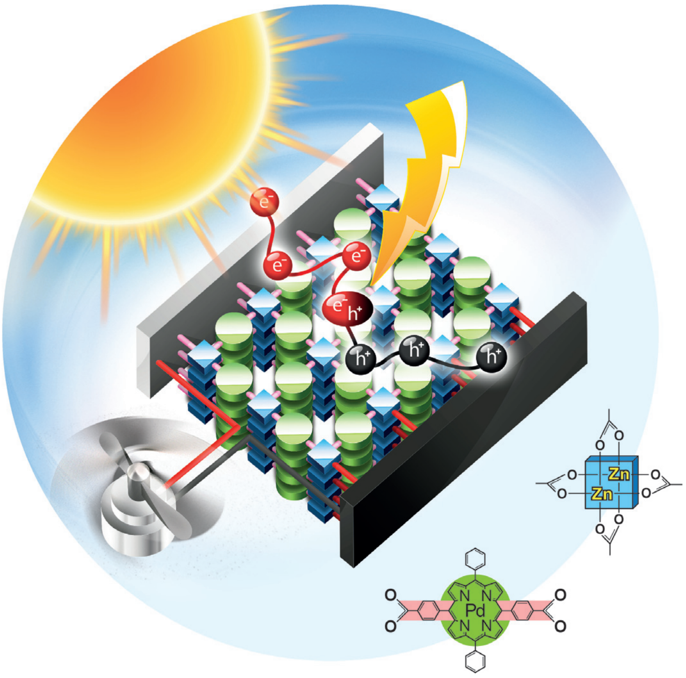
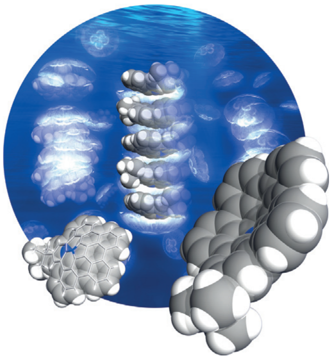
Strictly periodic assemblies …

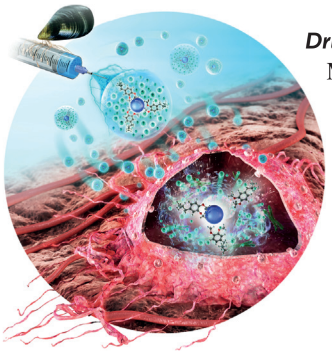


… of porphyrin units deposited on functionalized substrates can be used to realize solar cells with remarkable efficiency. In their Communication on page 7441 ff., J. Liu, C. Wöll, and co-workers show by electronic-structure calculations that ordered arrays of porphyrins have a small dispersion of occupied and unoccupied bands leading to the formation of a small indirect band gap. Such ordered porphyrin metal–organic frameworks (MOFs) are then grown using a layer-by-layer liquid-phase epitaxy.

Corannulene

S. Ito, K. Nozaki, and Y. Tokimaru describe in their Communication on page 7256 ff. the synthesis of a nitrogen-doped corannulene derivative that exhibits unique structural and physical properties and extended π conjugation compared to the parent corannulene.



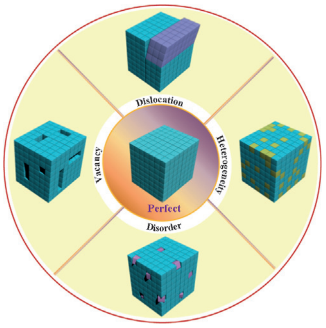


Drug Delivery

Mussel-inspired protein nanoparticles that are capable of pH-responsive drug release are described by H. J. Cha and co-workers in their Communication on page 7318 ff. These nanoparticles could be used for controlled drug delivery which is demonstrated by loading with doxorubicin.

Metal–Organic Frameworks

In their Review on page 7234 Z. L. Fang, B. Bueken, R. A. Fischer et al. give an overview of defects in coordination network compounds (CNCs), including their classification and characterization. The applications of defective CNCs are also presented.



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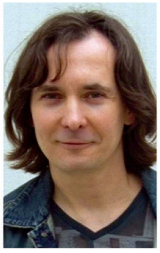
Author Profile

"My favorite place on earth is Yosemite National Park. My favorite piece of music is the Toreador Song from Carmen (Bizet) …"
This and more about Xingwei Li can be found on page 7224.

News

M. A. Kerr



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A. K. Yudin

A. Beauchemin

L. L. Schafer

J. Mauzeroll

D. A. Pratt

C.-J. Li

M. Murugesu

D. M. Perrin

Books

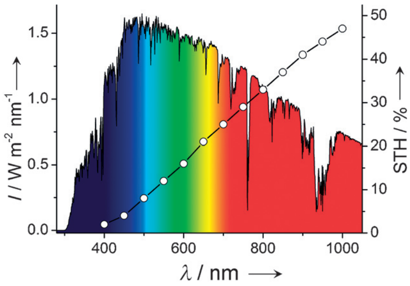
Highlights

Water Splitting

J. Zhang, X. Wang* ______ **7230 – 7232**

Solar Water Splitting at $\lambda = 600$ nm: A Step Closer to Sustainable Hydrogen Production

Overall water splitting with a semiconductor photocatalyst under visible-light irradiation is considered as a "dream reaction" in chemistry. The development of a 600 nm photocatalyst for solar water splitting highlighted here is not only an important milestone towards sustainable hydrogen production, but also a new starting point for artificial photosynthesis. STH = solar-to-hydrogen energy conversion efficiency.

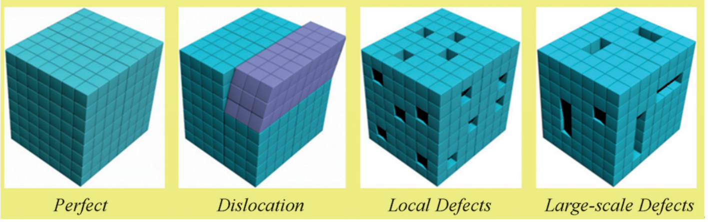


Reviews

Defect-Engineered CNCs

Z. L. Fang,* B. Bueken,* D. E. De Vos, R. A. Fischer* ______ **7234 – 7254**

Defect-Engineered Metal–Organic Frameworks



Designer defects: Defects in coordination network compounds (CNCs) are defined as "sites that locally break the regular periodic arrangement of atoms or ions of the static crystalline parent framework due to missing or incorrectly dislocated atoms or ions". This Review provides both a concise overview of defects in CNCs (including their classification and characterizations) and applications of defective CNCs/MOFs.

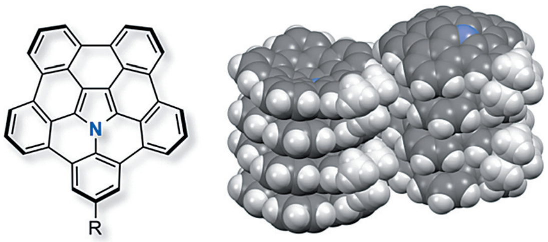
Communications

Corannulenes

S. Ito,* Y. Tokimaru, K. Nozaki* ______ **7256 – 7260**

Benzene-Fused Azacorannulene Bearing an Internal Nitrogen Atom

Frontispiece



Bowled over: A novel benzene-fused azacorannulene (left) was synthesized by the 1,3-dipolar cycloaddition of a polycyclic aromatic azomethine ylide with a diarylethyne and subsequent palladium-catalyzed intramolecular cyclization. This molecule represents the first example of a heteroatom-doped corannulene derivative and in the solid state bowl-in-bowl columnar π-stacking is observed (right).

For the USA and Canada:
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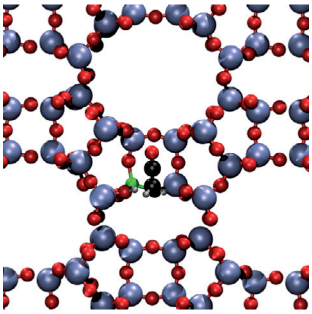


Ketene is seen: A theoretical prediction and experimental observation of ketene as a reaction intermediate in the carbonylation of dimethyl ether over Mordenite is reported. The formation of ketene is predicted by detailed DFT calculations and verified experimentally by the observation of doubly deuterated acetic acid (CH_2DCOOD), when D_2O is introduced in the feed during the carbonylation reaction.

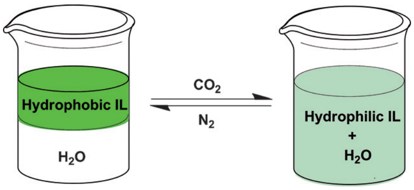
Reaction Mechanisms

D. B. Rasmussen, J. M. Christensen,*
B. Temel, F. Studt, P. G. Moses,
J. Rossmeisl, A. Riisager,
A. D. Jensen* **7261 – 7264**

Ketene as a Reaction Intermediate in the Carbonylation of Dimethyl Ether to Methyl Acetate over Mordenite

---

Three birds with one stone: ILs with strong hydrophobicity were developed. Their reversible hydrophobic–hydrophilic transition, switched by bubbling with and removal of CO_2 under ambient conditions, is due to the reversible reaction between CO_2 and anions to form hydrophilic ammonium salts. Homogeneous synthesis and heterogeneous separation of Au porous films as well as recovery of the ILs were coupled to achieve sustainable chemical processes.



Ionic Liquids

D. Xiong, G. Cui, J. Wang,* H. Wang, Z. Li,
K. Yao, S. Zhang **7265 – 7269**

Reversible Hydrophobic–Hydrophilic Transition of Ionic Liquids Driven by Carbon Dioxide

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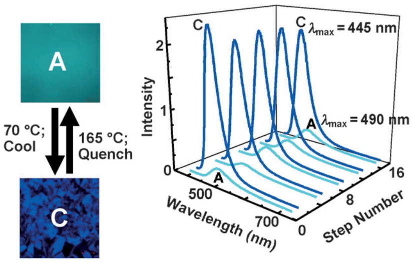

A subtle balance between robust supramolecular assembly and conformational flexibility is exploited in the development of a functional molecular phase change material showing reversible, thermally induced transformation between amorphous (A) and crystalline (C) states, together with a prominent change in the fluorescence emission color and intensity.

Phase-Change Materials

P. Srujana,
T. P. Radhakrishnan* **7270 – 7274**

Extensively Reversible Thermal Transformations of a Bistable, Fluorescence-Switchable Molecular Solid: Entry into Functional Molecular Phase-Change Materials

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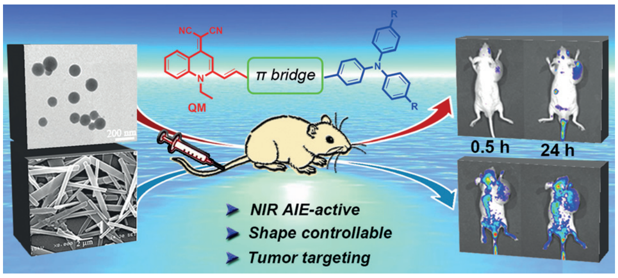


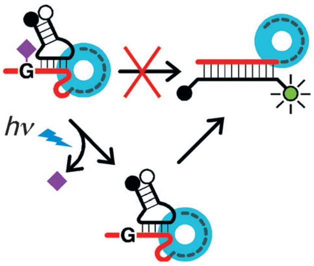
Tailoring long-wavelength aggregation-induced-emission-active molecules affords organic nanoaggregates with desired morphology, from rod-like to spherical. The latter are preferable for enhanced tumor-targeted bioimaging in vivo.

Aggregation-Induced Emission

A. Shao, Y. Xie, S. Zhu, Z. Guo,* S. Zhu,
J. Guo, P. Shi, T. D. James, H. Tian,
W. Zhu* **7275 – 7280**

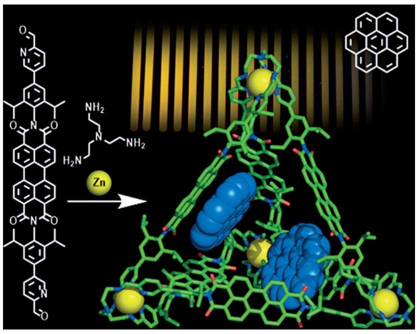
Far-Red and Near-IR AIE-Active Fluorescent Organic Nanoprobes with Enhanced Tumor-Targeting Efficacy: Shape-Specific Effects

RNA Chaperones



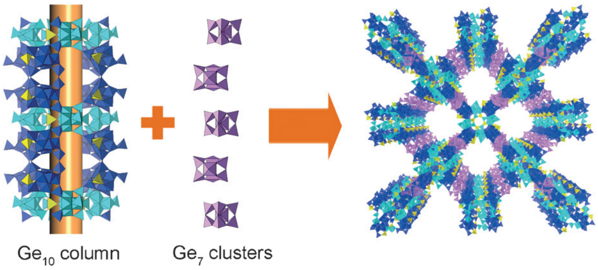
Caught in the act: Non-coding RNAs rely on a chaperone Hfq to find their targets in bacterial cells. Hfq-catalyzed base pairing is fast and hard to control. A new photocaged guanosine allows RNA base pairing to be controlled by light, catching Hfq in the act of forming a double helix. The results show that Hfq works by holding the initial base pairs in place until the remaining bases zipper together.

Luminescent Hosts



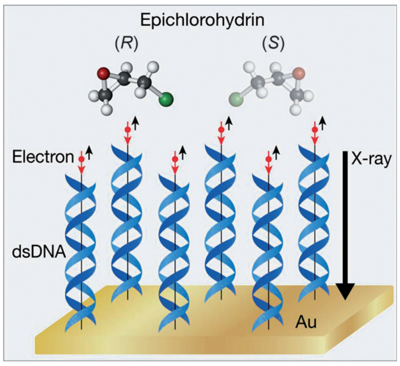
Fe^{II}-free and fluorescent: A highly luminescent ($\Phi_{em}=0.67$) Zn_4L_6 tetrahedron with perylene bisimide edges and hexadentate zinc–imine chelate vertices is accessed by dynamic imine–metal coordination self-assembly. Encapsulation of multiple perylene or coronene guest molecules is detected by quenching of the host emission. The chelate may be generalized to other dyes, improving access to brightly luminescent metallosupramolecular cages.

Zeolite Analogues

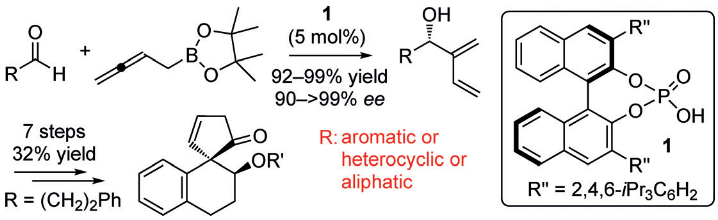


Germanate zeolites germinate: A novel mesoporous germanate PKU-17 with 3D 48×16×16-ring channels was designed by introducing two large building units (Ge_{10} and Ge_7 clusters) into the same framework. PKU-17 has the largest pore size among germanates. It is also the first germanate that shows a good selectivity toward CO_2 over N_2 and CH_4.

Selectivity at Surfaces



Secondary electrons from a substrate are transmitted through a chiral overlayer, causing enantiomeric selectivity in an adsorbed adlayer. Quantum yields (QYs) are determined for dissociation of (*R*)- or (*S*)-epichlorohydrin adsorbed on a chiral self-assembled layer of DNA on gold and on bare gold (for control). The QYs differ significantly between the two enantiomers when adsorbed on DNA, but not when they are adsorbed on bare Au.

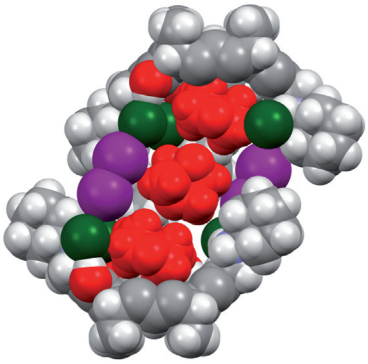


That important first step: The ability of chiral phosphoric acids to interact simultaneously with a 2,3-dienylboronic ester and an aldehyde through hydrogen bonding enabled enantiospecific C(sp)–C(sp^2) bond formation to give versatile synthetic intermediates. A chiral alkyl butadienyl adduct formed in this way on a gram scale was transformed into an optically pure benzo-fused spirocyclic cyclopentenone derivative (see scheme).

Organocatalysis

Y.-Y. Huang,* X. Yang, Z. Lv, C. Cai, C. Kai, Y. Pei,* Y. Feng ________ **7299 – 7302**

Asymmetric Synthesis of 1,3-Butadienyl-2-carbinols by the Homoallenylboration of Aldehydes with a Chiral Phosphoric Acid Catalyst

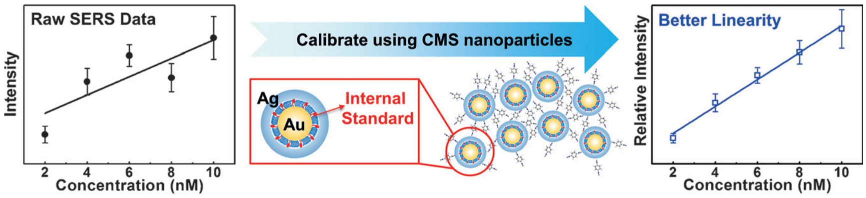


All in a nut shell: An entirely halogen-bonded dimeric capsule is isolated from the combination of I_2 as the bifunctional halogen-bond donor and *N*-cyclohexyl ammonium resorcinarene chloride as the tetravalent halogen-bond acceptor. Three 1,4-dioxane molecules as guests are bound in the single extended cavity (see picture; red molecules in center). Atom colors: C = gray; H = white; Cl = green; I = purple; O = red (edges).

Supramolecular Chemistry

N. K. Beyeh,* F. Pan, K. Rissanen* ________ **7303 – 7307**

A Halogen-Bonded Dimeric Resorcinarene Capsule

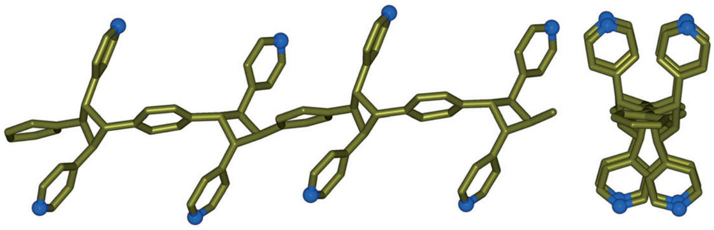


Core-molecule-shell (CMS) nanoparticles with embedded internal standards were designed for quantitative surface-enhanced Raman scattering (SERS) analysis. Quantitative analysis of target molecules that adsorb onto the shell with different affinities is possible because the internal standard corrects for signal fluctuation between samples and measuring conditions.

Analytical Methods

W. Shen, X. Lin, C. Y. Jiang, C. Y. Li, H. X. Lin, J. T. Huang, S. Wang, G. K. Liu, X. M. Yan, Q. L. Zhong, B. Ren* ________ **7308 – 7312**

Reliable Quantitative SERS Analysis Facilitated by Core–Shell Nanoparticles with Embedded Internal Standards



Pedaling for cylobutane polymers: A syndiotactic polymer ligand embedded inside a metal–organic framework (MOF) was formed through pedal motions of spacer ligands before undergoing a [2+2] cycloaddition reaction in the solid state.

Metal–Organic Frameworks

I.-H. Park, R. Medishetty, H.-H. Lee, C. E. Mulijanto, H. S. Quah, S. S. Lee,* J. J. Vittal* ________ **7313 – 7317**

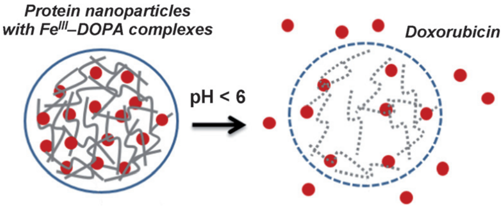
Formation of a Syndiotactic Organic Polymer Inside a MOF by a [2+2] Photo-Polymerization Reaction

Drug Delivery

B. J. Kim, H. Cheong, B. H. Hwang,
H. J. Cha* ________ 7318 – 7322

Mussel-Inspired Protein Nanoparticles Containing Iron(III)–DOPA Complexes for pH-Responsive Drug Delivery

Inside Back Cover

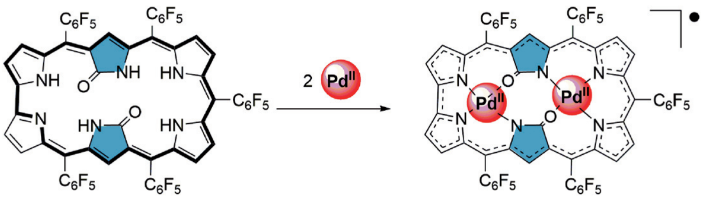


Mussel-inspired protein nanoparticles that are capable of pH-responsive drug release were obtained by exploiting the pH-dependent changes in the stoichiometry of iron(III)–DOPA complexes. Such doxorubicin-loaded polymeric nanoparticles were synthesized through a co-electrospraying process and shown to release doxorubicin at acidic pH values. DOPA = 3,4-dihydroxyphenylalanine.

Expanded Porphyrins

Y. Hisamune, K. Nishimura, K. Isakari,
M. Ishida, S. Mori, S. Karasawa, T. Kato,
S. Lee, D. Kim,* H. Furuta* 7323 – 7327

Stable π Radical from a Contracted Doubly N-Confused Hexaphyrin by Double Palladium Metalation

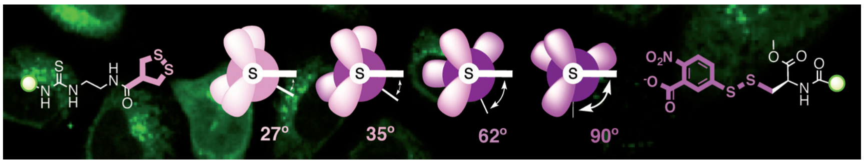


Who's afraid of a little water? A skeletally contracted doubly N-confused dioxohexaphyrin derivative served as a ligand for unsymmetrical dinuclear metal coordination. The complexation of two Pd^{II} cations led to the formation of a π-radical species that persisted in air in the presence of moisture (see scheme). Delocalization of the unpaired electron over the hexaphyrin backbone is thought to contribute to the chemical stability of the radical.

Cellular Uptake

G. Gasparini, G. Sargsyan, E.-K. Bang,
N. Sakai, S. Matile* ________ 7328 – 7331

Ring Tension Applied to Thiol-Mediated Cellular Uptake



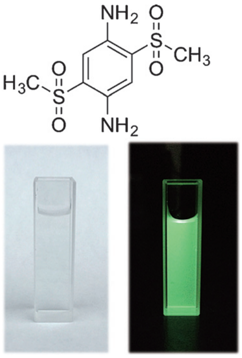
Mounting tension: Ring tension, which has been exploited for the modification of biological systems in many different ways, with click chemistry being a notable example, was applied to thiol-mediated cellular uptake. Fluorescent probes were conjugated to cyclic disulfides with varying degrees of ring tension and uptake into human cells was found to increase with increasing tension.

Fluorescence

T. Beppu, K. Tomiguchi, A. Masuhara,
Y.-J. Pu, H. Katagiri* ________ 7332 – 7335

Single Benzene Green Fluorophore: Solid-State Emissive, Water-Soluble, and Solvent- and pH-Independent Fluorescence with Large Stokes Shifts

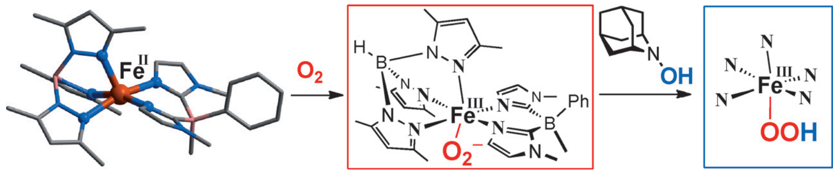
Evergreen: An effective push–pull system supported by intramolecular hydrogen bonding between amino and sulfonyl groups generated strong fluorescence properties. The achievement of a single-benzene-core fluorescent system (see picture) allowed steady green fluorescence, independent of the surrounding environment such as solvent polarity and pH, as well as extraordinarily large Stokes shifts of up to 140 nm.



Bioinorganic Chemistry

F. Oddon, Y. Chiba, J. Nakazawa,* T. Ohta, T. Ogura, S. Hikichi* ______ **7336–7339**

Characterization of Mononuclear Non-heme Iron(III)-Superoxo Complex with a Five-Azole Ligand Set



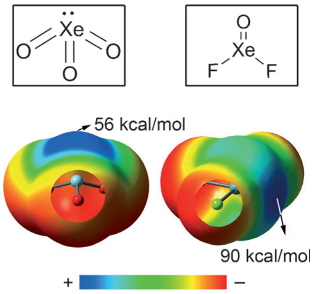
Reaction of O_2 with a mononuclear high-spin iron(II) complex supported by a five-azole donor set yields the corresponding mononuclear non-heme low-spin iron(III)–superoxo species. This species reacts with hydrogen-atom-donating reagents to give a low-spin iron(III)–hydroperoxo species.

Aerogen Bonding

A. Bauzá, A. Frontera* ______ **7340–7343**

Aerogen Bonding Interaction: A New Supramolecular Force?

A new noncovalent interaction between a covalently bonded atom of Group 18 and a negative site, for example, a lone pair of a Lewis base or an anion, is called an aerogen bonding. It involves a region of positive electrostatic potential (σ-hole). Energetically, aerogen bonds are comparable to hydrogen bonds and other σ-hole-based interactions but less directional. They might be important in xenon chemistry.

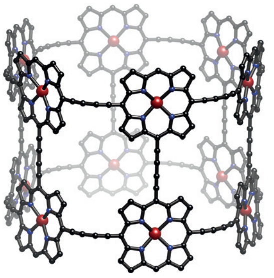


Porphyrin Tubes

P. Neuhaus, A. Cnossen, J. Q. Gong, L. M. Herz, H. L. Anderson* ______ **7344–7348**

A Molecular Nanotube with Three-Dimensional π-Conjugation

Joining together six staves creates a barrel-shaped nanotube consisting of twelve porphyrin units with continuous cylindrical π-conjugation. Fluorescence measurements reveal ultrafast migration of electronic excitation between different regions of the nanotube.

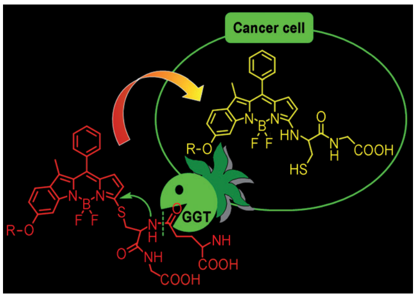


Cancer Diagnostics

F. Wang, Y. Zhu, L. Zhou, L. Pan, Z. Cui, Q. Fei, S. Luo, D. Pan, Q. Huang, R. Wang, C. Zhao,* H. Tian, C. Fan* ______ **7349–7353**

Fluorescent In Situ Targeting Probes for Rapid Imaging of Ovarian-Cancer-Specific γ-Glutamyltranspeptidase

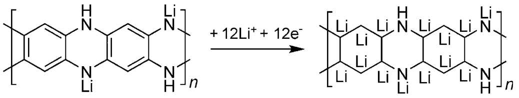
Localization of cancer: Novel fluorescent in situ targeting (FIST) probes were constructed for monitoring γ-glutamyltranspeptidase (GGT) activity. The enzyme-mediated aromatic hydrocarbon transfer between the sulfur and nitrogen atoms (see picture) induces photophysical responses to the GGT activity, thus enabling theses FIST probes to differentiate cancer cells from normal cells.



Lithium-Ion Batteries

J. Wu, X. Rui, G. Long, W. Chen, Q. Yan,* Q. Zhang* ______ **7354–7358**

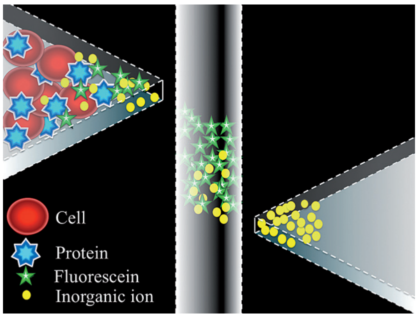
Pushing Up Lithium Storage through Nanostructured Polyazaacene Analogues as Anode



Nanoparticles of the conjugated ladder polymer poly(1,6-dihydropyrazino[2,3g]quinoxaline-2,3,8-triyl-7-(2*H*)-ylidene-7,8-dimethylidene) (PQL) were prepared through a reprecipitation method. The PQL has been tested as anode material for lithium-ion batteries and exhibits high capacity, good rate performance, and excellent cycle life, especially at a high temperature of 50 °C.

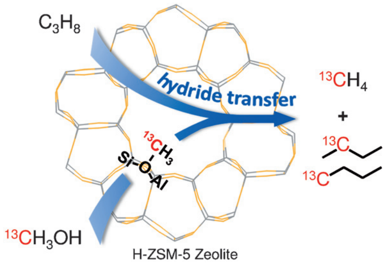
Microfluidics

Inside Cover



Trapped: The electrokinetic extraction, concentration, and purification of small molecules from biological samples is possible with size and mobility traps. These traps consist of two nanojunctions, with the extraction junction having a larger pore size than the purification junction. The direct analysis of ampicillin levels in a blood sample was achieved in 5 min using this method.

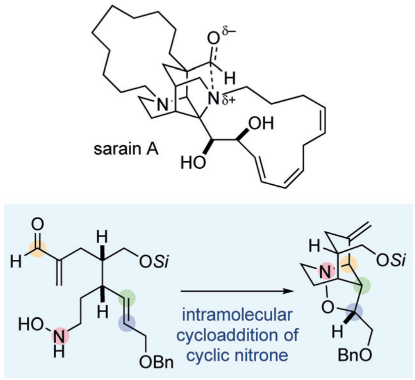
Reaction Mechanisms



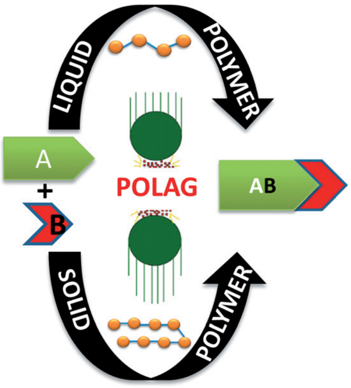
Put a label on it: ^{13}C-labeled methane and singly ^{13}C-labeled *n*-butanes were identified as the primary products from the initial reaction of propane and $^{13}CH_3OH$ over the zeolite H-ZSM-5. This result provides experimental evidence for the proposed hydride transfer between alkanes and surface alkoxy species over acidic zeolites, and also suggests a new possibility for alkane transformation at low temperatures.

Alkaloids

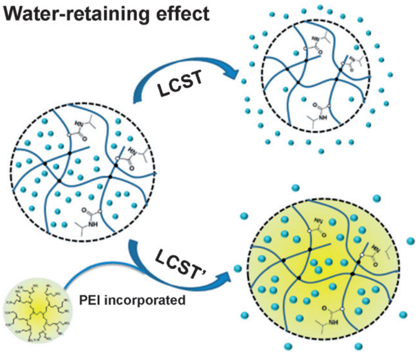
Skeleton construction: An enantioselective route to the tetracyclic skeleton of sarain A is reported, and features the intramolecular cycloaddition of an eight-membered cyclic nitrone to construct the 2-azabicyclo[3.3.1]nonane framework. The 13-membered ring and the pyrrolidine ring were formed by ring-closing metathesis and iodoamidation, respectively, thus leading to the tetracyclic, late-stage intermediate previously reported.



Mechanochemistry



Multicomponent crystals can be obtained by polymer-assisted grinding (POLAG), an alternative to the liquid-assisted grinding technique. POLAG is a new approach for the development of functional materials by mechanochemistry and may improve our understanding of the mechanisms and pathways of mechanochemical cocrystal formation.



A general drug carrier model with a tunable release rate is reported, which is formed by incorporating polyethyleneimine (PEI) into a thermally responsive poly(*N*-isopropylacrylamide) hydrogel. PEI plays an important role in tuning the water content in the hydrogel and controlling the water release rate of the hydrogel below the lower critical solution temperature (LCST; see picture).

Hybrid Hydrogels

C. Ma, Y. Shi, D. A. Pena, L. Peng,
G. Yu* ———— **7376 – 7380**

Thermally Responsive Hydrogel Blends: A General Drug Carrier Model for Controlled Drug Release

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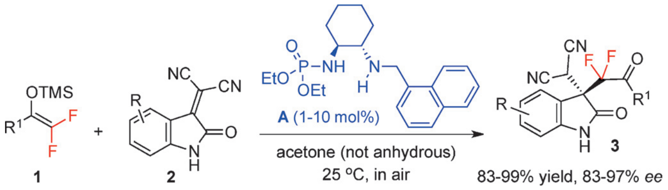

Four C's: The chiral secondary amine phosphoramide **A** was developed and serves as a powerful catalyst for the Michael addition of fluorinated enol silyl ethers to tetrasubstituted olefins. The resulting products are obtained with high enantioselectivities and contain a quaternary carbon stereocenter bearing either a difluoroalkyl or monofluoroalkyl group. TMS = trimethylsilyl.

Asymmetric Catalysis

J.-S. Yu, F.-M. Liao, W.-M. Gao, K. Liao,
R.-L. Zuo, J. Zhou* ———— **7381 – 7385**

Michael Addition Catalyzed by Chiral Secondary Amine Phosphoramide Using Fluorinated Silyl Enol Ethers: Formation of Quaternary Carbon Stereocenters

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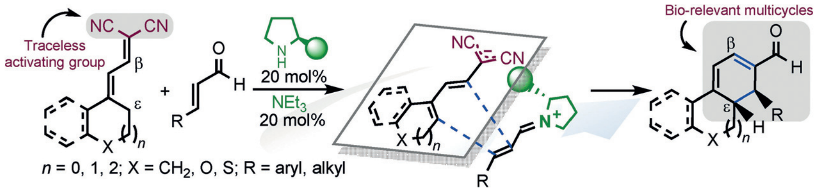

Without a trace: The covalent activation of α,β-unsaturated aldehydes with malononitrile produced remotely enolizable π-extended allylidene malononitriles. Their amine-catalyzed eliminative [4+2] cycloaddition to aromatic and aliphatic enals enabled the construction of cyclohexadiene-containing polycycles with outstanding diastereo- and enantioselectivities. The essential role of the malononitrile handle as a traceless activating moiety was demonstrated.

Organocatalysis

N. Brindani, G. Rassu,* L. Dell'Amico,
V. Zambrano, L. Pinna, C. Curti, A. Sartori,
L. Battistini, G. Casiraghi, G. Pelosi,
D. Greco, F. Zanardi* ———— **7386 – 7390**

Organocatalytic, Asymmetric Eliminative [4+2] Cycloaddition of Allylidene Malononitriles with Enals: Rapid Entry to Cyclohexadiene-Embedding Linear and Angular Polycycles

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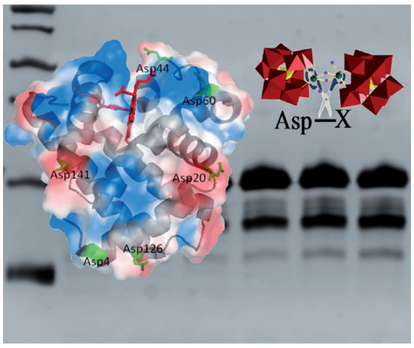


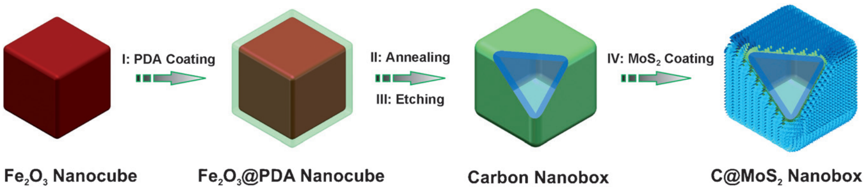
A clear-cut case: Asp-directed site-selective hydrolysis of horse-heart myoglobin occurred in the presence of zirconium(IV)-substituted polyoxometalates (POMs) in solution under mildly acidic and neutral conditions (see picture; Asp residues in hydrolyzable peptide bonds are shown in green). Electrostatic interactions between the negatively charged POMs and positively charged surface patches (blue areas) near the cleavage sites promoted hydrolysis.

Protein Hydrolysis

H. G. T. Ly, G. Absillis, R. Janssens,
P. Proost, T. N. Parac-Vogt* **7391 – 7394**

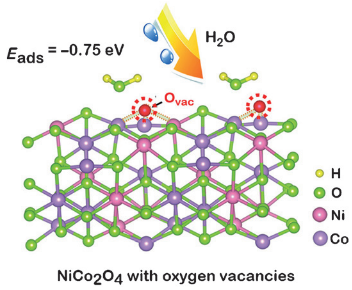
Highly Amino Acid Selective Hydrolysis of Myoglobin at Aspartate Residues as Promoted by Zirconium(IV)-Substituted Polyoxometalates

Nanostructures



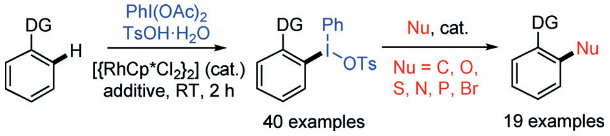
Nanosheets-on-Box: A hybrid structure composed of thin MoS_2 nanosheets supported on N-doped carbon nanoboxes has been synthesized. Because of the structural advantages, these well-defined C@MoS_2 nanoboxes exhibit superior electrochemical performance as electrode materials for both lithium-ion batteries and the hydrogen evolution reaction.

Oxygen Evolution Reaction



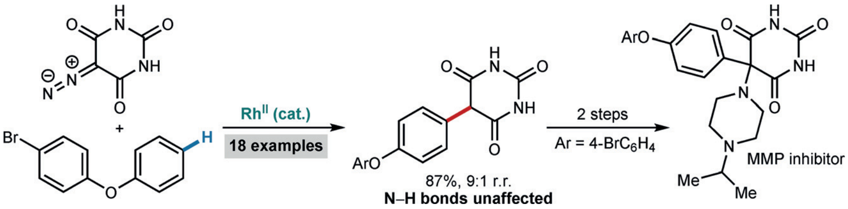
Beneficial deficiencies: A series of spinel-structured nanosheets with oxygen deficiencies (O_{vac}) and ultrathin thicknesses were synthesized for the first time. These features lead to an increase in the number of active sites and in the activity of the catalyst in water oxidation, which was confirmed by experimental and theoretical studies.

Hypervalent Compounds



Bonds aplenty: Diaryliodonium salts were synthesized for the first time from electron-poor arenes by the title reaction. The diaryliodoniums can be readily functionalized by nucleophiles with high chemoselectivity, thus leading to C–C, C–S, C–N, C–P, and C–Br bond formation. Cp* = C_5Me_5, DG = directing group, Ts = 4-toluenesulfonyl.

Arylation

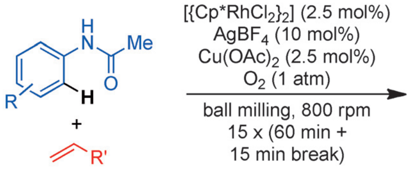


Direct is better: A commercially available rhodium(II) complex catalyzes the direct arylation of 5-diazobarbituric acids with arenes, providing straightforward access to 5-aryl barbituric acids. Free N–H groups are tolerated on the barbituric acid, with no complications arising from N–H insertion. This method was applied to the concise synthesis of a potent matrix metalloproteinase (MMP) inhibitor.

Solventless Cross-Coupling

G. N. Hermann, P. Becker,
C. Bolm* ______ 7414 – 7417

Mechanochemical Rhodium(III)-Catalyzed C–H Bond Functionalization of Acetanilides under Solventless Conditions in a Ball Mill

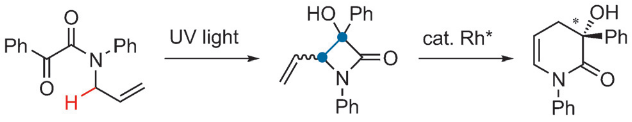


Home and dry: An oxidative Heck-type olefination of acetanilides in a planetary ball mill gave the corresponding products in moderate to good yield with high selectivity for monosubstitution (see scheme). Mechanochemical induction enabled C–H bond activation in the absence of a solvent as well as the use of a catalytic amount of a copper oxidant in an atmosphere of dioxygen. No additional heating was required.

Asymmetric Synthesis

N. Ishida, D. Nečas, Y. Masuda,
M. Murakami* ______ 7418 – 7421

Enantioselective Construction of 3-Hydroxypiperidine Scaffolds by Sequential Action of Light and Rhodium upon N-Allylglyoxylamides

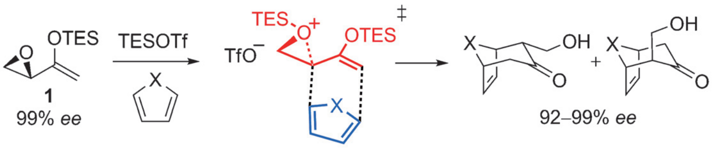


Action packed: 3-Hydroxypiperidine scaffolds were enantioselectively constructed in an atom-economical way by the title reaction. In a formal sense, the allylic C–H bond was selectively cleaved and added across the ketonic carbonyl group with migration of the double bond.

Reaction Mechanisms

E. H. Krenske,* S. Lam, J. P. L. Ng, B. Lo,
S. K. Lam, P. Chiu,*
K. N. Houk* ______ 7422 – 7425

Concerted Ring Opening and Cycloaddition of Chiral Epoxy Enolsilanes with Dienes

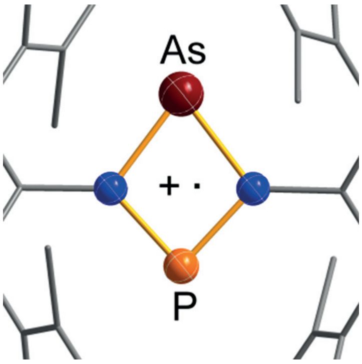


More than one way to add: Theoretical calculations indicate that the silyl-triflate-catalyzed (4+3) cycloadditions of epoxy enolsilane **1** do not generally proceed via an intermediate oxyallyl cation. Instead the reaction involves an S$_N$2-like epoxide ring opening in concert with remote C–C bond formation. TES = triethylsilyl, TfO = trifluoromethanesulfonyl.

Main-Group Radicals

A. Brückner, A. Hinz, J. B. Priebe,
A. Schulz,* A. Villinger ______ 7426 – 7430

Cyclic Group 15 Radical Cations

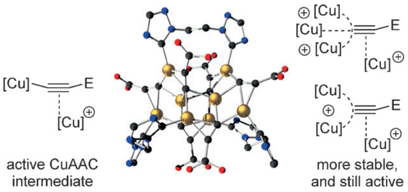


Positively radical: New radical cations of the type [E^1(μ-NTer)$_2$E^2] (E^{1,2} = P, As and E^1 = P, E^2 = As) were obtained by one-electron oxidation of Group 15 biradicaloids with silver salts. The structural features remain nearly unchanged upon oxidation. EPR and DFT studies show that there is an unpaired electron residing primarily on the heavy pnictogen atoms P and As, but in mixed species (see picture) it is to a larger extent at the As atom.

Click Mechanism

A. Makarem, R. Berg, F. Rominger,
B. F. Straub* ______________ **7431 – 7435**

A Fluxional Copper Acetylide Cluster in CuAAC Catalysis

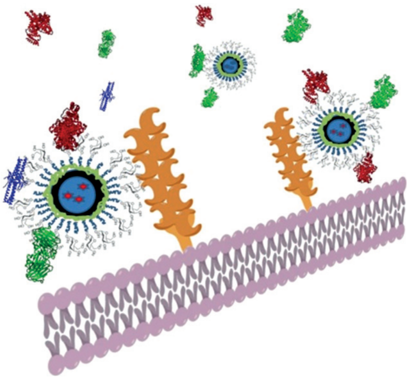


The complex chemistry of click reactions: Acetylide complexes are the central intermediates in copper-catalyzed azide–alkyne cycloadditions (CuAAC). A catalytically active octacopper(I) hexaacetylide salt was formed from a dinuclear copper complex and ethyl propiolate, thereby providing new insights into the influence of the coordination mode of the acetylide ligand on the stability and catalytic activity.

Nanocarriers

B. Kang, P. Okwieka, S. Schöttler,
S. Winzen, J. Langhanki, K. Mohr,
T. Opatz, V. Mailänder, K. Landfester,*
F. R. Wurm* ______________ **7436 – 7440**

Carbohydrate-Based Nanocarriers Exhibiting Specific Cell Targeting with Minimum Influence from the Protein Corona



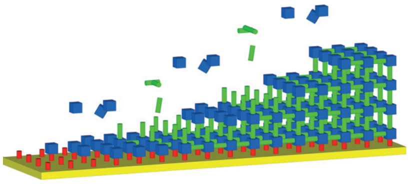
Stealth nanocarriers: The blood plasma interactions and targeting properties of PEGylated and mannose-functionalized hydroxyethyl starch (HES) nanocarriers were investigated. They exhibit colloidal stability in human plasma, low protein adsorption, a distinct protein pattern, and highly specific cellular uptake into dendritic cells both before and after contact with human plasma.

MOF Thin Films

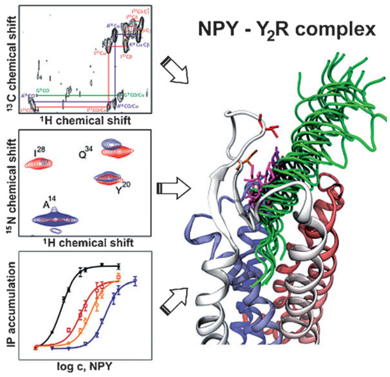
J. Liu,* W. Zhou, J. Liu, I. Howard,
G. Kilibarda, S. Schlabach, D. Coupry,
M. Addicoat, S. Yoneda, Y. Tsutsui,
T. Sakurai, S. Seki, Z. Wang, P. Lindemann,
E. Redel, T. Heine, C. Wöll* **7441 – 7445**

Photoinduced Charge-Carrier Generation in Epitaxial MOF Thin Films: High Efficiency as a Result of an Indirect Electronic Band Gap?

Front Cover



Mind the gap: electronic-structure calculations show that ordered arrays of porphyrins have a small dispersion of occupied and unoccupied bands leading to the formation of a small indirect band gap. Such ordered structures are formed by liquid-phase epitaxy (see picture) and exhibit superior photophysical properties. A prototype organic photovoltaic device based on this material is highly efficient.



Peptide–GPCR complex: The bioactive structure of the neuropeptide NPY was obtained from solid-state NMR measurements of the peptide in complex with its receptor (Y_2R), which was folded in vitro and reconstituted into lipid bicelles. The results reveal unwinding of the C-terminal α-helix. Additional solution NMR data, double-cycle mutagenesis, and molecular modeling enabled the construction of a detailed model of the peptide–receptor complex.

Peptide–Receptor Interactions

A. Kaiser, P. Müller, T. Zellmann,
H. A. Scheidt, L. Thomas, M. Bosse,
R. Meier, J. Meiler, D. Huster,
A. G. Beck-Sickinger,
P. Schmidt* ______ **7446 – 7449**

Unwinding of the C-Terminal Residues of Neuropeptide Y is critical for Y_2 Receptor Binding and Activation

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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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Angewandte Corrigendum

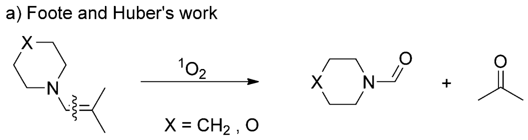
In this Communication, the sentence starting in line 8 of the first text paragraph on page 12201 must be replaced by the following two sentences: "The reactions of singlet oxygen with enamines were firstly disclosed by Foote and Lin[8a] and Huber[8b] in 1968 (Scheme 1 a). And the similar double bond cleavage reaction of enaminones by singlet oxygen was reported by Wasserman and Ives[9] in 1976 (Scheme 1 b)." Scheme 1 a and Ref. [8] need to be changed accordingly.

Visible-Light-Mediated 1,2-Acyl Migration: The Reaction of Secondary Enamino Ketones with Singlet Oxygen

W. Fan, P. Li* ______ **12201–12204**

Angew. Chem. Int. Ed. **2014**, *53*

DOI: 10.1002/anie.201407413



Scheme 1. Selected examples involving oxidation of enamines or enaminones.

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[8] a) C. S. Foote, J. W.-P. Lin, *Tetrahedron Lett.* **1968**, *9*, 3267; b) J. E. Huber, *Tetrahedron Lett.* **1968**, *9*, 3271.