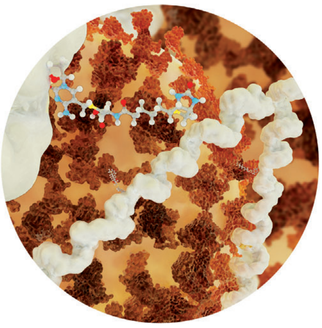
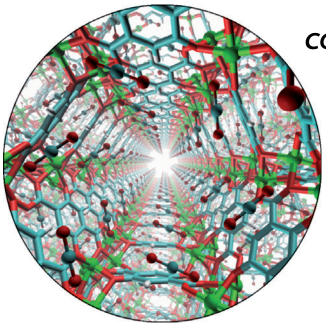
A recording industry patent …

… from the 1960s forms the inspiration for designing new core–shell Fischer–Tropsch catalysts. By tweaking the deposition and layer-growth process, G. Rothenberg et al. show in their Communication on page 4397 ff. how uniform spherical particles of iron oxide coated with a 1 nm cobalt shell can be prepared. Pelleted together with nanosized alumina particles, these catalysts are stable up to 673 K, and give good diesel fractions under Fischer–Tropsch conditions.

Epigenetic Modifications

5-Hydroxymethylcytosine (5hmC) is a recently discovered epigenetic modification that may be important in stem cell differentiation. In their Communication on page 4350 ff., H. Bayley et al. describe a method of detecting 5hmC in single molecules of DNA.



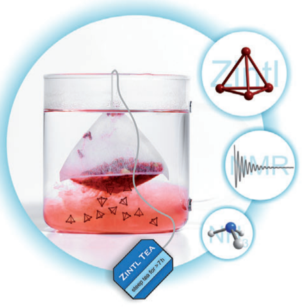


CO_2 Capture

The open metal sites in metal–organic frameworks interact strongly with CO_2, and this has been studied primarily in terms of adsorption properties. In their Communication on page 4410 ff., L.-C. Lin et al. now describe the dynamics of CO_2 absorption.

Zintl Anions

In their Communication on page 4483 ff., R. M. Gschwind, N. Korber et al. present NMR spectroscopic evidence for Sn_4^{4-} and Si_4^{4-} in liquid ammonia. The existence of these tetrahedral cages of tin and silicon is thus not limited to solid-state compounds with electropositive metals.



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Service

Author Profile

"If I were not a scientist, I would be an archeologist. The most important thing I learned from my parents is patience and modesty. …"
This and more about Yasushi Morita can be found on page 4298.

News

C. G. Willson

J. M. J. Fréchet

T. Betley

G. A. Somorjai

Books

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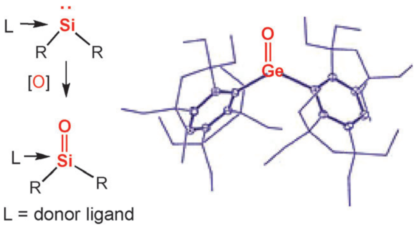
Minireviews

Heavier Ketones

Y. Xiong, S. Yao, M. Driess* **4302 – 4311**

Chemical Tricks To Stabilize Silanones and Their Heavier Homologues with E=O Bonds (E = Si–Pb): From Elusive Species to Isolable Building Blocks



Getting heavy: Recent progress in stable compounds with E=O bonds (E = Si, Ge, Sn, Pb) is presented. The synthesis of a series of silanone complexes and the first stable “genuine” germanone are the most noteworthy developments in the field of heavier ketone analogues. The structural and spectroscopic data obtained on these new species and their reactivity have greatly enriched the chemical knowledge on heavier ketones.

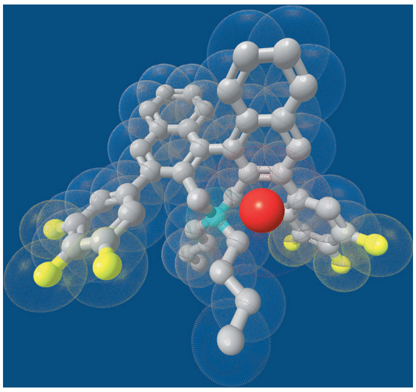
Reviews

Phase-Transfer Catalysis

S. Shirakawa, K. Maruoka* _ **4312 – 4348**

Recent Developments in Asymmetric Phase-Transfer Reactions

Work in process: The variations in the synthetic applications of phase-transfer reactions between 2006 and the middle of 2012 have been summarized to show the recent progress made in this field. The reactions have been applied to the synthesis of biologically active natural products and the large-scale preparation of drugs. The conceptually new catalyst design, reaction system, and reaction mode are also described.



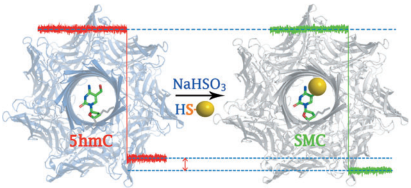
Communications

Epigenetic Markers

W. W. Li, L. Gong, H. Bayley* _______________ **4350 – 4355**

Single-Molecule Detection of 5-Hydroxymethylcytosine in DNA through Chemical Modification and Nanopore Analysis

DNA threading the needle: A new method of single-molecule detection of 5-hydroxymethylcytosine (5hmC) in DNA has been developed. Selective thiol substitution of 5hmC (giving SMC) in a single-step, bisulfite-mediated reaction (see scheme) allows the incorporation of a peptide (yellow sphere) or biotin into DNA. Modified 5hmC bases can be readily distinguished at the single-molecule level using protein nanopore analysis.



Frontispiece

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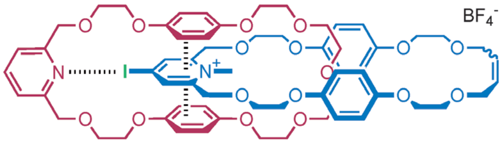
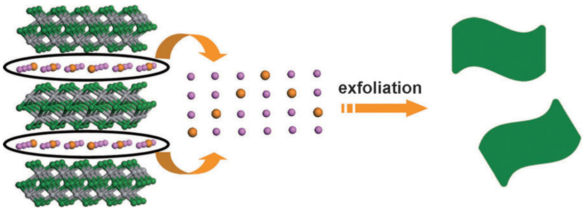


Getting connected: The formation of pseudorotaxane assemblies between a designed macrocyclic halogen bonding (XB) acceptor (red in scheme) and a series of XB donor threading components was templated by a single halogen bond. The strength of the XB assembly between the pyridine macrocycle and iodopyridinium thread was utilized in the ring-closing metathesis clipping synthesis of a [2]catenane.

Halogen Bonding

L. C. Gilday, T. Lang, A. Caballero,
P. J. Costa, V. Félix,
P. D. Beer* ——— **4356 – 4360**

A Catenane Assembled through a Single Charge-Assisted Halogen Bond

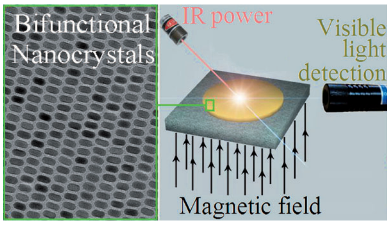


TSAC nanosheets: A substitutional solid solution based exfoliation method (see figure) has been developed for the preparation of ultrathin nanosheets of $Ti_3Si_{0.75}Al_{0.25}C_2$ (TSAC; Ti green, Si purple, Al yellow, C gray). The as-exfoliated nanosheets show excellent thermal and mechanical properties and can be used as effective fillers in polymer composites, such as with poly(methyl methacrylate).

Nanostructures

X. D. Zhang, J. G. Xu, H. Wang, J. J. Zhang,
H. B. Yan, B. C. Pan, J. F. Zhou,
Y. Xie* ——— **4361 – 4365**

Ultrathin Nanosheets of MAX Phases with Enhanced Thermal and Mechanical Properties in Polymeric Compositions: $Ti_3Si_{0.75}Al_{0.25}C_2$



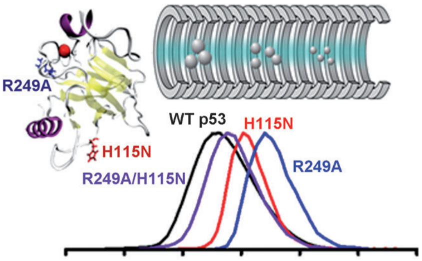
Nanocrystal clear: Optical-magnetic (OM) bifunctional $NaGdF_4{:}Nd^{3+},Yb^{3+},Er^{3+}$ nanocrystals were successfully synthesized that consist of luminescent Er^{3+} ions and a coordinating magnetic Gd^{3+} ion. The luminescence of $NaGdF_4{:}Nd^{3+},Yb^{3+},Er^{3+}$ nanocrystals was tuned by changing the applied magnetic field (see figure) both at room temperature and ultralow temperatures.

Bifunctional Materials

Y. Liu, D. Wang, J. Shi, Q. Peng,*
Y. Li* ——— **4366 – 4369**

Magnetic Tuning of Upconversion Luminescence in Lanthanide-Doped Bifunctional Nanocrystals

Conformational flexibility: The DNA-binding domain of tumor suppressor protein p53 (see picture) is characterized by using ion-mobility mass spectrometry. Wild-type p53 and common single-point carcinogenic mutations exhibit diverse conformational states upon transfer into a solvent-free environment of the mass spectrometer. DNA-binding properties of wild-type p53 and an engineered second-site suppressor mutation H115N were also investigated.



Protein Structures

E. Jurneczko, F. Cruickshank, M. Porrini,
D. J. Clarke, I. D. G. Campuzano,
M. Morris, P. V. Nikolova,
P. E. Barran* ——— **4370 – 4374**

Probing the Conformational Diversity of Cancer-Associated Mutations in p53 with Ion-Mobility Mass Spectrometry

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2012–124/4

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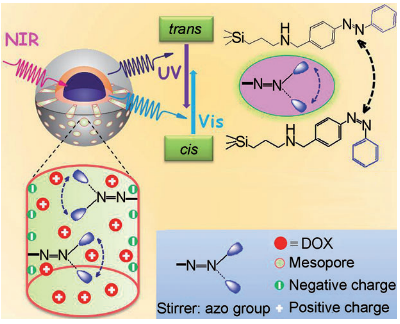
Photomediated drug release: Silica-coated upconverting nanoparticles with mesopores modified by azobenzene molecules were synthesized. The azobenzene molecules make possible the release of the anticancer drug doxorubicin from the pore network of the mesoporous silica outer layer by irradiation with near-infrared (NIR) laser light. The release is regulated by the *trans*–*cis* photoisomerization of the azobenzene molecules (see picture).



Drug Delivery

J. N. Liu, W. B. Bu,* L. M. Pan,
J. L. Shi* ———— **4375–4379**

NIR-Triggered Anticancer Drug Delivery by Upconverting Nanoparticles with Integrated Azobenzene-Modified Mesoporous Silica

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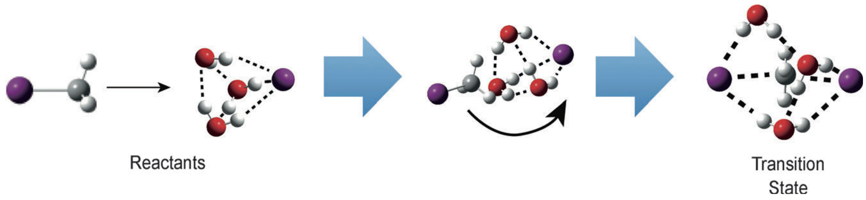


Water gets in the way: Hydrated $I^-(CH_3I)$ complexes, $I^-(CH_3I)(H_2O)_{1-3}$, are investigated by IR photodissociation spectroscopy to examine the stable structures of the intermediates of the $I^-+CH_3I \rightarrow ICH_3+I^-$ S_N2 reaction under hydrated conditions. The structures and the energetics of the complexes suggest that just one or two H_2O molecules will effectively inhibit this S_N2 reaction.

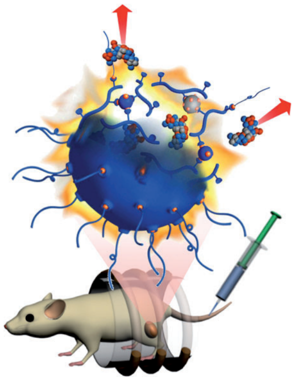
Solvent Effects

K. Doi, E. Togano, S. S. Xantheas,
R. Nakanishi, T. Nagata, T. Ebata,
Y. Inokuchi* ———— **4380–4383**

Microhydration Effects on the Intermediates of the S_N2 Reaction of Iodide Anion with Methyl Iodide

---

On-demand drug release: Magnetothermally responsive drug-encapsulated supramolecular nanoparticles for on-demand drug release in vivo have been developed. The remote application of an alternative magnetic field heats the magnetic particles that effectively trigger the release of the drug. An acute drug concentration can be delivered to the tumor in vivo, resulting in an improved therapeutic outcome.



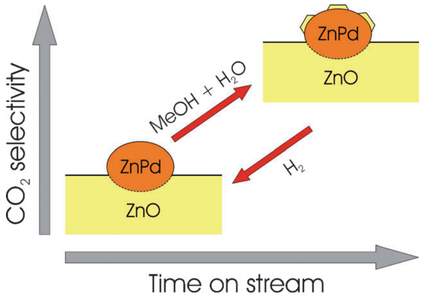
Drug Delivery

J.-H. Lee, K.-J. Chen, S.-H. Noh,
M. A. Garcia, H. Wang, W.-Y. Lin, H. Jeong,
B. J. Kong, D. B. Stout, J. Cheon,*
H.-R. Tseng* ———— **4384–4388**

On-Demand Drug Release System for In Vivo Cancer Treatment through Self-Assembled Magnetic Nanoparticles

---

Together we are strong: Immediately after high-temperature reduction, ZnPd/ZnO catalysts are not notably CO_2 selective in the methanol steam reforming process. Under methanol steam reforming conditions, high CO_2 selectivity can only be achieved by the rather slow formation of ZnO patches on the surface of intermetallic ZnPd nanoparticles to create a highly synergistic interface.



Methanol Steam Reforming

M. Friedrich, S. Penner, M. Heggen,
M. Armbrüster* ———— **4389–4392**

High CO_2 Selectivity in Methanol Steam Reforming through ZnPd/ZnO Teamwork

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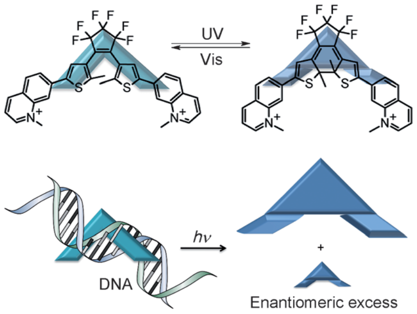
Supramolecular Chemistry

T. C. S. Pace, V. Müller, S. Li, P. Lincoln,
J. Andréasson* ———— 4393 – 4396

Enantioselective Cyclization of Photochromic Dithienylethenes Bound to DNA

Guiding light: Enantioselectivity is obtained for the photocyclization of a photochromic dithienylethene when isomerization is carried out in the presence of DNA (see scheme).



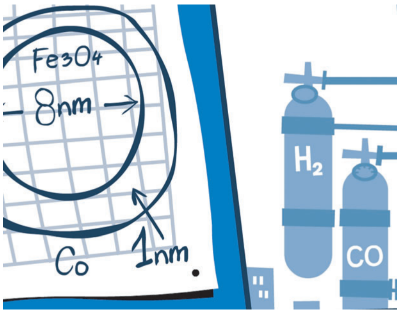
Core–Shell Catalysts

V. R. Calderone, N. R. Shiju,
D. Curulla-Ferré, S. Chambrey,
A. Khodakov, A. Rose, J. Thiessen, A. Jess,
G. Rothenberg* ———— 4397 – 4401

De Novo Design of Nanostructured Iron–Cobalt Fischer–Tropsch Catalysts

Front Cover

Audio cassettes hold the key to enhancing Fischer–Tropsch catalysis. Catalysts based on ultra-thin cobalt shells surrounding cheap iron oxide cores (see picture) are developed, an approach previously optimized for preparing magnetic tape for audio cassettes. These particles are easily made on a large scale, and are excellent Fischer–Tropsch catalysts, giving good diesel fractions.

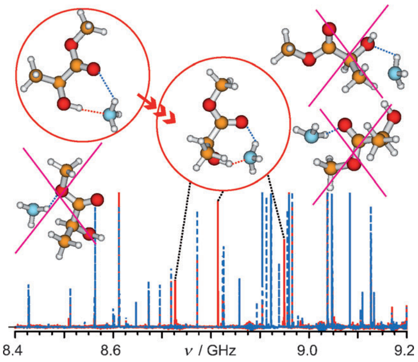


Molecular Recognition

J. Thomas, O. Sukhorukov, W. Jäger,
Y. Xu* ———— 4402 – 4405

Chirped-Pulse and Cavity-Based Fourier Transform Microwave Spectra of the Methyl Lactate···Ammonia Adduct

Internal rotations: Using a broadband chirped-pulse and a cavity-based microwave spectrometer, the delicate balance between intra- and intermolecular hydrogen-bonding interactions in the methyl lactate···NH_3 adduct was investigated (see picture). The adduct is a prototype lock-and-key system consisting of a lock with two "spinning" tops and a key which is also a spinning top itself.

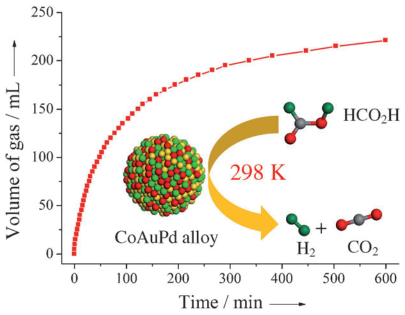


Hydrogen Storage

Z.-L. Wang, J.-M. Yan,* Y. Ping,
H.-L. Wang, W.-T. Zheng,
Q. Jiang* ———— 4406 – 4409

An Efficient CoAuPd/C Catalyst for Hydrogen Generation from Formic Acid at Room Temperature

Less noble: The $Co_{0.30}Au_{0.35}Pd_{0.35}$ nanoalloy supported on carbon is reported as a stable, low-cost, and highly efficient catalyst for the CO-free hydrogen generation from formic acid dehydrogenation at room temperature (see picture). The method may strongly encourage the practical application of formic acid as a hydrogen storage material for fuel cells.



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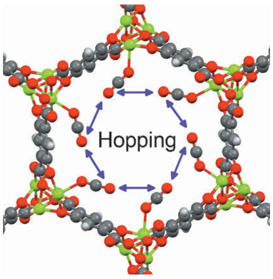
CO_2 Dynamics

L.-C. Lin,* J. Kim, X. Kong, E. Scott,
T. M. McDonald, J. R. Long, J. A. Reimer,
B. Smit ______ 4410 – 4413

Understanding CO_2 Dynamics in Metal–Organic Frameworks with Open Metal Sites



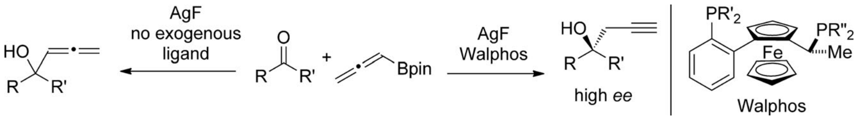
Hopping along: Metal–organic frameworks such as Mg-MOF-74 possess open metal sites that interact strongly with CO_2. Molecular simulations reveal detailed CO_2 dynamics (hops between metal sites and localized fluctuations), which can be used to accurately explain the experimentally measured ^{13}C NMR chemical shift anisotropy pattern.

Inside Back Cover

Asymmetric Catalysis

B. L. Kohn, N. Ichiishi,
E. R. Jarvo* ______ 4414 – 4417

Silver-Catalyzed Allenylation and Enantioselective Propargylation Reactions of Ketones

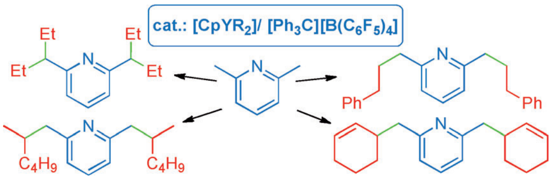


More than a silver lining: Certain silver complexes are capable of selective catalysis of either allenylation or asymmetric propargylation reactions of ketones. Ligand-free conditions lead to allenyl alcohols as the major product, whereas ligation with Walphos-8 gives enantioenriched homopropargyl alcohols. This method can be applied to reactions of prochiral diarylketones to provide optically enriched tertiary diaryl alcohols.

C–H Alkylation

B.-T. Guan, B. Wang, M. Nishiura,
Z. Hou* ______ 4418 – 4421

Yttrium-Catalyzed Addition of Benzylic C–H Bonds of Alkyl Pyridines to Olefins

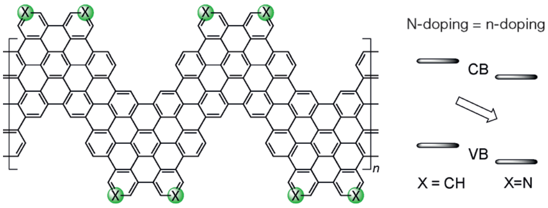


Cationic half-sandwich yttrium alkyl complexes catalyze the *ortho*-selective benzylic C–H addition of dialkyl pyridines to various olefins, such as ethylene, 1-hexene, styrenes, and 1,3-conjugated dienes, to afford new alkylated and allylated pyridine derivatives (see scheme; $Cp = C_5Me_5$). A cationic half-sandwich yttrium picolyl species, such as $[CpY(2\text{-}CH_2\text{-}6\text{-}CH_3C_5H_3N)]^+$, has been confirmed to be a key active species in this transformation.

Carbon Materials

C. Bronner,* S. Stremlau, M. Gille,
F. Brauße, A. Haase, S. Hecht,*
P. Tegeder* ______ 4422 – 4425

Aligning the Band Gap of Graphene Nanoribbons by Monomer Doping



A matter of doping: Graphene nanoribbons (GNRs) were generated through an on-surface bottom-up synthesis and selectively doped at their edges by introducing nitrogen atoms in the precursor monomers. While the size of the band gap of 2.8 eV remains almost unchanged upon N substitution, a linear shift of the band structure is observed and corresponds to n-type doping (see picture; CB = conduction band and VB = valence band).

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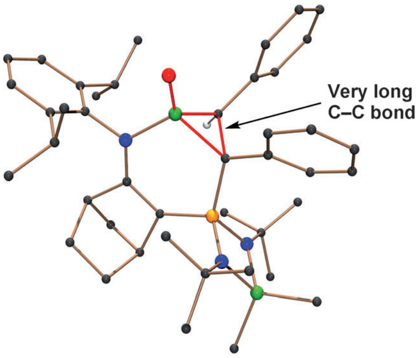
Small-Ring Systems

R. Rodriguez, T. Troadec, D. Gau,
N. Saffon-Merceron, D. Hashizume,
K. Miqueu, J.-M. Sotiropoulos,
A. Baceiredo,* T. Kato* ____ **4426 – 4430**

Synthesis of a Donor-Stabilized Silacyclopropan-1-one

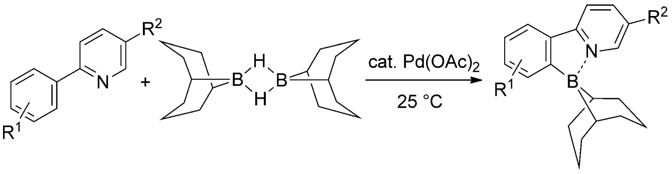


As intriguing as the Bermuda Triangle: The synthesis and characterization of an isolable silacyclopropan-1-one (see structure; red O, blue N, green Si, yellow P) was made possible by stabilization through intramolecular coordination by a Lewis base. However, this silacyclopropan-1-one, which contains a significantly elongated endocyclic C–C σ bond, remains highly reactive and underwent an unprecedented silanone–silenol rearrangement under mild conditions.

Borylation Reactions

Y. Kuninobu,* T. Iwanaga, T. Omura,
K. Takai* ________________ **4431 – 4434**

Palladium-Catalyzed *ortho*-Selective C–H Borylation of 2-Phenylpyridine and Its Derivatives at Room Temperature

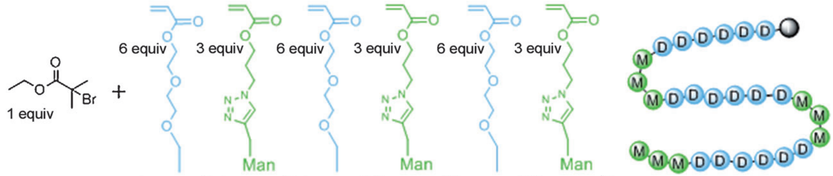


Boron delivery: C–H borylation at the *ortho*-position of aromatic compounds is promoted by the treatment of 2-phenylpyridine, or its derivatives, with 9-borabicyclo[3.3.1]nonane in the presence of a palladium catalyst. This reaction proceeds at room temperature and can be conducted without the palladium catalyst at higher temperatures. In both cases, the regioselectivity is controlled by Lewis acid–base interaction between the boron and nitrogen atoms.

Glycopolymers

Q. Zhang, J. Collins, A. Anastasaki,
R. Wallis, D. A. Mitchell, C. R. Becer,
D. M. Haddleton* _________ **4435 – 4439**

Sequence-Controlled Multi-Block Glycopolymers to Inhibit DC-SIGN-gp120 Binding

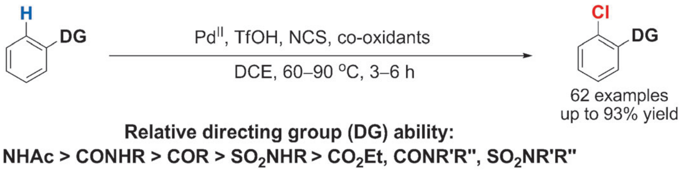


Chain of command: Multi-block glycopolymers made of mannose (M, see figure), glucose, and di(ethylene glycol) ethyl ether (D) monomers were synthesized using a technique to control the polymer sequence. These highly monodisperse glycopolymers were then tested for binding and inhibition of DC-SIGN, a protein important for HIV infection.

C–H Activation

X. Sun, G. Shan, Y. Sun,
Y. Rao* ________________ **4440 – 4444**

Regio- and Chemoselective C–H Chlorination/Bromination of Electron-Deficient Arenes by Weak Coordination and Study of Relative Directing-Group Abilities



It's all relative: A practical and efficient Pd^{II}-catalyzed regio- and chemoselective chlorination/bromination has been developed for the facile synthesis of a broad range of aromatic chlorides. The reaction demonstrates excellent reactivity, good functional-group tolerance, and high yields. A preliminary study was conducted to evaluate relative directing-group abilities of various functionalities.

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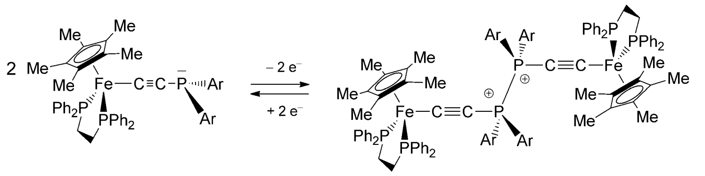
Alkynyl Diphosphane Complexes

A. Tohmé, G. Grelaud, G. Argouarch, T. Roisnel, S. Labouille, D. Carmichael,* F. Paul* **4445 – 4448**

Redox-Induced Reversible P–P Bond Formation to Generate an Organometallic σ^{4}λ^4-1,2-Biphosphane Dication

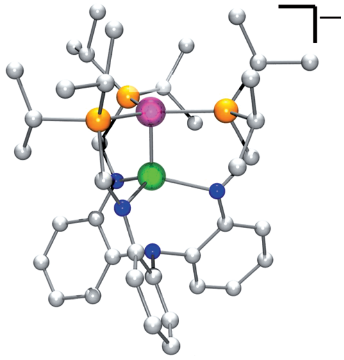


Twice the fun: Dimeric Fe^{II} diphosphonium bis(alkynyl) complexes are formed by oxidation of the corresponding Fe^{II} alkynyl phosphine complexes. The structure of these organometallic diphosphonium salts and their monomeric precursors were established by X-ray crystallography. The P–P bond can be cleaved by two-electron reduction to regenerate the monomers.

Heterometallic Complexes

P. A. Rudd, S. Liu, N. Planas, E. Bill, L. Gagliardi,* C. C. Lu* **4449 – 4452**

Multiple Metal–Metal Bonds in Iron–Chromium Complexes



Mix and match: The first structural examples of M–M multiple bonds between different first-row transition metals are elucidated using X-ray crystallography (see picture; Fe pink, Cr green, P yellow, N blue), spectroscopic methods, and calculations. The Fe–Cr bonds are ultrashort (< 2 Å) with highly delocalized σ and π bonds and unusually large quadrupole splittings in Mössbauer spectroscopy.

C-H Functionalization

D. Liu, C. Liu, H. Li, A. Lei* **4453 – 4456**

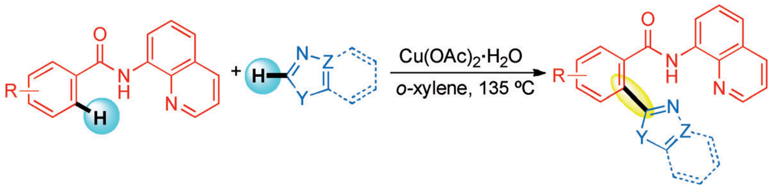
Direct Functionalization of Tetrahydrofuran and 1,4-Dioxane: Nickel-Catalyzed Oxidative C(sp^3)–H Arylation

CHoose nickel: The nickel-catalyzed oxidative arylation of C(sp^3)–H bonds has been achieved. Several substituted arylboronic acids and various C(sp^3)–H bonds were found to be suitable substrates for this novel transformation, which is likely to proceed through a radical pathway. This method allows the introduction of simple ether derivatives to construct α-arylated ethers. FG = functional group.

Synthetic Methods

M. Nishino, K. Hirano,* T. Satoh, M. Miura* **4457 – 4461**

Copper-Mediated C–H/C–H Biaryl Coupling of Benzoic Acid Derivatives and 1,3-Azoles



Hot couple: A precious-metal-free copper-mediated intermolecular direct biaryl coupling of benzoic acid derivatives and 1,3-azoles has been developed. The key to success is the installation of an amide-based bidentate coordinating group, which is easily removed and transformed into the parent ester groups after the coupling reaction. Kinetic studies indicate that the rate-limiting step is the aromatic C–H bond cleavage of benzoic acid derivatives.

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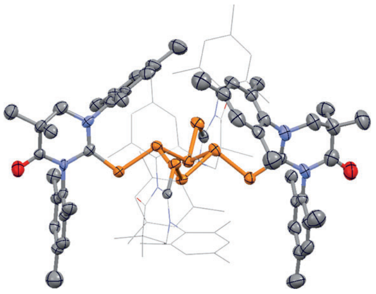
Phosphorus Clusters

C. L. Dorsey, B. M. Squires,
T. W. Hudnall* ____________ **4462 – 4465**

Isolation of a Neutral P_8 Cluster by [2+2] Cycloaddition of a Diphosphene Facilitated by Carbene Activation of White Phosphorus

Inside Cover

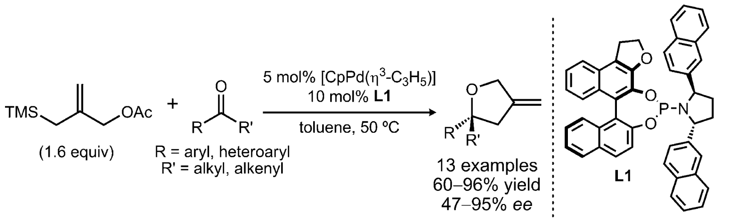
P-cing it together: Carbonyl-decorated carbenes readily activate white phosphorus to afford carbene-stabilized P_4 and P_8 clusters. Mechanistic evidence suggests the P_8 cluster (see structure from X-ray diffraction: C gray, P orange, N blue, O red) forms by a [2+2] cycloaddition of a transient diphosphene species.



Asymmetric Catalysis

B. M. Trost,* D. A. Bringley . **4466 – 4469**

Enantioselective Synthesis of 2,2-Disubstituted Tetrahydrofurans: Palladium-Catalyzed [3+2] Cycloadditions of Trimethylenemethane with Ketones

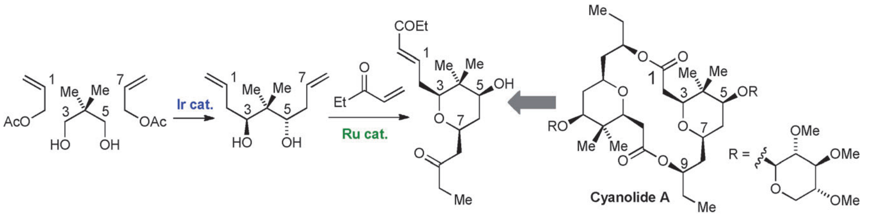


O rings: An approach to the title compounds has been developed utilizing a cycloaddition of trimethylenemethane with aryl ketones. The products are formed in up to a 96% yield with 95% *ee*. The reaction is catalyzed by palladium in the presence of **L1**, which possesses a stereogenic phosphorus atom, and only a single epimer at the phosphorus atom yields the active catalyst. Cp = cyclopentadiene, TMS = trimethylsilyl.

Natural Products Synthesis

A. R. Waldeck,
M. J. Krische* ____________ **4470 – 4473**

Total Synthesis of Cyanolide A in the Absence of Protecting Groups, Chiral Auxiliaries, or Premetalated Carbon Nucleophiles

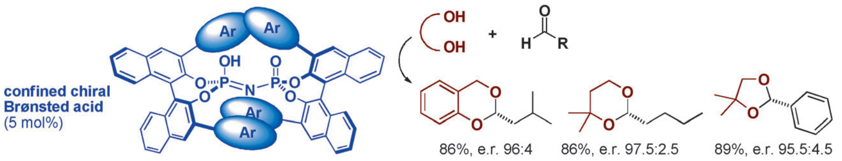


No protection, no problem: The C_2-symmetric macrodiolide cyanolide A is prepared in six steps from neopentyl glycol and allyl acetate by iridium-catalyzed double asymmetric allylation and a tandem cross-metathesis/oxa-Michael cyclization to form the substituted pyran. The synthesis is accomplished in the absence of any protecting groups, chiral auxiliaries, or premetalated carbon nucleophiles in fewer than half the steps of any prior approach.

Acetals

J. H. Kim, I. Čorić, S. Vellalath,
B. List* ____________ **4474 – 4477**

The Catalytic Asymmetric Acetalization



In straitened circumstances: In an asymmetric version of the acid-catalyzed acetalization of aldehydes, a novel member of the chiral confined Brønsted acid family significantly outperformed previously established catalysts, providing cyclic acetals with excellent enantioselectivity (see scheme; Ar = 2-*i*Pr-5-MeC_6H_3).

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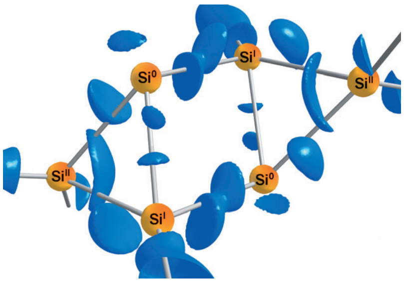
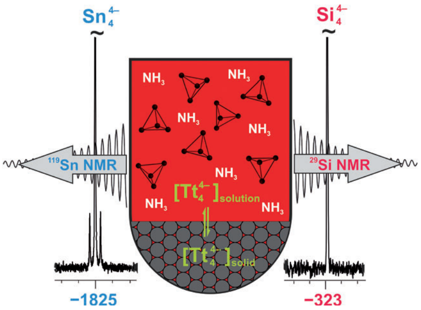


The aromaticity of the ring and cage isomer of a hexasilabenzene derivative was investigated by experimentally determined charge-density distribution. Topological analysis and valence-shell charge concentrations reflect the degree of delocalization in the various bonds. A transannular Si^0–Si^I bond was found in the ring conformer, while an interstitial Si^0–Si^0 bond along the hub in the silapropellane moiety of the cage conformer was not detected.

Hexasilabenzene

D. Kratzert, D. Leusser, J. J. Holstein,
B. Dittrich, K. Abersfelder,
D. Scheschkewitz,
D. Stalke* ______ **4478 – 4482**

An Experimental Charge Density Study of Two Isomers of Hexasilabenzene



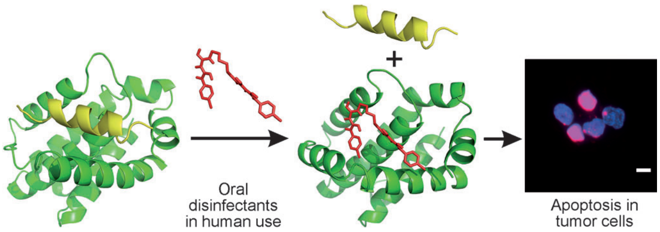
It's detected! The existence of the prototypical Zintl ions Tt_4^{4-} (Tt = Group 14 element), which are isoelectronic to the P_4 molecule, used to be confined to the solid state. Recently, circumstantial evidence for a solution chemistry in liquid ammonia emerged. Direct spectroscopic observation of the dissolved anions has now been achieved. In the case of Si_4^{4-}, this is the first solution detection of any homoatomic silicide.

Main-Group Chemistry

M. Neumeier, F. Fendt, S. Gärtner,
C. Koch, T. Gärtner, N. Korber,*
R. M. Gschwind* ______ **4483 – 4486**

Detection of the Elusive Highly Charged Zintl Ions Si_4^{4-} and Sn_4^{4-} in Liquid Ammonia by NMR Spectroscopy

Back Cover



Chlorhexidine and alexidine have long been used as oral disinfectants by humans. Both compounds inhibit protein–protein interactions mediated by the anti-apoptotic protein Bcl-x_L at physiologically relevant concentrations and induce apoptosis in a series of tumor cell lines derived from the tongue and pharynx (see picture). Inhibition of protein–protein interactions is a potential mode of action of drugs in current human use.

Protein–Protein Interactions

M. Gräber, M. Hell, C. Gröst, A. Friberg,
B. Sperl, M. Sattler, T. Berg* **4487 – 4491**

Oral Disinfectants Inhibit Protein–Protein Interactions Mediated by the Anti-Apoptotic Protein Bcl-x_L and Induce Apoptosis in Human Oral Tumor Cells

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

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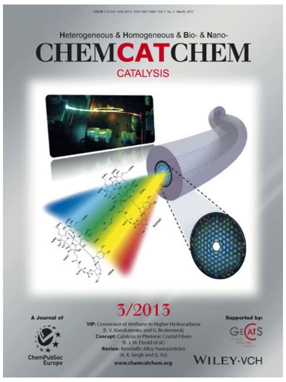

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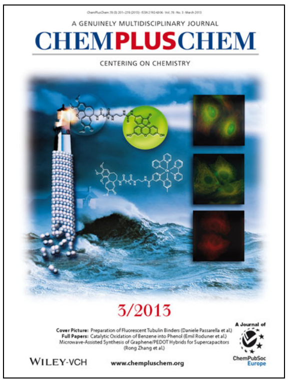

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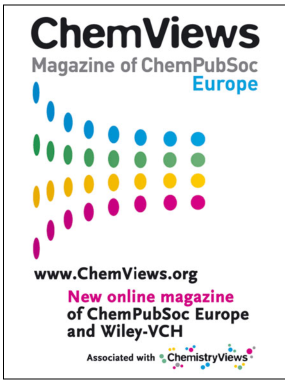
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