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:

*B. L. Merner, L. N. Dawe, G. J. Bodwell**
1,1,8,8-Tetramethyl[8](2,11)teropyrenophane: Half of an Aromatic Belt and a Segment of an (8,8) Single-Walled Carbon Nanotube

*B. Liu, H. Wang, H. Xie, B. Zeng, J. Chen, J. Tao, T. B. Wen, Z. Cao, H. Xia**
Osmapyridine and Osmapyridinium from a Formal [4+2] Cycloaddition Reaction

*J. L. Alonso-Gómez, P. Rivera-Fuentes, N. Harada, N. Berova, F. Diederich**
An Enantiomerically Pure Alleno-Acetylenic Macrocycle: Synthesis and Rationalization of Its Outstanding Chiroptical Response

*P. García-García, M. A. Fernández-Rodríguez, E. Aguilar**
Gold-Catalyzed Cycloaromatization of 2,4-Dien-6-yne Carboxylic Acids: Synthesis of 2,3-Disubstituted Phenols and Unsymmetrical Bi- and Terphenyls

*H. Jiang, P. Elsner, K. L. Jensen, A. Falcicchio, V. Marcos, K. A. Jørgensen**
Achieving Molecular Complexity by Organocatalytic One-Pot Strategies: A Fast Entry for the De Novo Synthesis of Sphingoids, Amino Sugars and Polyhydroxylated α-Amino Acids

P. A. Rupar, R. Bandyopadhyay, B. F. T. Cooper, M. R. Stinchcombe, P. J. Ragogna, C. L. B. Macdonald, K. M. Baines**
Cationic Crown Ether Complexes of Germanium(II)

*T. J. Kucharski, Z. Huang, Q.-Z. Yang, Y. Tian, N. C. Rubin, C. D. Concepcion, R. Boulatov**
Kinetics of Thiol/Disulfide Exchange Correlates Weakly with the Restoring Force in the Disulfide Moiety

*W. Xu, X. Xue, T. Li, H. Zeng, X. Liu**
Ultrasensitive and Selective Colorimetric DNA Detection by Nicking Endonuclease-Assisted Nanoparticle Amplification

Author Profile

"My favorite subject at school was mathematics, although I have forgotten most of it. When I was eighteen I wanted to be 19 and to finish school. …"
This and more about Christoph A. Schalley can be found on page 4888.

News

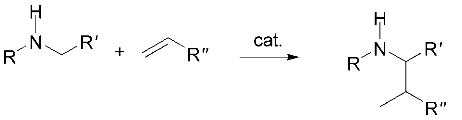
A. Müller

M. Kappes

Books

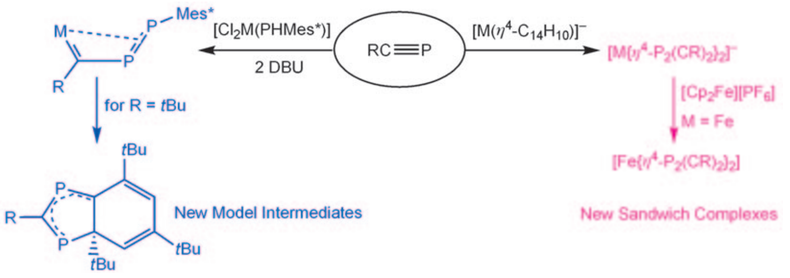
Highlights

C—H Activation



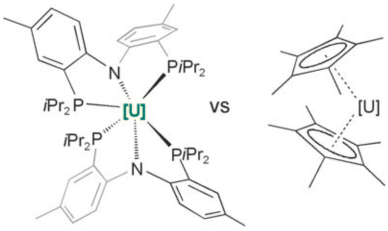
Excellent couplings: Recent developments in the metal-catalyzed C—H activation of sp^3 centers in an α position relative to an amine nitrogen atom are presented. Their reaction with alkenes to give alkylamines (hydroaminoalkylation) is also summarized (see general scheme).

Phosphorus Chemistry



Teaching old dogs new tricks: Recent developments in low-coordinate phosphorus chemistry reveal the capacity of this element for surprises. For example, P for CR substitution in new phosphaalkynes was used to stabilize purported intermediates in an important synthetic transformation, and also to form new diphosphacyclobutadiene sandwich complexes (see scheme).

Actinides



Pincers do something for U that sandwiches don't: The dead-ends in the metallocene chemistry of the actinides can be circumvented by using a soft PNP pincer ligand (see scheme). The PNP ligand has been shown to be flexible, hemilabile, and capable of stabilizing low- and high-valent uranium species. The bis(PNP) framework is a valuable alternative to the $(C_5Me_5)_2$ ligand set, offering distinct structures and reaction patterns.

For the USA and Canada:
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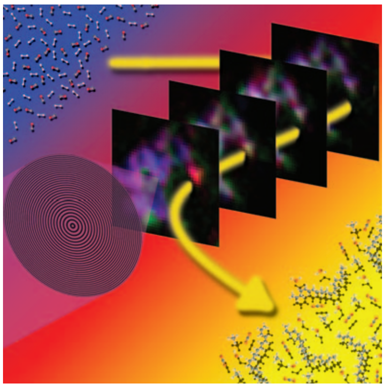
Minireviews

No copper needed: In recent years, a large number of metal-free click reactions have been reported based on thiol-ene radical additions, Diels–Alder reactions, and Michael additions. In this Minireview, special attention is given to the advantages and limitations of the different methods to evaluate whether they have the potential to surpass the overwhelming success of the copper(I)-catalyzed azide-alkyne cycloaddition.

Click Chemistry

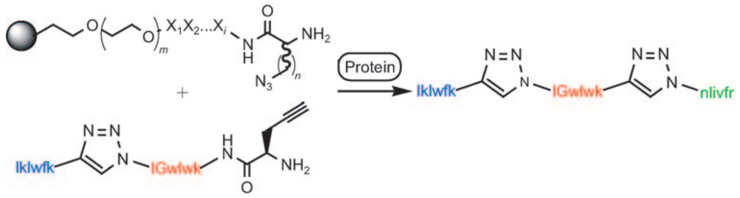
Reviews

Catalytic solids in the spotlight: Detailed insight into the working principles of heterogeneous catalysts is essential for the design of improved or totally new ones. Such insight can be provided by making use of chemical imaging techniques, which yield spatiotemporal information about the workings of catalytic solids at different length scales: at the level of reactors, catalyst bodies, catalyst grains, and nanoparticles.



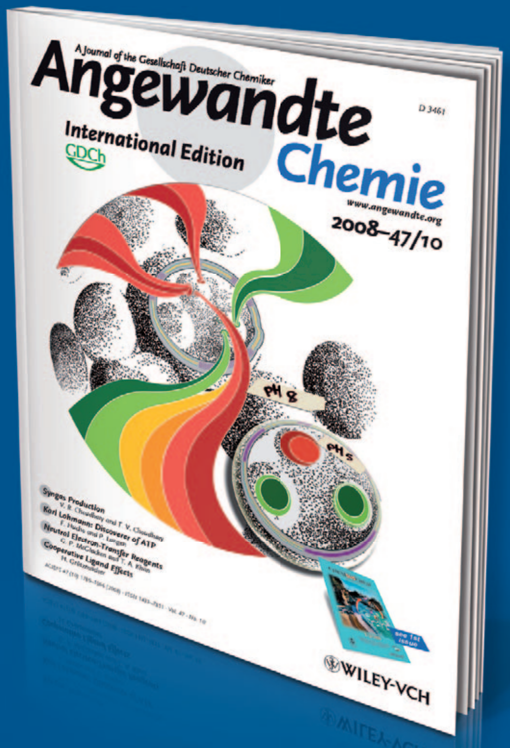
Heterogeneous Catalysts

Communications



Special agents for protein capture: Iterative in situ click chemistry (see scheme for the tertiary ligand screen) and the one-bead–one-compound method for the creation of a peptide library enable the fragment-based assembly of selective high-affinity protein-capture agents. The resulting ligands are water-soluble and stable chemically, biochemically, and thermally. They can be produced in gram quantities through copper(I)-catalyzed cycloaddition.

Affinity Agents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pH 5
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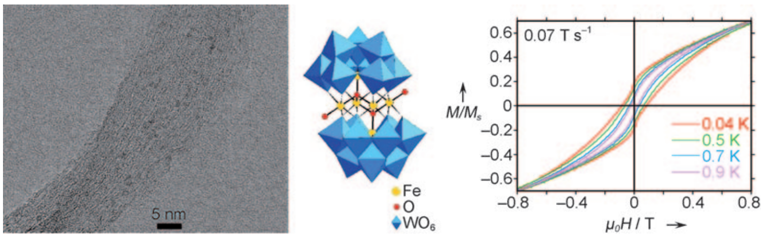
Single-Molecule Magnets

A. Giusti, G. Charron,* S. Mazerat, J.-D. Compain, P. Mialane, A. Dolbecq, E. Rivière, W. Wernsdorfer, R. Ngo Biboum, B. Keita, L. Nadjo, A. Filoramo, J.-P. Bourgoin, T. Mallah* ———— **4949 – 4952**

Magnetic Bistability of Individual Single-Molecule Magnets Grafted on Single-Wall Carbon Nanotubes

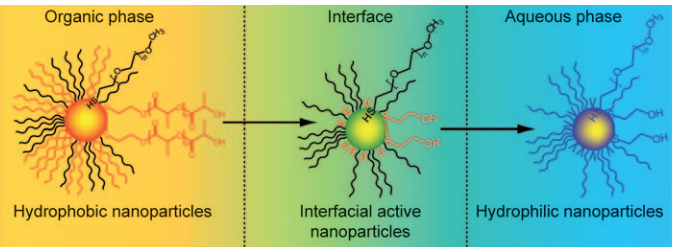


A POM to remember: Hexanuclear Fe^{III} polyoxometalate (POM) single-molecule magnets (see structure) can be noncovalently assembled on the surface of single-wall carbon nanotubes. Complementary characterization techniques (see TEM image and magnetic hysteresis loops) demonstrate the integrity and bistability of the individual molecules, which could be used to construct single-molecule memory devices.

Biotechnology

Z. Mao, J. Guo, S. Bai, T.-L. Nguyen, H. Xia, Y. Huang,* P. Mulvaney, D. Wang* ———— **4953 – 4956**

Hydrogen-Bond-Selective Phase Transfer of Nanoparticles across Liquid/Gel Interfaces



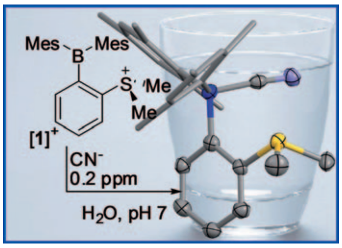
In the swim: Colloidal nanoparticles coated with polylactide (PLA, red) and poly(ethylene glycol) brushes (PEG, black) can transfer from organic to aqueous phases across liquid/liquid or liquid/gel interfaces during degradation of the PLA coating (see picture: first step), which is driven selectively by the hydrogen bonding of the PEG coating with the aqueous phase (second step).

Receptors

Y. Kim, H. Zhao, F. P. Gabbaï* ———— **4957 – 4960**

Sulfonium Boranes for the Selective Capture of Cyanide Ions in Water

Going fishing! The sulfonium borane $[\mathbf{1}]^+$ complexes cyanide in pure water at the maximum allowable concentration of 50 ppb recommended by the European Union. The high cyanide ion affinity displayed by this compound arises from favorable Coulombic effects augmented by a direct bonding interaction between the cyano and sulfonio groups.

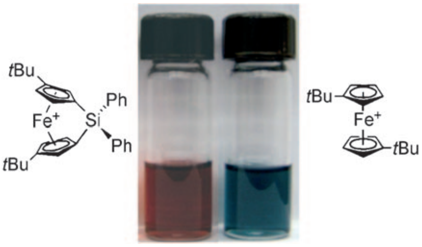


Cationic Metallocenophanes

G. Masson, D. E. Herbert, G. R. Whittell, J. P. Holland, A. J. Lough, J. C. Green,* I. Manners* ———— **4961 – 4964**

Synthesis and Reactivity of a Strained Silicon-Bridged [1]Ferrocenophanium Ion

Not blue but red-brown: A [1]ferrocenophanium ion has been synthesized and isolated as a red-brown crystalline salt, surprisingly different in color from characteristically blue-green unstrained ferrocenium ions. Compared to the neutral iron(II) counterpart, the [1]ferrocenophanium ion displays a considerably higher ring tilt and an increased propensity for ring-opening reactions.

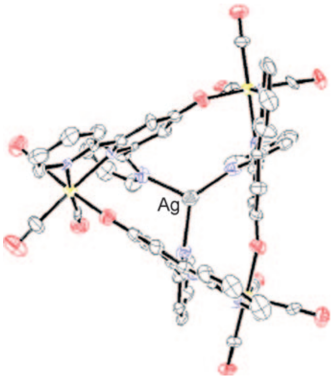


Coordination Chemistry

M. P. Coogan,* V. Fernández-Moreira,
B. M. Kariuki, S. J. A. Pope,
F. L. Thorp-Greenwood ____ **4965 – 4968**

A Rhenium Tricarbonyl 4′-Oxo-terpy Trimer as a Luminescent Molecular Vessel with a Removable Silver Stopper

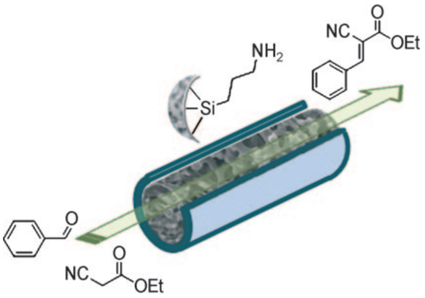
Shining metal cups: A luminescent tube of triangular cross-section and stoppered by a silver ion (see picture: Re yellow, N blue, O red) is formed in two steps from commercial materials. The silver ion can be removed to give a tube, and both species are potential hosts for small ions and molecules; a change in luminescence is triggered by the encapsulation of silver.



Microreactors

A. El Kadib, R. Chimenton, A. Sachse,
F. Fajula, A. Galarneau,
B. Coq* ____ **4969 – 4972**

Functionalized Inorganic Monolithic Microreactors for High Productivity in Fine Chemicals Catalytic Synthesis

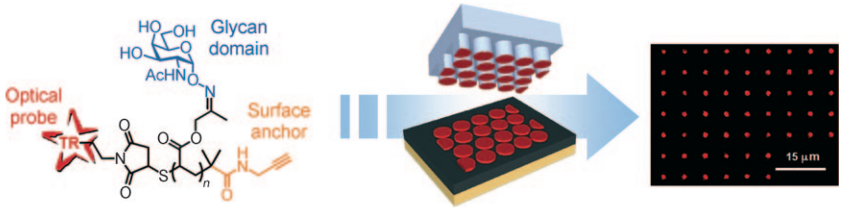


Highly productive: Grafted monolith silica skeleton microreactors process bulky molecules more efficiently than a batch mode reactor. This efficiency is due to a higher contact area, shorter diffusion path, and lower inhibition by products in the thin monolith skeleton. These materials provide a new approach in the field of heterogeneous catalysis for the synthesis of fine chemicals.

Microarrays

K. Godula, D. Rabuka, K. T. Nam,
C. R. Bertozzi* ____ **4973 – 4976**

Synthesis and Microcontact Printing of Dual End-Functionalized Mucin-like Glycopolymers for Microarray Applications

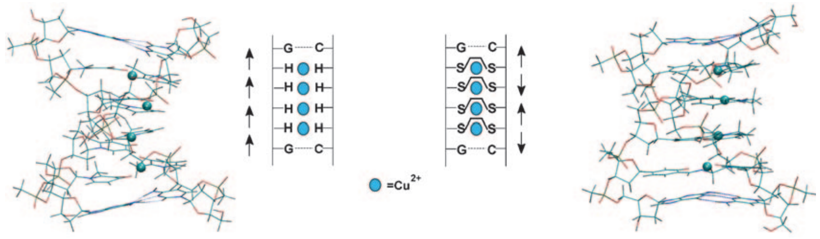


Click to view: Glycopolymers can be used to display glycans on microarrays in native-like architectures. The structurally uniform alkyne-terminated mucin mimetic glycopolymers (see picture; TR = fluorophore) were printed on azide-functionalized chips by microcontact printing in the presence of a copper catalyst. The surface-bound glycopolymers bind lectins in a ligand-specific manner.

Bioinorganic Chemistry

S. S. Mallajosyula,
S. K. Pati* ____ **4977 – 4981**

Conformational Tuning of Magnetic Interactions in Metal–DNA Complexes

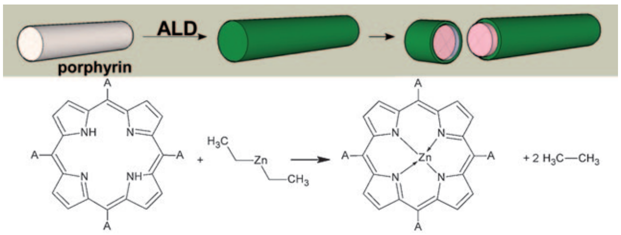


The alignment of Cu^{2+} ions along a modified DNA helix is studied with either hydroxypyridone (H) or bis(salicylaldehyde)ethylenediamine (S-en) metalated base pairs (MBPs). The conformational motion of H-MBP leads to the interlinking of the H-MBPs by an extended Cu-O network that is ferromagnetic, whereas the conformational freezing of the S-en-MBP leads to an ordered pairwise-stacked arrangement that is weakly antoferrimagnetic.

Hybrid Nanostructures

L. Zhang,* A. J. Patil, L. Li, A. Schierhorn, S. Mann, U. Gösele, M. Knez* ________ **4982 – 4985**

Chemical Infiltration during Atomic Layer Deposition: Metalation of Porphyrins as Model Substrates

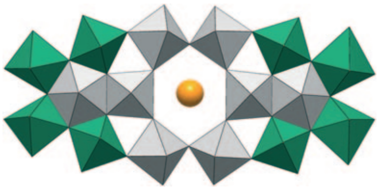


New uses for ALD: By applying standard metal oxide atomic layer deposition (ALD) to two types of porphyrins, site-specific chemical infiltration of substrate molecules is achieved: Diethylzinc can diffuse into the interior of porphyrin supramolecular structures and induce metalation of the porphyrin molecules from the vapor phase. A = Ph, p-$HO_3SC_6H_4$.

Keggin Structures

N. Leclerc-Laronze, J. Marrot, R. Thouvenot,* E. Cadot* __ **4986 – 4989**

Structural Link between Giant Molybdenum Oxide Based Ions and Derived Keggin Structure: Modular Assemblies Based on the $[BW_{11}O_{39}]^{9-}$ Ion and Pentagonal $\{M'M_5\}$ Units (M′ = W; M = Mo,W)

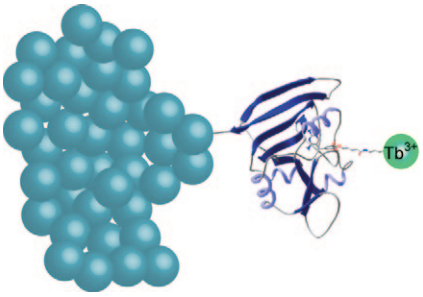


Linked to the Pentagon: The addition of molybdate to $[HBW_{11}O_{39}]^{8-}$ ions leads to the formation of mixed pentagonal units $\{W(Mo_5)\}$ and $\{W(WMo_4)\}$ trapped as linkers in the resulting modular assemblies, thus establishing the first link between the conventional Keggin ion derivatives and the giant molybdenum oxide and keplerate ions.

Live-Cell Imaging

H. E. Rajapakse, D. R. Reddy, S. Mohandessi, N. G. Butlin, L. W. Miller* ________ **4990 – 4992**

Luminescent Terbium Protein Labels for Time-Resolved Microscopy and Screening

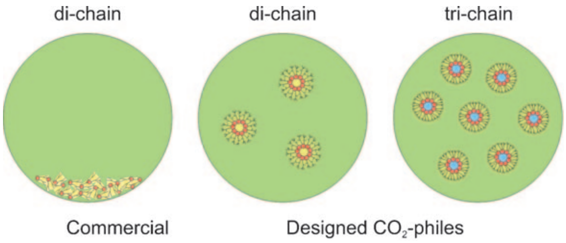


Brilliance of terbium: Heterodimeric conjugates of trimethoprim covalently linked to sensitized terbium chelates bind to *Escherichia coli* dihydrofolate reductase fusion proteins with nanomolar affinity (see picture). Terbium luminescence enables sensitive and time-resolved detection of labeled proteins in vitro and on the surface of living mammalian cells.

Micellar Modifiers

M. J. Hollamby, K. Trickett, A. Mohamed, S. Cummings, R. F. Tabor, O. Myakonkaya, S. Gold, S. Rogers, R. K. Heenan, J. Eastoe* __ **4993 – 4995**

Tri-Chain Hydrocarbon Surfactants as Designed Micellar Modifiers for Supercritical CO_2

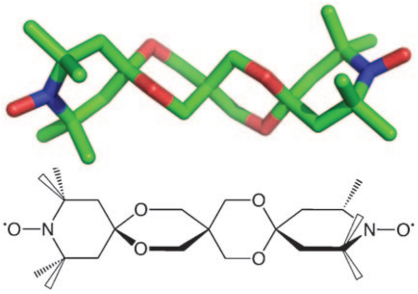


Getting their feet wet: Low-cost hydrocarbon surfactants act as fluid modifiers for supercritical carbon dioxide ($scCO_2$). Increased terminal branching of the surfactant chains aids micelle formation (see middle picture: CO_2 green), and more chains allows water to be incorporated (right, blue).

Dynamic Nuclear Polarization

Y. Matsuki, T. Maly, O. Ouari, H. Karoui, F. Le Moigne, E. Rizzato, S. Lyubenova, J. Herzfeld, T. Prisner, P. Tordo, R. G. Griffin* ______ **4996 – 5000**

Dynamic Nuclear Polarization with a Rigid Biradical



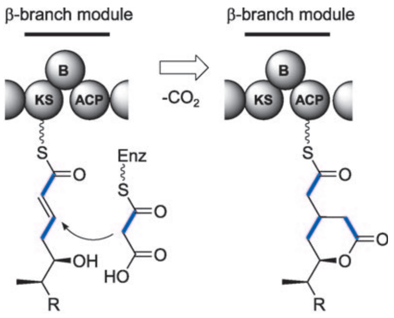
A new polarizing agent with superior performance in dynamic nuclear polarization experiments is introduced, and utilizes two TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) moieties connected through a rigid spiro tether (see structure). The observed NMR signal intensities were enhanced by a factor of 1.4 compared to those of TOTAPOL, a previously described TEMPO-based biradical with a flexible tether.

Polyketide Biosynthesis

B. Kusebauch, B. Busch, K. Scherlach, M. Roth, C. Hertweck* ______ **5001 – 5004**

Polyketide-Chain Branching by an Enzymatic Michael Addition

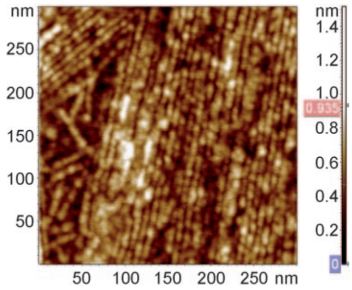
A new “branch” for polyketide synthases was discovered in the biosynthesis of the antimitotic rhizoxin complex in the endofungal bacterium *Burkholderia rhizoxinica*. Genetic engineering and the structural elucidation of pathway intermediates revealed that a complex polyketide chain is branched at the β position by an unprecedented conjugate addition of an acetyl building block to an acryloyl precursor (see scheme).



Amyloid Nanostructures

M. Lepère, C. Chevallard, G. Brezesinski, M. Goldmann, P. Guenoun* ______ **5005 – 5009**

Crystalline Amyloid Structures at Interfaces

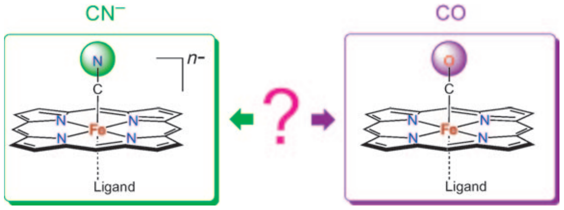


Laying the groundwork: The interfacial self-assembly properties of an amyloid peptide were used to develop crystalline nanostructures at air–water interfaces, which were studied by both AFM microscopy and X-ray diffraction (see image). These structures generate regular arrays of functional groups and pave the way to controlled deposition of inorganic materials like that observed in biomineralization.

Structure and Bonding

J. Li, B. C. Noll, C. E. Schulz, W. R. Scheidt* ______ **5010 – 5013**

Comparison of Cyanide and Carbon Monoxide as Ligands in Iron(II) Porphyrinates

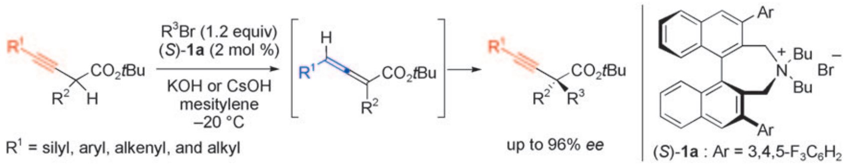


Spot the difference: The five-coordinate iron(II) cyanoporphyrinates, which are spin-crossover compounds, can be used to synthesize previously unknown six-coordinate complexes. Bis(cyano) and (cyano)imidazole complexes are presented, and the five- and six-coordinate (cyano)iron(II) derivatives are compared with analogous CO complexes.

Asymmetric Synthesis

T. Hashimoto, K. Sakata, K. Maruoka* ______ **5014 – 5017**

α-Chiral Acetylenes Having an All-Carbon Quaternary Center: Phase Transfer Catalyzed Enantioselective α Alkylation of α-Alkyl-α-alkynyl Esters

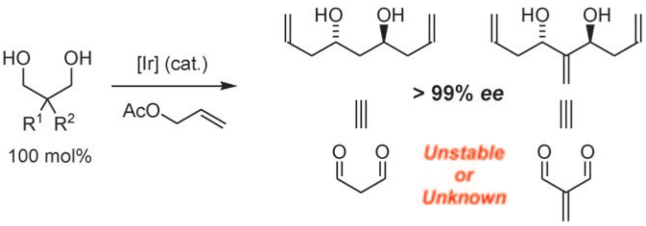


Going through the phases: The title reaction was found to proceed by an initial base-mediated isomerization to allenyl esters and subsequent phase transfer catalyzed alkylation at the α position of the ester (see scheme).

Synthetic Methods

Y. Lu, I. S. Kim, A. Hassan, D. J. Del Valle, M. J. Krische* ______ **5018 – 5021**

1,*n*-Glycols as Dialdehyde Equivalents in Iridium-Catalyzed Enantioselective Carbonyl Allylation and Iterative Two-Directional Assembly of 1,3-Polyols

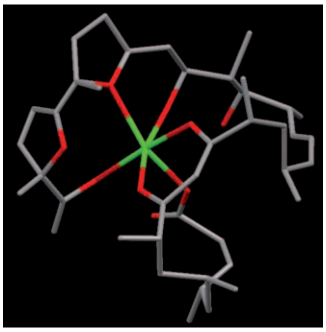


Unstable? We're able! 1,*n*-Glycols serve as synthetic equivalents to unstable dialdehydes in two-directional carbonyl allylation from the alcohol oxidation level under iridium-catalyzed transfer hydrogenation conditions. Iterative asymmetric allylation employing 1,3-propanediol enables the rapid assembly of protected 1,3-polyol substructures with exceptional levels of stereocontrol.

Total Synthesis

Z. Gao, Y. Li, J. P. Cooksey, T. N. Snaddon, S. Schunk, E. M. E. Viseux, S. M. McAteer, P. J. Kocienski* ______ **5022 – 5025**

A Synthesis of an Ionomycin Calcium Complex

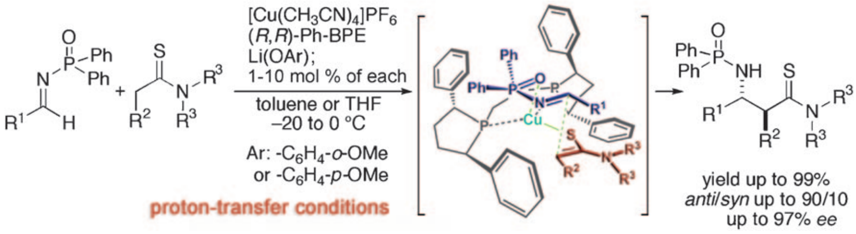


Caught in the middle: The ionomycin calcium complex (see structure; O red, Ca green) was the target of an approach featuring the efficient asymmetric synthesis of an allene by a copper(I)-mediated *anti*-selective $\mathrm{S_N}2'$ reaction, a highly stereoselective gold(III)-catalyzed cycloisomerization of an α-hydroxyallene, and a Rh-catalyzed rearrangement of an α-diazo-β-hydroxyketone.

Asymmetric Catalysis

Y. Suzuki, R. Yazaki, N. Kumagai,* M. Shibasaki* ______ **5026 – 5029**

Direct Catalytic Asymmetric Mannich-Type Reaction of Thioamides

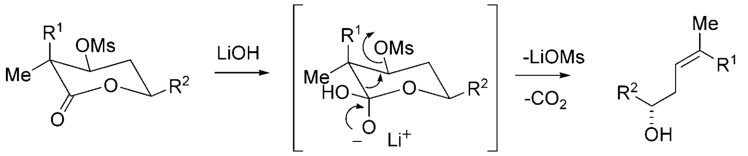


Taking the reins: The title transformation of thioamides and *N*-diphenylphosphinoyl imines is described. By harnessing the power of cooperative catalysis between a soft Lewis acid and a hard Brønsted base, thioamide carbon pronucleophiles can furnish Mannich products (see scheme). Divergent transformation of the thioamide functionality highlights the utility of this methodology.

Olefin Synthesis

K. Prantz, J. Mulzer* ______ 5030 – 5033

Decarboxylative Grob-Type Fragmentations in the Synthesis of Trisubstituted *Z* Olefins: Application to Peloruside A, Discodermolide, and Epothilone D

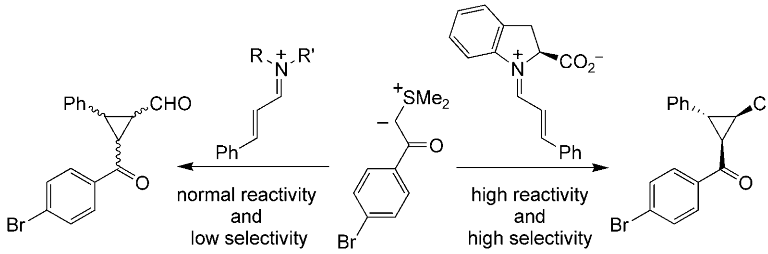


Discriminating elimination: A new method for the synthesis of methyl-branched trisubstituted *Z* olefins, a structural motif in many polyketides with anticancer activity, relies on an $^-$OH-induced decarboxylative Grob-type fragmentation (see scheme; Ms = mesyl). The starting materials are β-mesyloxy lactones with a quaternary α center, which are prepared by aldol reactions in a diastereo- and enantioselective manner.

Organocatalysis

S. Lakhdar, R. Appel, H. Mayr* ______ 5034 – 5037

How Does Electrostatic Activation Control Iminium-Catalyzed Cyclopropanations?

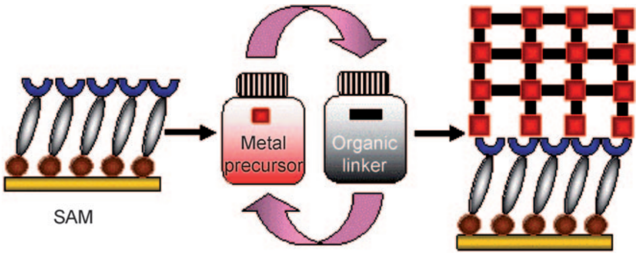


Prediction of $\lg k = s(N+E)$ verified: In contrast to previous statements, ordinary α,β-unsaturated iminium ions do react with sulfur ylides. Electrostatic interactions accelerate the reactions by a factor of more than 10^5 and are responsible for the high stereoselectivity.

MOFs on Surfaces

O. Shekhah, H. Wang, D. Zacher, R. A. Fischer, C. Wöll* ______ 5038 – 5041

Growth Mechanism of Metal–Organic Frameworks: Insights into the Nucleation by Employing a Step-by-Step Route

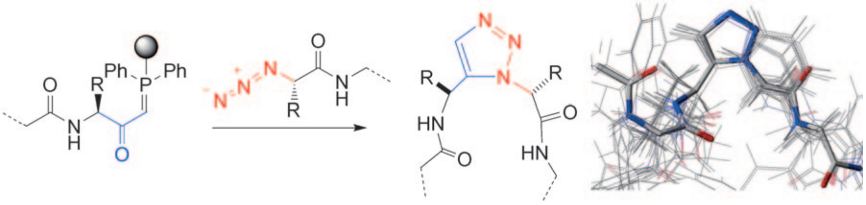


One step at a time: The in situ monitoring of the step-by-step formation of metal–organic frameworks (MOFs) by using surface plasmon resonance (SPR), allows the nucleation process and the formation of the secondary building units to be investigated. Growth rates on functionalized organic surfaces with different crystallographic orientations can also be studied.

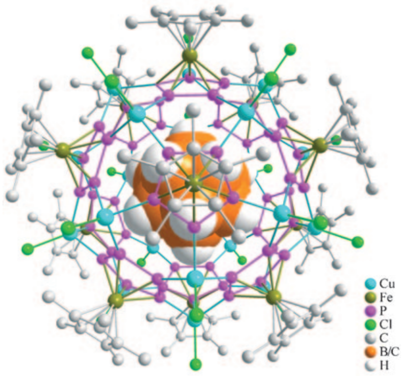
Biocompatible Ligations

Ahsanullah, P. Schmieder, R. Kühne, J. Rademann* ______ 5042 – 5045

Metal-Free, Regioselective Triazole Ligations that Deliver Locked *cis* Peptide Mimetics



Metal-free triazole turns: 1,5-Disubstituted peptidyl triazoles are obtained regioselectively from the 1,3-dipolar cycloaddition of peptidyl phosphoranes and azides. Peptide turns are thus formed that contain a conformationally locked *cis* peptide bond. Being regioselective and free of heavy metals, this reaction may find broad application in chemical biology and medicinal chemistry.



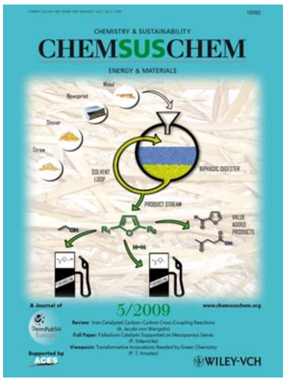
The complete encapsulation of *ortho*-carborane by a fullerene-like building-block system consisting of pentaphosphaferrocene and $Cu^{I}Cl$ leads to the formation of the spherical supermolecule $C_2B_{10}H_{12}@\text{-}[\{Cp^*Fe(\eta^5\text{-}P_5)\}_{12}(CuCl)_{20}]$. This product of template-controlled aggregation represents the first example of a carbon-free C_{80} analogue possessing icosahedral symmetry.

Host–Guest Compounds

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).

Service



Corrigendum

Copper-Catalyzed Direct C-Arylation of Heterocycles with Aryl Bromides: Discovery of Fluorescent Core Frameworks

D. Zhao, W. Wang, F. Yang, J. Lan,
L. Yang, G. Gao, J. You* ___ **3296–3300**

Angew. Chem. Int. Ed. **2009**, *48*

DOI 10.1002/anie.200900413

The authors would like to correct the following claims made in their article which misrepresent data that was published prior to our work.

1) It was claimed that the system previously developed by others is efficient only for reactions with aryl iodides. However, it has been previously shown that arylation of heterocycles by aryl bromide is possible with their system.[1] Additionally, multiple examples of the arylation of electron-deficient arenes by aryl bromides have been reported, and the method employs the exact reaction conditions which were used for the arylation of electron-rich heterocycles.[1,2] Even activated aryl chlorides have been shown to be reactive for copper-catalyzed arylation. Hence, the claim that the previously reported system is effective only with aryl iodides is incorrect.
2) It was claimed that regioselectivity and functional-group tolerance of the previously reported method[1,2] are compromised because of the use of strong bases, and that the method described is compatible with functional groups such as esters, cyanos, aldehydes, and others. However, it has been previously demonstrated that the method is compatible with most of these functional groups.[1,2] Hence, the claim of improved functional group tolerance is incorrect.
3) The prior use of K_3PO_4 base in copper-catalyzed arylations was overlooked, and the reaction conditions that were reported are almost identical to the ones reported earlier.[1] Catalytic CuI/phenanthroline in combination with ArBr in DMF/xylene solvent was shown to be efficient for the arylation of electron-deficient arenes.[1,2] Hence, the claims of developing a new catalytic system are incorrect.

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[1] H.-Q. Do, R. K. M. Khan, O. Daugulis, *J. Am. Chem. Soc.* **2008**, *130*, 15185.

[2] H.-Q. Do, O. Daugulis, *J. Am. Chem. Soc.* **2008**, *130*, 1128.