enhanced Absorption and Circular Dichroism

G-Quadruplex DNA

D. Monchaud, P. Yang, L. Lacroix, M.-P. Teulade-Fichou, J.-L. Mergny* — 4858–4861

A Metal-Mediated Conformational Switch Controls G-Quadruplex Binding Affinity

C–C Coupling

M. Carril, A. Correa, C. Bolm* — 4862–4865

Iron-Catalyzed Sonogashira Reactions

Cross-Coupling Reactions

M. Tobisu,* T. Shimasaki, N. Chatani* — 4866–4869

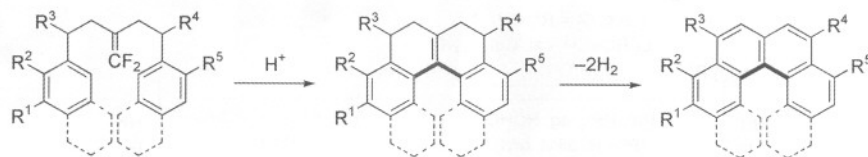
Nickel-Catalyzed Cross-Coupling of Aryl Methyl Ethers with Aryl Boronic Esters

Helical Compounds

J. Ichikawa,* M. Yokota, T. Kudo,
S. Umezaki ————— 4870–4873



Efficient Helicene Synthesis: Friedel–Crafts-type Cyclization of 1,1-Difluoro-1-alkenes



The unique properties of fluorine substituents, leaving groups that also stabilize an α carbocation, are exploited in a high-yielding synthesis of substituted [4]- to [6]helicenes in three or four steps from commercially available compounds: Two

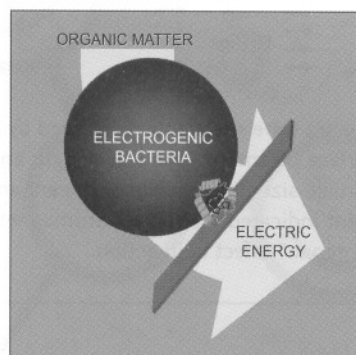
fused benzene rings are constructed in the title reaction of readily prepared 1,1-difluoro-1-alkenes containing two aryl groups followed by dehydrogenation (see scheme).

Microbial Fuel Cells

J. P. Busalmen,* A. Esteve-Núñez,*
A. Berná, J. M. Feliu ————— 4874–4877



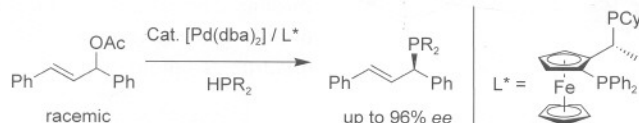
C-Type Cytochromes Wire Electricity-Producing Bacteria to Electrodes



Down to the wire: electro-active bacteria that exchange electrons with solid electrodes are studied by electrochemical and infrared techniques. The approach allows the identification of cell-surface molecules involved in the direct electron transfer to the electrode, a development that is crucial for future utilization of these electricity-producing microorganisms.

Allylic Phosphination

P. Butti, R. Rochat, A. D. Sadow,
A. Togni* ————— 4878–4881



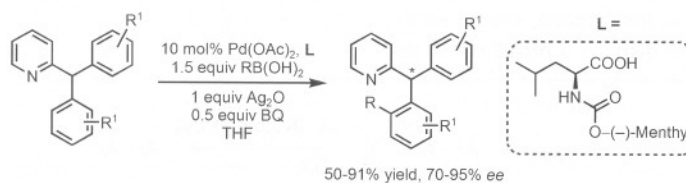
Palladium-Catalyzed Enantioselective Allylic Phosphination

A new cat. for chiral phosphines: A highly enantioselective allylic phosphination reaction is realized using the Pd–Josiphos(L) catalyst system. This C–P bond

forming reaction provides a new access to chiral phosphines (see scheme) that may be further functionalized. Cy=cyclohexyl, dba=*trans,trans*-dibenzylideneacetone.

C–H Activation

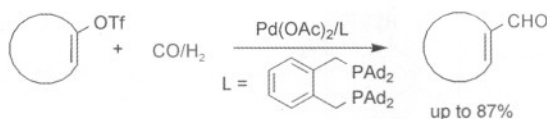
B.-F. Shi, N. Maugel, Y.-H. Zhang,
J.-Q. Yu* ————— 4882–4886



Pd^{II}-Catalyzed Enantioselective Activation of C(sp²)–H and C(sp³)–H Bonds Using Monoprotected Amino Acids as Chiral Ligands

The relay of chiral information from the α -carbon atom of the amino acid ligand is believed to be crucial for chiral induction in the Pd^{II}-catalyzed enantioselective C–H

activation/C–C coupling reaction of diphenyl(2-pyridyl)methane with boronic acids (see scheme; BQ = benzoquinone).



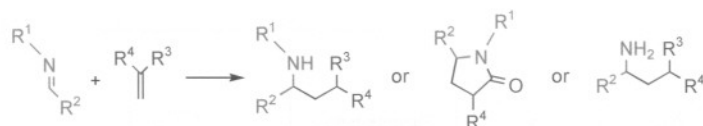
What a gas! Synthesis gas is the formylating agent in the efficient one-step title transformation promoted by a palladium catalyst with the bidentate ligand 1,2-bis(di-1-adamantylphosphinomethyl)benzene (see scheme). This method enables

the conversion of six- to eight-membered ring triflates into α,β -unsaturated aldehydes and the introduction of a formyl group into derivatives of elaborate natural compounds. Tf = trifluoromethanesulfonyl.

Synthetic Methods

H. Neumann, A. Sergeev,
M. Beller* — 4887–4891

Palladium Catalysts for the Formylation of Vinyl Triflates To Form α,β -Unsaturated Aldehydes



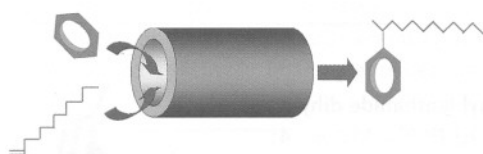
A couple of alternatives: An efficient method has been developed for the synthesis of γ -amino derivatives and pyrrolidinones from readily available starting materials by using a nickel–phenanthroline complex (see scheme). The reaction

proceeds by the formation of a C–C bond at the β -carbon atom, instead of the more usual α -carbon atom, of a conjugated alkene via an azanickelacycle intermediate.

Synthetic Methods

C.-H. Yeh, R. Prasad Korivi,
C.-H. Cheng* — 4892–4895

Regioselective Synthesis of γ -Amino Esters, Nitriles, Sulfones, and Pyrrolidinones by Nickel-Catalyzed Reductive Coupling of Aldimines and Activated Alkenes



Tantal(izing) catalysis: Mesoporous tantalum oxides were treated with 1.0 M sulfuric acid and evaluated for their catalytic activity and selectivity to 2-phenyl isomers in the alkylation of benzene with bulky olefins (see scheme). The sulfated mesoporous Ta oxide showed comparable

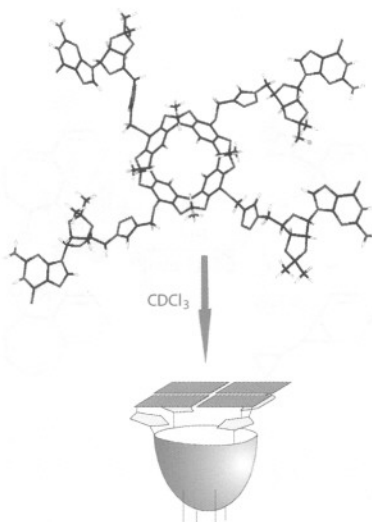
activity to H-Y zeolite, but much higher 2-phenyldodecane selectivity in mild reaction conditions. The high activity and selectivity was rationalized by the eased diffusion of bulky reactants in the mesoporous frames.

Alkylation

J. Kang, Y. Rao, M. Trudeau,
D. Antonelli* — 4896–4899

Sulfated Mesoporous Tantalum Oxides in the Shape Selective Synthesis of Linear Alkyl Benzene

An unusual quartet: Four guanine residues have been efficiently “clicked” onto a cavitand to create a lipophilic template-assembled synthetic G-quartet (TASQ) structure in CDCl_3 . The TASQ manifests unusual cation-free structural integrity and stability. This cation-free basket, as well as corresponding potential cation-bound quartets and cation-induced quadruplexes may find applications in health therapies.



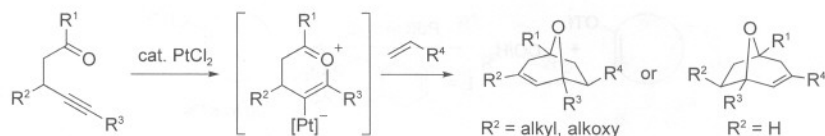
Supramolecular Chemistry

M. Nikan, J. C. Sherman* — 4900–4902

Template-Assembled Synthetic G-Quartets (TASQs)

Cycloaddition

H. Kusama, K. Ishida, H. Funami,
N. Iwasawa* 4903–4905



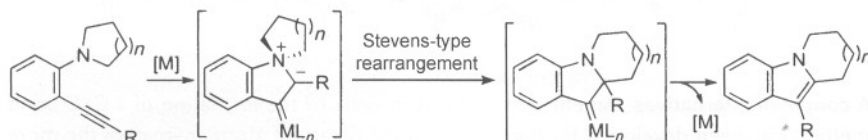
Platinum(II)-Catalyzed Reaction of γ,δ -Ynones with Alkenes for the Construction of 8-Oxabicyclo[3.2.1]octane Skeletons: Generation of Platinum-Containing Carbonyl Ylides from Acyclic Precursors

Two types of bicycles can be prepared selectively by the title reaction, depending on whether or not a substituent is present at the propargylic position of the ynone substrate (see scheme). The cycloaddition of carbonyl ylides derived from

γ,δ -ynones with vinyl ethers (or styrene) gave intermediate bicyclic carbene complexes, which underwent a 1,2-hydrogen-atom shift or rearrangement to provide the products. R^1 = alkyl, Ph; R^3 = alkyl.

Heterocycle Synthesis

J. Takaya, S. Udagawa, H. Kusama,
N. Iwasawa* 4906–4909



Synthesis of N-Fused Tricyclic Indoles by a Tandem [1,2] Stevens-Type Rearrangement/1,2-Alkyl Migration of Metal-Containing Ammonium Ylides

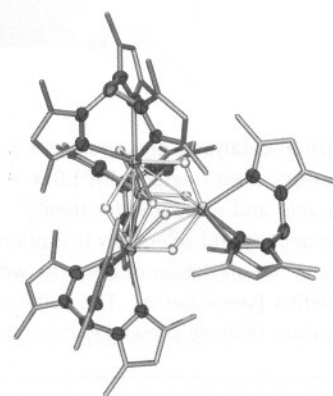
An alkyne moiety is activated efficiently with a $[W(CO)_6]$ or $[ReBr(CO)_5]$ catalyst in the presence of an amine functionality in the title reaction of *N*-(2-alkynylphenyl)-

amines. The resulting ammonium ylides undergo rearrangement to form a variety of *N*-fused polycyclic indole derivatives (see scheme; $n = 1, 2$; R = alkyl, Ph).

Lanthanide Complexes

J. Cheng, K. Saliu, G. Y. Kiel,
M. J. Ferguson, R. McDonald,
J. Takats* 4910–4913

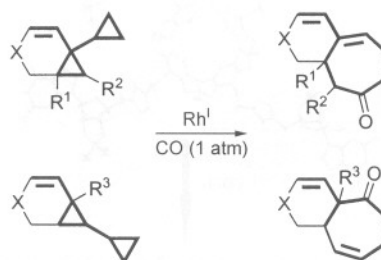
Non-cyclopentadienyl lanthanide dihydrides $[(Tp^{R,R'})LnH_2]_n$ ($R, R' = Me$, $n = 4$; $R, R' = H$, $n = 6$) and $[(Tp^{Me_2})YH_2]_3(thf)_{2-3}$ were isolated and characterized. Their polynuclear frameworks are maintained in solution, and their nuclearity depends on the ligand and the solvent used in their preparation. The structure of $[(Tp^{Me_2})YH_2]_4$ is shown (B red, H white, N blue, Y orange). $Tp^{R,R'} = \text{tris}(3-R-5-R'-\text{pyrazolyl})\text{borate}$.



Scorpionate-Supported Dialkyl and Dihydride Lanthanide Complexes: Ligand- and Solvent-Dependent Cluster Hydride Formation

Cycloaddition

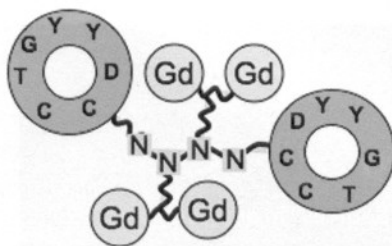
S. Y. Kim, S. I. Lee, S. Y. Choi,
Y. K. Chung* 4914–4917



Rhodium-Catalyzed Carbonylative [3+3+1] Cycloaddition of Biscyclopropanes with a Vinyl Substituent To Form Seven-Membered Rings

Choose your catalyst wisely: Depending on the position of the cyclopropyl substituent on the bicyclo[4.1.0]hept-2-ene substrate, a different rhodium complex was used to catalyze the title reaction, which leads to bicyclic dienones in reasonable to excellent yields (see scheme). The products contain a highly substituted seven-membered ring with useful functionality for further manipulation. $R^1 = H, Me$; $R^2 = H, Me, Ph$; $R^3 = Me, Et$; $X = NR, O$.

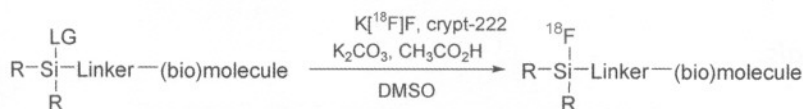
Probing in contrast: Four gadolinium-DTPA moieties (DTPA = diethylenetriami-nepentaacetic acid) and two fibrin-specific cyclic peptides are linked by a compact triethylenetetraamine core (see scheme) to create a highly sensitive probe for molecular MR imaging of thrombosis. The contrast agent has a high molecular relaxivity, and the dual peptide construct provides five-fold higher fibrin affinity than the monovalent analogue. This bivalent probe showed significant specific thrombus uptake in an in vivo model of thrombosis.



Medical Imaging

S. A. Nair, A. F. Kolodziej, G. Bhole, M. T. Greenfield, T. J. McMurry, P. Caravan* — 4918–4921

Monovalent and Bivalent Fibrin-specific MRI Contrast Agents for Detection of Thrombus



Linker: alkyl, aryl

R: Me, *i*Pr, *t*Bu

LG: Leaving group such as alkoxy, OH, H

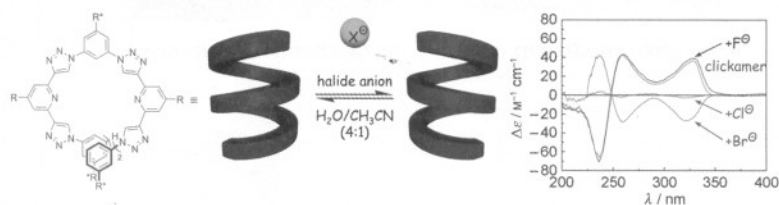
Radio-controlled landing of F: The facile ^{18}F labeling of biomolecules has been achieved under mild conditions by using a unique silicon-based one-step approach (see scheme). A di-*tert*-butylsilyl derivative with an aryl linker was attached to a

tetrapeptide. The assembly shows a hydrolytic stability that appears to be within the range required for in vivo positron emission tomography (PET) imaging applications.

Labeling with Radioactive Fluorine

L. Mu, A. Höhne, P. A. Schubiger, S. M. Ametamey,* K. Graham, J. E. Cyr, L. Dinkelborg, T. Stellfeld, A. Srinivasan, U. Voigtmann, U. Klar* — 4922–4925

Silicon-Based Building Blocks for One-Step ^{18}F -Radiolabeling of Peptides for PET Imaging



A surprising about-face: Click chemistry was used for the efficient synthesis of a new class of foldamers, referred to as clickamers, that display unusual folding

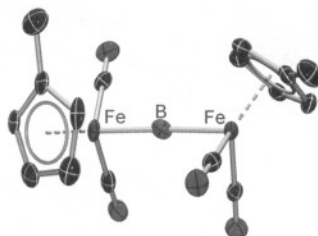
and recognition properties. In the presence of halide ions—achiral species—they undergo an unprecedented helix inversion.

Molecular Recognition

R. M. Meudtner, S. Hecht* — 4926–4930

Helicity Inversion in Responsive Foldamers Induced by Achiral Halide ion Guests

The first cationic metallaborylene complexes, $[(\text{OC})_5\text{Mn}]_2(\mu\text{-B})[\text{BARf}_4]$ and $[(\eta^5\text{-C}_5\text{H}_4\text{R})(\text{OC})_2\text{Fe}]_2(\mu\text{-B})[\text{BARf}_4]$ ($\text{R}=\text{H}, \text{Me}$; see structure) were synthesized by halide abstraction from bridged haloborylene complexes and structurally characterized. The boron atom is located in the coordination sphere of two transition-metal centers and is highly unsaturated.



Borylene Complexes

H. Braunschweig,* K. Kraft, T. Kupfer, K. Radacki, F. Seeler — 4931–4933

B^+ in the Coordination Sphere of Two Transition Metals

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).