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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:

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Robust Self-Assembly of Highly Ordered Complex Structures by Controlled Evaporation of Confined Microfluids

*W. M. Czaplik, M. Mayer, A. Jacobi von Wangelin**
Domino Iron Catalysis: Direct Aryl–Alkyl Cross-Coupling

Z. You, A. H. Hoveyda, M. L. Snapper**
Catalytic Enantioselective Silylation of Acyclic and Cyclic Triols and Application to Total Syntheses of Cleroindicins D, F, and C

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*K. M. Gericke, D. I. Chai, N. Bieler, M. Lautens**
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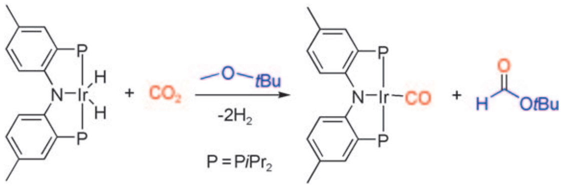
Highlights

Carbon Dioxide Fixation



A quick fix: The recently reported process of “oxygen-atom metathesis”, which is akin to olefin metathesis, may be involved in the activation of carbon dioxide. Nucleophilic attack by the d^8 metal center of an in situ generated Fischer carbene complex on carbon dioxide affords an unstable metallacycle. Elimination of an organic component, *tert*-butyl formate, results in the concurrent formation of an iridium–carbonyl complex.

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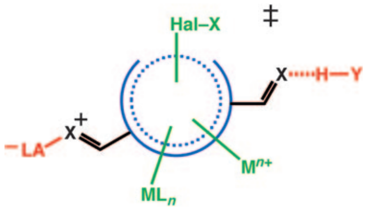
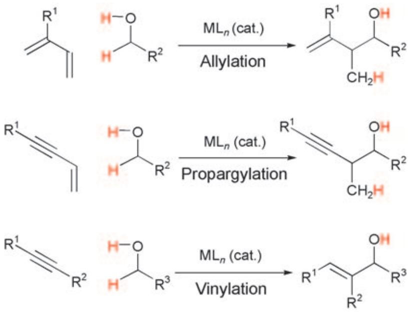
Pericyclic Reactions



Going full circle: Pericyclic reactions can be catalyzed by groups that can bind selectively to a pericyclic transition-state structure (blue) either by interacting directly with rearranging electrons (green) or interacting with substituents (red). The recent success in accelerating six-electron electrocyclizations by using Lewis acids (LAs) is discussed in this Highlight. Future prospects for catalyst design are also emphasized.

Minireviews

C–C Coupling

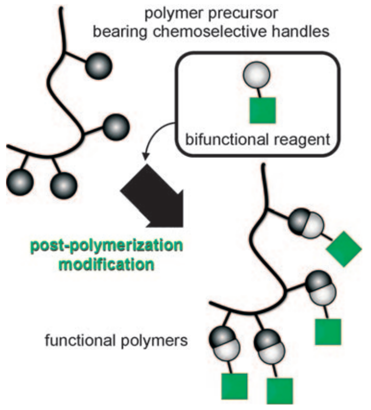


Classical protocols for carbonyl allylation, propargylation, and vinylation typically rely upon the use of preformed allyl metal, allenyl metal, and vinyl metal reagents, respectively, mandating stoichiometric generation of metallic by-products. Through transfer hydrogenative C–C coupling, carbonyl addition may be achieved from the aldehyde or alcohol oxidation level in the absence of stoichiometric organometallic reagents or metallic reductants.

Reviews

Post-Polymerization Modification

More than an afterthought: Functional polymers possessing precisely controlled molecular weight, composition, and architecture remain difficult to synthesize, despite the advent of modern polymerization techniques. This Review surveys different classes of reactive polymer precursors that bear chemoselective side groups and discusses reactions suitable for their post-polymerization modification into functional polymers.



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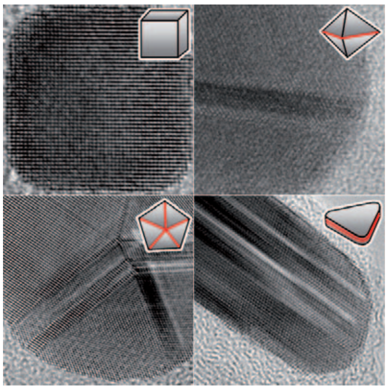
Nanostructures

Y. Xia,* Y. Xiong, B. Lim,
S. E. Skrabalak ______ **60 – 103**

Shape-Controlled Synthesis of Metal Nanocrystals: Simple Chemistry Meets Complex Physics?



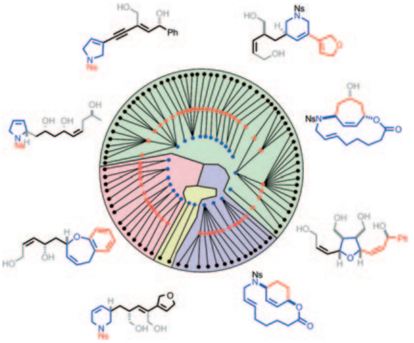
Function follows form: Controlling the shape of nanocrystals may initially seem like a scientific curiosity, but its goal goes far beyond aesthetic appeal. For metal nanocrystals, shape not only determines their intrinsic physical and chemical properties but also their relevance for electronic, magnetic, optical, catalytic, and sensing applications.

Communications

Scaffold Diversity

D. Morton, S. Leach, C. Cordier,
S. Warriner, A. Nelson* ______ **104 – 109**

Synthesis of Natural-Product-Like Molecules with Over Eighty Distinct Scaffolds

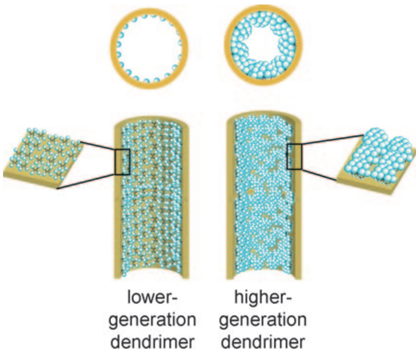


Seeking scaffold diversity: A synthetic approach for the combinatorial variation of the scaffolds of small molecules is described. Using just six basic reaction types, compounds with 84 distinct scaffolds were prepared. The compounds had many natural-product-like structural features including rich stereochemistry, heterocyclic and unsaturated ring systems, and dense functionalization.

Dendritic Nanopores

E. N. Savariar, M. M. Sochat, A. Klaikherd,
S. Thayumanavan* ______ **110 – 114**

Functional Group Density and Recognition in Polymer Nanotubes



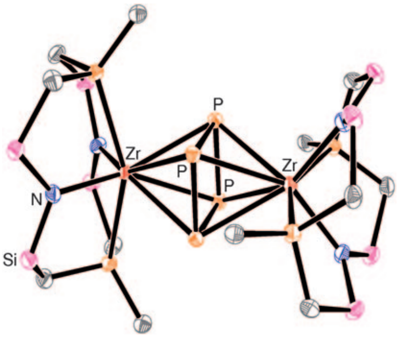
Branching out: The use of polypropylene–imine dendrimers as scaffolds leads to the precise control of the pore size of functionalized nanoporous membranes, which can be used for molecular recognition. The nanopores show a finite transition in generation-dependent molecular discrimination capabilities, which arises not only from the size of the final pores, but also from the functional group density of the dendrimers (see picture).

Activation of P_4

W. W. Seidel, O. T. Summerscales,
B. O. Patrick, M. D. Fryzuk* ______ **115 – 117**

Activation of White Phosphorus by Reduction in the Presence of a Zirconium Diamidodiphosphine Macrocycle: Formation of a Bridging Square-Planar *cyclo*-P_4 Unit

It's hip to be square: A perfectly planar square of phosphorus atoms is prepared by the reduction of $[ZrCl_2\{PhP(CH_2SiMe_2NSiMe_2CH_2)_2PPh\}]$ in the presence of P_4 (see structure). On the basis of the P–P single bond lengths and oxidation state of the Zr centers, this unit is formulated as a $[P_4]^{4-}$ fragment.



Incredibly

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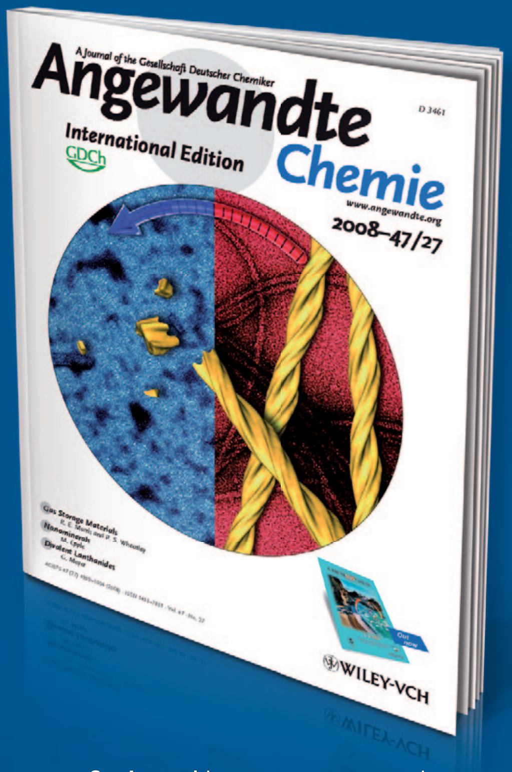

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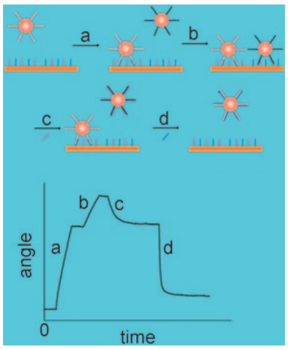
Functionalized Surfaces

Z. Zhang, Q. Cheng, P. Feng* **118 – 122**

Selective Removal of DNA-Labeled Nanoparticles from Planar Substrates by DNA Displacement Reactions

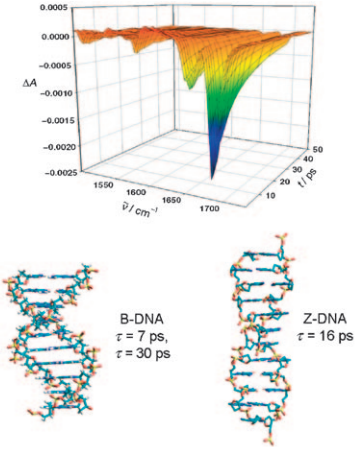


Touching the surface: DNA-labeled gold nanoparticles can be removed from a planar substrate by using a heterogeneous DNA displacement reaction. An advantage of using a planar substrate is that quantitative and kinetic studies of the displacement process could be achieved. This provides a fascinating way to control nanomaterials and to develop novel nanodevices on planar substrates by combining DNA hybridization and displacement reactions.

Time-Resolved Spectroscopy

G. W. Doorley, D. A. McGovern, M. W. George, M. Towrie, A. W. Parker, J. M. Kelly, S. J. Quinn* **123 – 127**

Picosecond Transient Infrared Study of the Ultrafast Deactivation Processes of Electronically Excited B-DNA and Z-DNA Forms of $[\text{poly(dG-dC)}]_2$

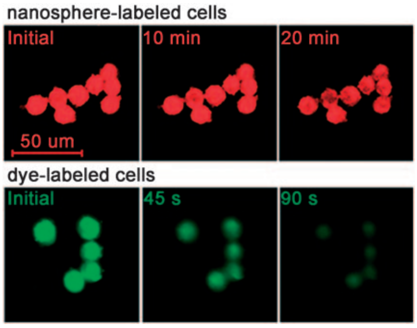


Very fast: UV excitation of the right-handed B form or the left-handed Z form of $[\text{poly(dG-dC)}]_2$ results in transient IR absorption bands that remain long after the $^1\pi\pi^*$ state is predicted to have decayed (see picture). A biexponential decay is observed for B-DNA, which is assigned to the vibrationally excited ground state and the $^1n_N\pi^*$ state. The decay of Z-DNA is dominated by single-exponential decay, which is assigned to an exciplex state.

Silicon Quantum Dots

Y. He, Z.-H. Kang, Q.-S. Li, C. H. A. Tsang, C.-H. Fan,* S.-T. Lee* **128 – 132**

Ultrastable, Highly Fluorescent, and Water-Dispersed Silicon-Based Nanospheres as Cellular Probes



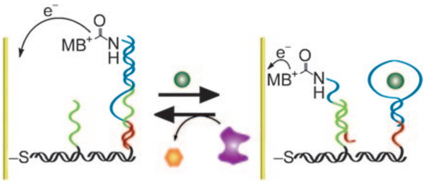
In silico to in vivo: The design strategy for silicon-based fluorescent nanospheres with controllable sizes was based on the results of theoretical calculations. These nanospheres are fully water dispersible, highly photoluminescent, extremely photostable, and suitably biocompatible. Cell imaging results further demonstrate the nanospheres are remarkably efficacious for real-time and long-term cell monitoring (see picture).

Molecular Devices

J. Elbaz, R. Tel-Vered, R. Freeman, H. B. Yildiz, I. Willner* **133 – 137**

Switchable Motion of DNA on Solid Supports

Tracking the changes: The switchable translocation of a nucleic acid strand with a methylene blue (MB$^+$) redox group on a DNA track associated with a surface can be triggered by adenosine monophosphate (AMP, green) and adenosine deaminase (purple, see picture); the latter converts AMP into inosine monophosphate (orange). The motion of the nucleic acid can be followed by the electrochemical, photo-electrochemical, and fluorescence signals.



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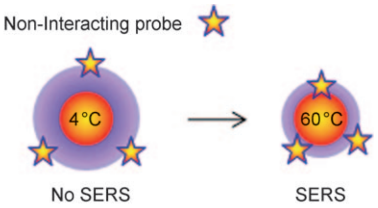
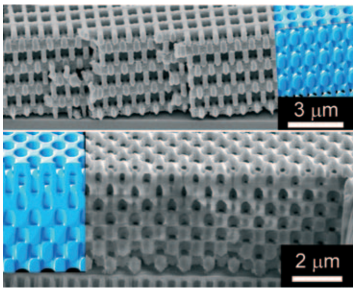
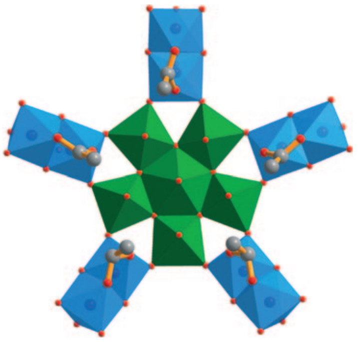
Caught in a trap: Colloids of gold nanoparticles coated with a thermally responsive poly-(*N*-isopropylacrylamide) (pNIPAM) microgel can trap molecules in different ways as a function of temperature (see scheme). The porous pNIPAM shells prevent electromagnetic coupling between metal particles, thus providing highly reproducible surface-enhanced Raman scattering (SERS) signals and intensity.

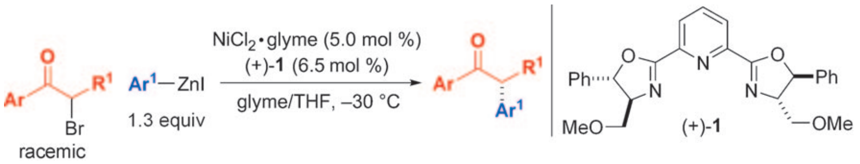


Nitty gritty: A chemically amplified poly-(methylsilsesquioxane) resist based on the acid-catalyzed condensation of silanol end groups was developed for direct fabrication of hybrid 3D microstructures (see picture) by conformal and maskless proximity-field nanopatterning. Fibers, colloidal particles, helical arrays, and photonic crystals were fabricated by varying phase-mask design and exposure conditions.





Magic pentagons: Exploitation of versatile pentagonal units/ligands has previously led to giant molybdenum oxide based curved species, including spherical Keplerates. Similar methodology is now also applicable to the related tungstate scenario (see corresponding basic central pentagonal unit in green).



Nickel box: The first catalytic asymmetric method for cross-coupling arylzinc reagents with α-bromoketones has been developed (see scheme). This stereoconvergent carbon–carbon bond-forming process occurs under unusually mild conditions and without activators, thereby allowing the generation of potentially labile tertiary stereocenters.

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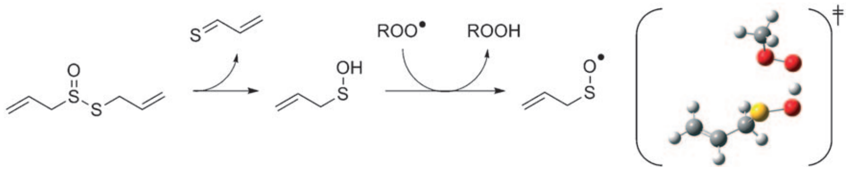
Radical Scavengers

V. Vaidya, K. U. Ingold,
D. A. Pratt* ______ 157 – 160

Garlic: Source of the Ultimate Antioxidants—Sulfenic Acids

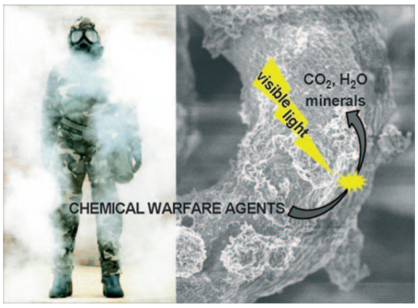


The medicinal properties of garlic, thought to derive at least in part from the antioxidant activity of its sulfur-containing secondary metabolites, have been recognized for hundreds of years. The ability of garlic to scavenge peroxyl radicals can be accounted for in terms of the action of transient sulfenic acids, which are predicted to react by diffusion-controlled five-center proton-coupled electron transfer (see scheme and transition state).

Photocatalytic Decontamination

M. Grandcolas, A. Louvet, N. Keller,
V. Keller* ______ 161 – 164

Layer-by-Layer Deposited Titanate-Based Nanotubes for Solar Photocatalytic Removal of Chemical Warfare Agents from Textiles

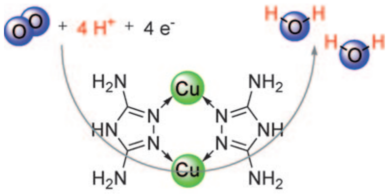


Self-decontaminating textiles were prepared using layer-by-layer deposition of highly active WO_3/titanate nanotubes for photocatalytic removal of sulfide and organophosphonate simulants and authentic chemical warfare agents by using solar light.

Electrocatalysis

M. S. Thorum, J. Yadav,
A. A. Gewirth* ______ 165 – 167

Oxygen Reduction Activity of a Copper Complex of 3,5-Diamino-1,2,4-triazole Supported on Carbon Black

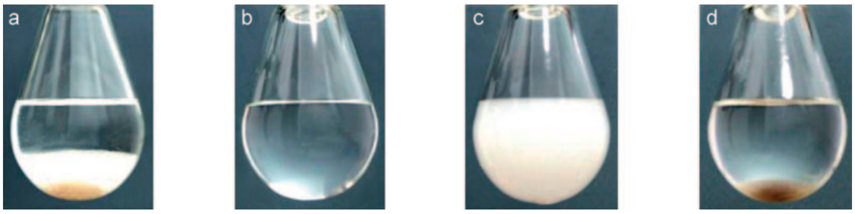


Reduction deduction: Precipitation of an insoluble copper triazole complex onto a carbon black support leads to the formation of an efficient catalyst for the four-electron reduction of O_2 to H_2O. The oxygen-reduction activity is reported over a wide pH range from 1 to 13 and the onset of the reaction occurs at potentials as high as 0.86 V. Ex situ magnetic susceptibility measurements demonstrate the presence of multicopper sites.

Catalysis

Y. Leng, J. Wang,* D.-R. Zhu, X.-Q. Ren,
H.-Q. Ge, L. Shen ______ 168 – 171

Heteropolyanion-Based Ionic Liquids: Reaction-Induced Self-Separation Catalysts for Esterification



It comes out in the wash: In the esterification of citric acid with *n*-butanol, heteropolyanion-based ionic liquid (IL) catalysts show high catalytic activity, self-separation, and easy reuse. The good solubility in reactants, nonmiscibility with ester product, and high melting point of the IL catalysts enable the reaction-induced switching from homogeneous (b in the picture) to heterogeneous (c) with subsequent precipitation of the catalyst (d).

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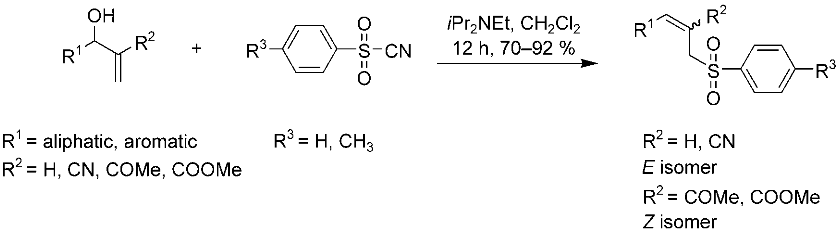
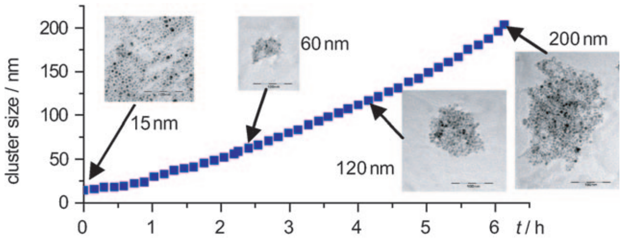
Synthetic Methods



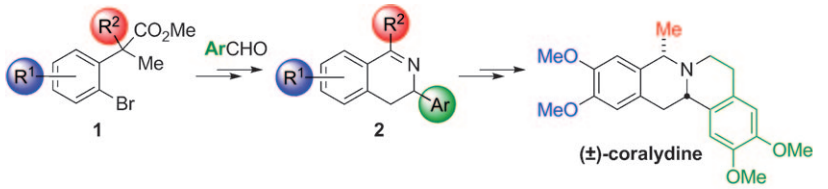
An efficient and practical protocol for the highly selective preparation of substituted allyl sulfones has been developed. Arenesulfonyl cyanides, Baylis–Hillman adducts, and simple allylic alcohols give an unforeseen outcome (see scheme).

Nanoparticle Clusters



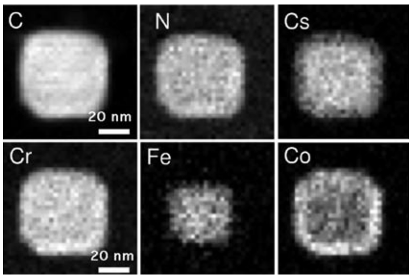
Size-controlled clusters: Clusters of preformed 15 nm oleic acid coated superparamagnetic iron oxide nanoparticles were prepared through partially destabilizing suspensions of the dispersed nanoparticles with CN-modified silica. This effect induced gradual formation of monodisperse, superparamagnetic clusters by competition between the solid phases for the surfactant. The cluster size can be controlled within the range 15–200 nm as the growth process can be stopped and restarted.

Synthetic Methods



Thanks to C–H activation: 3-Aryl-3,4-dihydroisoquinolines (**2**) are synthesized from bromobenzenes (**1**) by a sequence comprising a C(sp^3)–H activation, a Curtius rearrangement, and a tandem electrocyclic ring-opening/6π electrocyclization. This method is applied to the synthesis of various isoquinoline-containing molecules, including the tetrahydroprotoberberine alkaloid coralydine.

Nanoparticles



Simple epitaxial growth of a cyano-bridged coordination network on different core particles can lead to core–multishell nanoparticles. Shell growth is controlled on the nanometer scale and can be repeated with different metal ions. Particles can be prepared with a distinct composition in each layer (see images), and synergy is observed between their magnetic properties.

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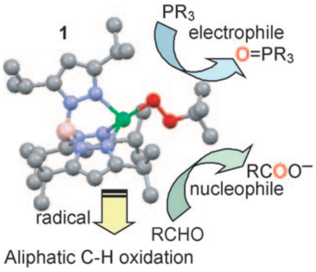
Peroxonickel Complexes

S. Hikichi,* H. Okuda, Y. Ohzu,
M. Akita ―――――――― 188 – 191

Structural Characterization and Oxidation Activity of a Nickel(II) Alkylperoxo Complex

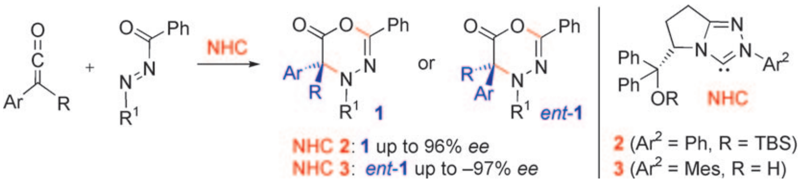


Substrate-dependent reactivity: The nickel(II) alkylperoxo complex **1** (see structure), obtained by the dehydrative condensation of the nickel(II) hydroxo complex with *tert*-butylhydroperoxide has a unique structure; the coordination mode of the O–O moiety is an intermediate between η^1 and η^2. Compound **1** exhibits substrate-dependent reactivity toward aliphatic C–H, phosphines, carbon monoxide, and aldehydes.

Asymmetric Catalysis

X.-L. Huang, L. He, P.-L. Shao,
S. Ye* ―――――――― 192 – 195

[4+2] Cycloaddition of Ketenes with *N*-Benzoyldiazenes Catalyzed by N-Heterocyclic Carbenes

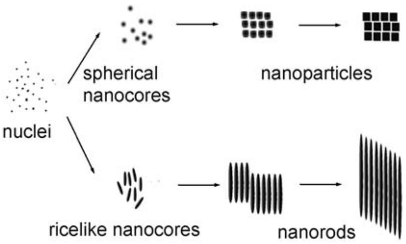


Enantioselectivity switch: A catalytic enantioselective [4+2] cycloaddition reaction of alkylarylketenes with *N*-aryl-*N*′-benzoyldiazenes or *N*,*N*′-dibenzoyldiazenes to give 1,3,4-oxadiazin-6-ones **1** was developed by employing N-heterocyclic carbene (NHC) catalysts. The enantioselectivities could be switched for most reactions by changing the substituents on the NHC catalyst. TBS = *tert*-butyldimethylsilyl, Mes = 2,4,6-trimethylphenyl.

Crystal Growth

T. Xie, S. Li, Q. Peng, Y. D. Li* 196 – 200

Monodisperse BaF$_2$ Nanocrystals: Phases, Size Transitions, and Self-Assembly

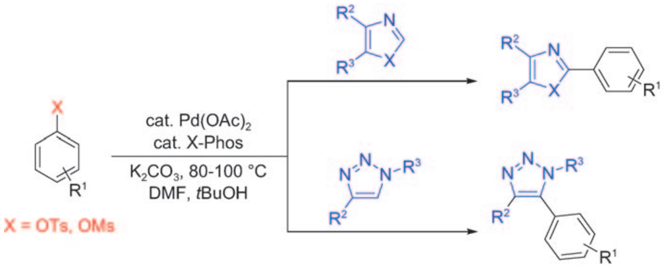


BaF$_2$fled no more: Monodisperse cubic- and orthorhombic-phase BaF$_2$ nanocrystals were formed readily by the liquid–solid–solution approach. Nucleus growth of BaF$_2$ occurs under kinetic control, whereby their size and morphology depend greatly on the ripening time and concentration of surfactants (see scheme). The phase of the BaF$_2$ crystals is under thermodynamic control.

C–H Bond Functionalization

L. Ackermann,* A. Althammer,
S. Fenner ―――――――― 201 – 204

Palladium-Catalyzed Direct Arylations of Heteroarenes with Tosylates and Mesylates



A toss up: A highly active palladium complex enabled the first direct arylation of heteroarenes through C–H bond functionalization using tosylates or mesylates as electrophiles with ample scope.

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Synthetic Methods

G. Manolikakes, P. Knochel* — **205 – 209**

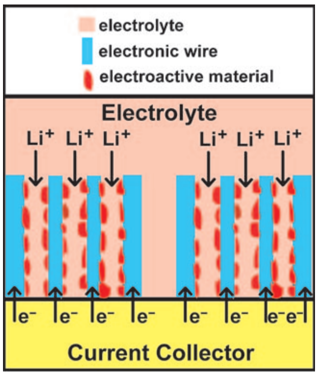
Radical Catalysis of Kumada Cross-Coupling Reactions Using Functionalized Grignard Reagents

Palladium, radically different: A wide range of polyfunctional aryl- and heteroarylmagnesium reagents undergo fast Kumada cross-couplings (see scheme) with functionalized aryl bromides in the presence of a palladium catalyst and an alkyl iodide as additive. These reactions proceed by a radical pathway.

Nanostructured Electrodes

Y.-S. Hu,* X. Liu, J.-O. Müller, R. Schlögl, J. Maier,* D. S. Su* ——— **210 – 214**

Synthesis and Electrode Performance of Nanostructured V_2O_5 by Using a Carbon Tube-in-Tube as a Nanoreactor and an Efficient Mixed-Conducting Network



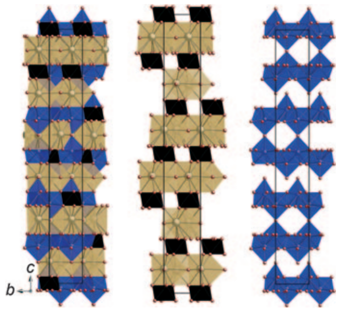
Totally tubular electrodes: A new design is proposed for nanostructured electrodes for high-performance lithium batteries (see picture) based on the use of carbon tube-in-tube (CTIT) as both a nanoreactor and an efficient ion- and electron-conducting network. A V_2O_5/CTIT nanocomposite electrode is prepared to demonstrate this concept. The resulting materials exhibit a significant improved lithium-storage performance.

Solid-State Chemistry

S. J. Mugavero, III, M. D. Smith, W.-S. Yoon, H.-C. zur Loye* —— **215 – 218**

$Nd_2K_2IrO_7$ and $Sm_2K_2IrO_7$: Iridium(VI) Oxides Prepared under Ambient Pressure

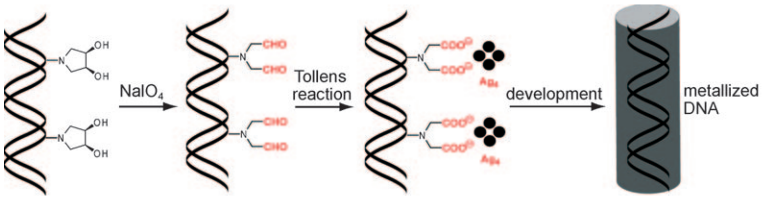
No pressure: The most-oxidized iridium oxides known to date are prepared in a hydroxide flux under normal pressure. They contain iridium centers exclusively in the +VI oxidation state and are characterized crystallographically. The picture shows the structure of the $Ln_2K_2IrO_7$ ($Ln = Nd, Sm$) and its structural components: IrO_6 octahedra (black), KO_{10} polyhedra (beige), LnO_{10} polyhedra (blue).



Nanotechnology

C. T. Wirges, J. Timper, M. Fischler, A. S. Sologubenko, J. Mayer, U. Simon, T. Carell* ——— **219 – 223**

Controlled Nucleation of DNA Metallization



Silver-plated DNA: The deposit of a thin metal layer on biomolecules, such as DNA, requires the formation of small, "magic-sized" metal nuclei. Through the careful design of a reducing chemical functionality in the form of a dialdehyde, the nucleation process and thus the metallization step can be controlled (see scheme).

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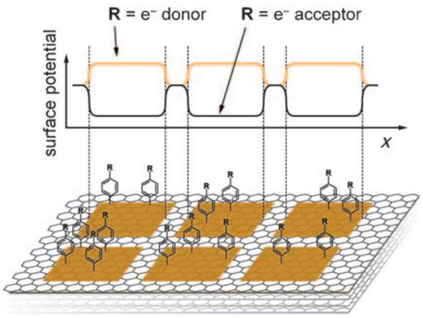
Surface Chemistry

Beyond the age of silicon: A combination of radical chemistry under standard conditions and clean-room lithography can alter the electronic structure of graphene layers permanently through covalent chemical functionalization. The potential change follows the Hammett correlation. This simple method is a promising approach for graphene-based electronics.



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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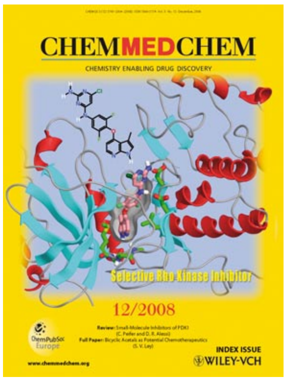

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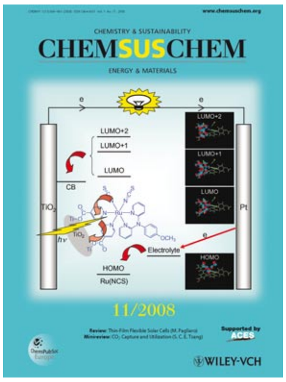

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