Screening methodologies ...





... can greatly accelerate the discovery of new chemical reactions. In their Communication on page 4361 ff., F. Glorius et al. describe a conceptually novel mechanism-based screening approach using luminescence spectroscopy to directly investigate the key quenching step in photocatalysis. As illustrated in the cover image, various photocatalysts and potential substrates undergo "speed dating" with the observation of quenching signifying a promising combination that can be applied in new light-promoted reactions.

Sustainable Polymers

In their Communication on page 4188 ff., E. Y.-X. Chen et al. report the organocatalytic polymerization of γ-butyrolactone to give a high-molecularweight metal-free polyester with complete recyclability.





Photovoltaic Devices

In their Communication on page 4280 ff., Z. Lin et al. report a strategy for integrating NaYF₄:Yb/ Er upconversion nanoparticles as a mesoporous electrode into organolead halide perovskite solar cells.

C-H Activation

In their Communication on page 4308 ff., C.-H. Cheng et al. describe the diastereoselective synthesis of pentacyclic fluorenones from secondary amides and bicyclic alkenes by cobalt-catalyzed C-H activation.



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Spotlight on Angewandte's Sister Journals

4120 - 4123



Zhenfeng Xi ______ 4124



"My favorite food is noodles.

My favorite piece of music is Going Home (Kenny G) ..."

This and more about Zhenfeng Xi can be found on page 4124.



J. S. Siegel



P. J. Stang



M. Antonietti



S. Schlemmer

News

Friendship Award:
J. S. Siegel and P. J. Stang ______ 4125

International Science and Technology
Cooperation Award: P. J. Stang _____ 4125

Gay-Lussac Humboldt Prize: M. Antonietti and S. Schlemmer _____ 4125

Books

Never Lose Your Nerve Alan J. Heeger reviewed by G. Wegner* ____



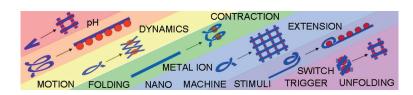


Reviews

Molecular Motion

M. Barboiu, A.-M. Stadler, J.-M. Lehn* ______ 4130 – 4154

Controlled Folding, Motional, and Constitutional Dynamic Processes of Polyheterocyclic Molecular Strands



This Review discusses the structural and functional features of polyheterocyclic ligand strands that display designed specific shapes, undergo shape changes on binding of metal cations, and perform various types of pH-responsive motions induced by metal ions.

Contiguous Quaternary C Atoms

M. Büschleb, S. Dorich, S. Hanessian,* D. Tao, K. B. Schenthal,

L. E. Overman* _____ 4156 – 4186



Synthetic Strategies toward Natural Products Containing Contiguous Stereogenic Quaternary Carbon Atoms Raising the bar: The impressive achievements in the total synthesis of complex natural products containing two or three stereogenic contiguous quaternary carbon centers since 1953 are showcased by many creative strategies. The height of the "synthesis bar" can now be raised to consider hitherto unconquered molecules with multiple contiguous quaternary carbon atoms, each residing on a stereogenic carbon atom.

Communications



Sustainable Polymers

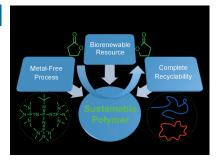
M. Hong, E. Y.-X. Chen* ____ 4188 - 4193



Towards Truly Sustainable Polymers: A Metal-Free Recyclable Polyester from Biorenewable Non-Strained γ -Butyrolactone



Frontispiece



Recyclable and renewable: The fast organopolymerization of the biorenewable non-strained γ -butyrolactone has led to a high-molecular-weight metal-free polyester with complete recyclability. The monomer has been long believed to be a non-polymerizable monomer because of its stable five-membered ring structure.

For the USA and Canada:

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electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.







Let it go... The two major limitations for theranostics of the *p*-hydroxyphenacyl (pHP) phototrigger were overcome by incorporating a benzothiazole appendage to enable rapid excited-state intramolecular proton transfer (ESIPT; see picture).

The ESIPT effect had two key advantages: It assisted the deprotonation of pHP group for faster release of the anticancer drug chlorambucil and led to a fluorescence color change upon photorelease.

Photoregulated Drug Release

S. Barman, S. K. Mukhopadhyay,

S. Biswas, S. Nandi, M. Gangopadhyay,

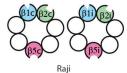
S. Dey,* A. Anoop,*

N. D. P. Singh* _____ 4194 - 4198

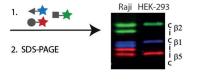
A p-Hydroxyphenacyl-Benzothiazole-Chlorambucil Conjugate as a Real-Time-Monitoring Drug-Delivery System Assisted by Excited-State Intramolecular Proton Transfer







(immune cell)



inhibitors for each subunit were developed. Specific inhibition of the immunoproteasome subunits $\beta5i$ and $\beta1i$ proved to be cytotoxic to primary cells from acute lymphocytic leukemia patients.

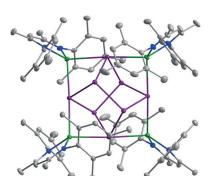
Activity-Based Protein Profiling



A Set of Activity-Based Probes to Visualize Human (Immuno)proteasome Activities



A cocktail of activity-based probes enables the visualization and relative quantification of the six catalytically active subunits of the constitutive proteasome and the immunoproteasome. Proteasome inhibitors were thus characterized, and specific



Reduction reactions of distibines Sb_2R_4 (R=Me, Et) with monovalent magnesium complexes $[(L^{1,2}Mg)_2]$ yielded the first tetraanionic polystibides $[(L^{1,2}Mg)_4Sb_8]$ ($L^1=HC[C(Me)N(2,4,6\cdot Me_3C_6H_2)]_2$, $L^2=HC[C(Me)N(2,6\cdot iPr_2C_6H_3)]_2$), in which the central Sb_8 cores adopt realgar-type structures. Atom colors: Mg=green; Sb=purple; N=blue; C=gray.

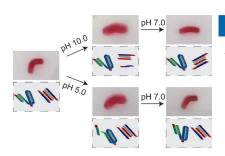
Polystibides

C. Ganesamoorthy, C. Wölper,
A. S. Nizovtsev, S. Schulz* 4204 – 4209

Synthesis and Structural Characterization of Magnesium-Substituted Polystibides $[(LMg)_4Sb_8] \label{eq:synthesis} % \begin{substituted} \begin{$



An acrylamide–DNA hydrogel of a defined shape has been synthesized by crosslinking the polymer chains with two different pH-responsive oligonucleotide units. The hydrogel was transformed into a soft, shapeless state by a pH-induced selective dissociation of one of the crosslinker types, while the second crosslinking unit was retained as internal memory.



DNA Nanostructures



Y. Hu, W. Guo, J. S. Kahn, M. A. Aleman-Garcia, I. Willner* ______ **4210–4214**

A Shape-Memory DNA-Based Hydrogel Exhibiting Two Internal Memories





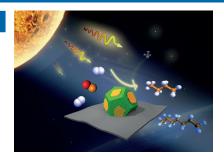




Photocatalysis



Oxide-Modified Nickel Photocatalysts for the Production of Hydrocarbons in Visible Light



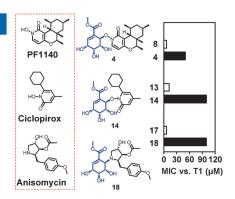
Production of hydrocarbons: Oxide-decorated metal nickel nanoparticle catalysts were prepared and used for the photocatalytic hydrogenation of carbon monoxide to C₂₊ hydrocarbons in visible light. The work highlights the possibility of using solar energy to produce fuels and chemicals under mild reaction conditions.

Natural Products

L. Du, J. You, K. M. Nicholas, R. H. Cichewicz* ______ **4220 – 4225**



Chemoreactive Natural Products that Afford Resistance Against Disparate Antibiotics and Toxins



Electrophilic warheads: Fungus-derived shikimate analogues, pericoxide and pericosine A (see picture; blue), have been identified as archetypal chemoreactive natural products that neutralize the antagonistic properties of chemically diverse synthetic and naturally derived antifungal agents and toxins (see picture; left).



Biomaterials

B. G. Cooper, R. C. Stewart, D. Burstein, B. D. Snyder,

M. W. Grinstaff* _____ 4226-4230



A Tissue-Penetrating Double Network Restores the Mechanical Properties of Degenerated Articular Cartilage



Recovery of strength, wear resistance

Double network (in situ synthesis)



Bring in the reinforcements: Softened and wear-prone articular cartilage is reinforced by a semi-natural—semi-synthetic interpenetrating polymer network. In situ photopolymerization of biomimetic mon-

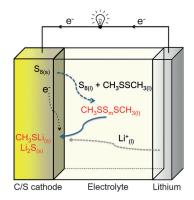
omers within the tissue increases cartilage strength and wear-resistance. This biomaterials-based approach may hold promise for treating early stage osteoarthritis.

Batteries

S. Chen, F. Dai, M. L. Gordin, Z. Yu, Y. Gao, J. Song, D. Wang* _ **4231 – 4235**



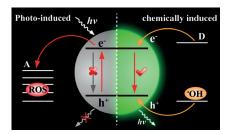
Functional Organosulfide Electrolyte Promotes an Alternate Reaction Pathway to Achieve High Performance in Lithium— Sulfur Batteries



Finding the right electrolyte: Dimethyl disulfide (DMDS) was reported as a functional co-solvent for Li-S electrolytes. DMDS enabled an alternative discharge pathway for sulfur cathodes by formation and subsequent reduction of dimethyl polysulfide (DMPS) intermediates, showing a much higher capacity and more stable cycling performance than that of conventional Li-S cells.

Contents





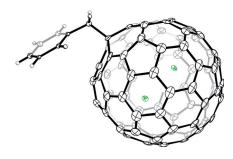
HO' selective: A novel quantum dot (QD) based turn-on luminescent probe for the specific detection of hydroxyl radicals was designed and used for monitoring the endogenous release of such species in living cells. Metal citrate complexes on the surfaces of the QDs play a crucial role as electron donors. Importantly, this luminescent probe does not respond to other reactive oxygen species (ROS).

Luminescent Probes

W. J. Zhou, Y. Q. Cao, D. D. Sui, 4236-4241

Turn-On Luminescent Probes for the Real-Time Monitoring of Endogenous Hydroxyl Radicals in Living Cells





A stable fullerene radical $La_2@I_h-C_{80}(C_7H_7)$ was synthesized and fully characterized. The stability of the radical is attributed to the localization of the unpaired electron inside the cage, as suggested by EPR spectroscopy and DFT calculations. Metal-metal bonding is indicated by the La-La distance, which is consistent with the calculated distance, and the localization of the SOMO on the La2 unit.

Fullerene Radicals

L. Bao, M. Chen, C. Pan, T. Yamaguchi, T. Kato, M. M. Olmstead, A. L. Balch, T. Akasaka, X. Lu* _____ 4242 - 4246

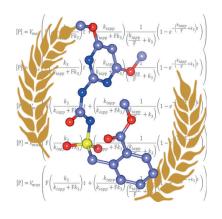
Crystallographic Evidence for Direct



Metal-Metal Bonding in a Stable Open-Shell $La_2@I_h$ - C_{80} Derivative

How AHAS-inhibiting herbicides work:

Acetohydroxyacid synthase (AHAS) inhibitors, such as bensulfuron methyl (see picture), are successful commercial herbicides; however, their mechanism of inhibition is poorly understood. To address this issue, a new equation is proposed that both accounts for the accumulative and reversible inhibition of AHAS and explains all previous experimental data. Atom colors: C = blue; N = dark blue; O = red; S = yellow.



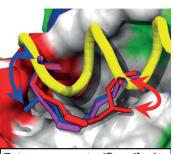
Enzyme Kinetics

T. Lonhienne,* A. Nouwens, C. M. Williams, J. A. Fraser, Y. Lee, N. P. West, L. W. Guddat* _ 4247 - 4251

Commercial Herbicides Can Trigger the Oxidative Inactivation of Acetohydroxyacid Synthase



Branching out: γ-Branched stapling amino acids were synthesized and incorporated into peptides to produce highaffinity inhibitors of the estrogen receptor/steroid receptor coactivator interaction. Some branched stapled peptides were more effective than the unfunctionalized peptide. The influence of 1,5-interactions on peptide conformation was analyzed by circular dichroism, X-ray crystallography, and molecular dynamics.



Estrogen receptor/Coactivator IC₅₀: 89 nM 390 nM 1800 nM

Peptidomimetics



T. E. Speltz, S. W. Fanning, C. G. Mayne, C. Fowler, E. Tajkhorshid, G. L. Greene, T. W. Moore* _____ 4252 – 4255

Stapled Peptides with γ-Methylated Hydrocarbon Chains for the Estrogen

Receptor/Coactivator Interaction



Inside Cover



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Anticancer Agents

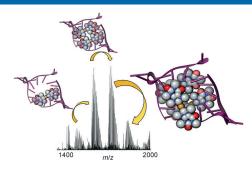
C. Bazzicalupi, M. Ferraroni,* F. Papi,

L. Massai, B. Bertrand, L. Messori,

P. Gratteri,* A. Casini _____ 4256 - 4259



Determinants for Tight and Selective Binding of a Medicinal Dicarbene Gold(I) Complex to a Telomeric DNA G-Quadruplex: a Joint ESI MS and XRD Investigation



Ready for takeoff: A crystal structure analysis of the adduct formed between [Au(9-methylcaffein-8-ylidene)₂]⁺ and Tel 23 DNA G-quadruplex is presented. In the

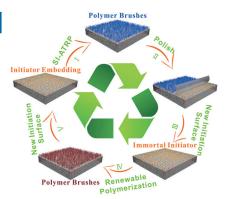
adduct, Tel 23 maintains a characteristic propeller conformation, while binding three gold(I) dicarbene moieties at two distinct sites.

Surface Modifications

T. Du, B. Li, X. Wang, B. Yu, X. Pei, W. T. S. Huck, F. Zhou* _____ 4260 – 4264



Bio-Inspired Renewable Surface-Initiated Polymerization from Permanently Embedded Initiators



A simple and robust method is reported to repeatedly modify surfaces with polymer brushes through SI-ATRP, based on an initiator-embedded polystyrene sheet. This method outpaces traditional surface grafting technologies owing to unlimited grafting cycles, and it can be combined with carving, micromachining, and hot embossing, and allows stereoselective polymer grafting and metal deposition.

Superhydrophobic Surfaces

J. Liu, H. Guo, B. Zhang, S. Qiao, M. Shao, X. Zhang, X. Feng, Q. Li,* Y. Song, L. Jiang, J. Wang* _______ 4265 – 4269



Guided Self-Propelled Leaping of Droplets on a Micro-Anisotropic Superhydrophobic Surface



Jumping Jack Flash: Water microdroplets can coalesce and leap over the surface spontaneously along a prescribed direction upon introducing anisotropic micropatterns onto superhydrophobic surfaces.

These surfaces offer efficient self-powered and relatively long-distance transport of microdroplets by "relay" coalescence-induced leaping and effective self-sustained microcarriers.

Boronic Ester Reactions



Y. Wang, A. Noble, E. L. Myers, V. K. Aggarwal* ______ 4270-4274



Enantiospecific Alkynylation of Alkylboronic Esters



1) LDA 2) I₂ / MeOH



or LDA

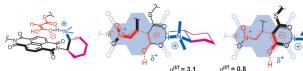


Enantiospecific alkynylation: Enantioenriched secondary and tertiary alkyl pinacolboronic esters undergo enantiospecific deborylative alkynylation through a Zwei-

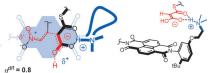
fel-type alkenylation followed by a 1,2elimination reaction to give alkynes in high yield and essentially complete enantiospecificity.







Served on a platter: Simple, compact, and precisely sculpted Leonard turns are introduced to firmly and reliably place reactions on aromatic surfaces, minimizing entropic costs to maximize enthalpic gains. The significant change in selectivity



 $(\eta^{d/f})$ from less desirable decarboxylation with loose turns (right) to more relevant enolate addition pathways on π -acidic surfaces with rigidified Leonard turns (left) demonstrates the power of this concept.

Preorganization

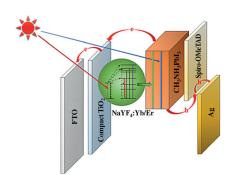


Y. Cotelle, S. Benz, A.-J. Avestro, T. R. Ward, N. Sakai,

S. Matile* _____ 4275 – 4279

Anion- π Catalysis of Enolate Chemistry: Rigidified Leonard Turns as a General Motif to Run Reactions on Aromatic Surfaces





A strategy for integrating NaYF₄:Yb/Er upconversion nanoparticles as a mesoporous electrode into CH₃NH₃PbI₃ perovskite solar cells makes it possible to operate the cells with near-infrared light. The in situ integration of upconversion materials as functional components in perovskite solar cells offers flexibility for engineering the device architecture and broadening the use of solar radiation.

Photovoltaic Devices



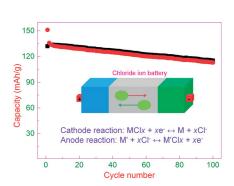
M. He, X. Pang, X. Liu, B. Jiang, Y. He, H. Snaith, Z. Lin* ______ 4280 – 4284

Monodisperse Dual-Functional Upconversion Nanoparticles Enabled Near-Infrared Organolead Halide Perovskite Solar Cells



Inside Back Cover





Chloride shuttle: A rechargeable chloride ion battery is based on the reversible transfer of chloride ions between a VOCl cathode and lithium anode. A reversible capacity of 113 mAh g⁻¹ can be retained after 100 cycles even at a high current density rating of 2 C. Key: ● Cl⁻, ■ MClx (cathode), ■ M' (anode), → discharging, ← charging.

Rechargeable Batteries

P. Gao, M. A. Reddy, X. Mu, T. Diemant,
L. Zhang, Z. Zhao-Karger,
V. S. K. Chakravadhanula, O. Clemens,
R. J. Behm, M. Fichtner* — 4285 – 4290

VOCI as a Cathode for Rechargeable Chloride Ion Batteries



Resistance is futile: The natural product aspergillomarasmine A (AMA) is a potent inhibitor of metallo- β -lactamase-1, which mediates resistance to β -lactam antibiotics. The presented total synthesis of AMA allowed a reassignment of its stereo-

chemical configuration. The synthetic route is amenable to the efficient preparation of analogues for the development of potent and selective metallo- β -lactamase inhibitors.

Antibiotics

D. Liao, S. Yang, J. Wang, J. Zhang,B. Hong, F. Wu, X. Lei* ____ 4291 – 4295

Total Synthesis and Structural Reassignment of Aspergillomarasmine A



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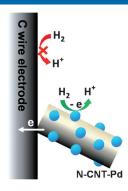
Electrochemistry

X. Li, C. Batchelor-McAuley, S. A. I. Whitby, K. Tschulik, L. Shao, __ 4296 - 4299 R. G. Compton* _



Single Nanoparticle Voltammetry: Contact Modulation of the Mediated Current

Catalysis at the nanoscale: The cyclic voltammetric responses of individual palladium-coated nitrogen-doped multiwalled carbon nanotubes (N-CNT-Pd; see picture) were studied. The nanoparticles acted as individual nanoelectrodes that catalyzed the hydrogen-oxidation reaction.

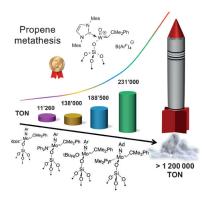


Supported Catalysts

M. Pucino, V. Mougel, R. Schowner, A. Fedorov, M. R. Buchmeiser,* C. Copéret* _____ 4300 - 4302



Cationic Silica-Supported N-Heterocyclic Carbene Tungsten Oxo Alkylidene Sites: Highly Active and Stable Catalysts for Olefin Metathesis



Like a rocket: A well-defined silica-supported cationic N-heterocyclic carbene tungsten oxo alkylidene catalyst $(B(Ar^F)_4 = B(3,5-(CF_3)_2C_6H_3)_4$, Mes = mesityl) was synthesized and fully characterized by elemental analysis, infrared spectroscopy, and solid-state NMR spectroscopy. The catalyst demonstrated very high activity for the metathesis of olefins.

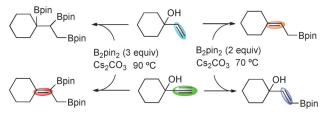
Borylation



N. Miralles, R. Alam, K. J. Szabó,* E. Fernández* ______ 4303 – 4307



Transition-Metal-Free Borylation of Allylic and Propargylic Alcohols



A transition-metal-free allylic borylation of tertiary allylic alcohols provides access to new allylic boronates. The reactions were carried out in the presence of 15 mol% of Cs₂CO₃ and MeOH to promote the Lewis

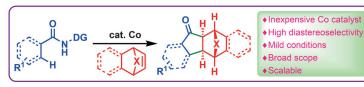
acid-base adduct formation [Hbase]+[MeO-B₂pin₂]-, which may be responsible for generating unprecedented 1,2,3polyborated products.

C-H Activation

P. Gandeepan, P. Rajamalli, C.-H. Cheng* _____ 4308 - 4311



Diastereoselective [3+2] Annulation of Aromatic/Vinylic Amides with Bicyclic Alkenes through Cobalt-Catalyzed C-H Activation and Intramolecular **Nucleophilic Addition**



[3+2] instead of [4+2] or [4+1]: The diastereoselective [3+2] annulation of secondary amides with alkenes proceeds by cobalt-catalyzed C-H activation and intramolecular nucleophilic addition to

the amide functional group under mild conditions. Mechanistic studies suggest that the C-H bond cleavage is the ratelimiting step.



Back Cover

Contents



network of cooperative hydrogen bonds

J. M. Saá* _____ 4312 - 4316

Organocatalysis by Networks of

Caught in the net: The standard roles that the actors (nucleophile, electrophile, and catalyst) perform during the catalytic act in the arena of bifunctional catalysis were switched in the search for bioinspired organocatalysts. It was thus found that

the network of hydrogen bonds provided by salan derivatives catalyzed the Mannich reaction of arylideneureas with acetoacetates in an enantioselective, biomimetic manner (see scheme).

up to 95% ee

Cooperative Hydrogen Bonds: Enantioselective Direct Mannich Addition to Preformed Arylideneureas

Asymmetric Catalysis

V. J. Lillo, J. Mansilla,

Me
$$R'$$
 R''
 $NHAr_F$
 $NHAR_$

Pd^{II}-catalyzed arylation of γ-C(sp³)—H bonds of aliphatic acid-derived amides was developed by using quinoline-based ligands. Various γ-aryl- α -amino acids were

Catalysis combo: A highly selective mul-

ticomponent carbonyl allylation reaction

of 1,3-butadienes, aryldiazonium tetra-

fluoroborates, and aldehydes has been

established under combined palladium

prepared from natural amino acids using this method. The influence of ligand structure on reactivity was also systematically investigated.

C-H Activation

S. Li, R.-Y. Zhu, K.-J. Xiao, J.-Q. Yu* _______ 4317 – 4321

Ligand-Enabled Arylation of γ -C-H Bonds





acetate and chiral anion phase-transfer catalysis. The protocol leads to the assembly of chiral Z-configured homoallylic alcohols in high yields and with excellent levels of enantioselectivity.

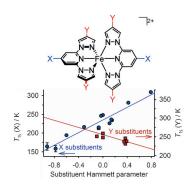
Asymmetric Catalysis

Z.-L. Tao, A. Adili, H.-C. Shen, Z.-Y. Han, L.-Z. Gong* ______ 4322 – 4326

Catalytic Enantioselective Assembly of Homoallylic Alcohols from Dienes, Aryldiazonium Salts, and Aldehydes



Highs and lows: The low-spin state of the complex shown is stabilized by electron-withdrawing pyridyl "X" substituents, but also by electron-donating pyrazolyl "Y" substituents. DFT calculations reproduce these results, which arise from competing influences of pyridyl and pyrazolyl ligand substituents on Fe–L σ and π bonding.



Spin State

L. J. Kershaw Cook, R. Kulmaczewski, R. Mohammed, S. Dudley, S. A. Barrett, M. A. Little, R. J. Deeth,*

M. A. Halcrow* _____ 4327 – 4331

A Unified Treatment of the Relationship Between Ligand Substituents and Spin State in a Family of Iron(II) Complexes



O

4115





Marine Alkaloids

J. S. Clark,* C. Xu _____ 4332 - 4335



Total Synthesis of (-)-Nakadomarin A

The later the better: A highly efficient 12step synthesis of (—)-nakadomarin A is reported. The key tetracyclic ketone intermediate was constructed from a simple enyne in seven steps. As the furan is introduced at a later synthetic stage, this intermediate may have potential in the syntheses of related marine alkaloids such as manzamine A and ircinal A.

FLP Catalysis

S. Tamke, Z.-W. Qu, N. A. Sitte, U. Flörke, S. Grimme, J. Paradies 4336 – 4339



Frustrated Lewis Pair-Catalyzed Cycloisomerization of 1,5-Enynes via a 5-endo-dig Cyclization/Protodeborylation Sequence **Cycloisomerization without a metal**: The first FLP-catalyzed C—C bond forming reaction is described as proceeding through a cycloisomerization/protode-borylation sequence. The reaction mechanism is supported by X-ray crystal structure analysis of intermediates, kinetic experiments, and by quantum-mechanical calculations.

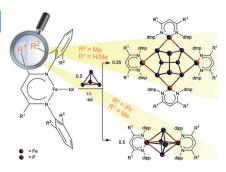
P₄ Activation



F. Spitzer, C. Graßl, G. Balázs, E. M. Zolnhofer, K. Meyer, M. Scheer* ______ 4340 – 4344



Influence of the nacnac Ligand in Iron(I)-Mediated P₄ Transformations



Depending on the size of the substituents of the N,N'-diarylated β -diketiminato ligands, iron(I) complexes activate white phosphorus in different ways. Small substituents result in dimerization with formation of a realgar-like P_8 ligand at the center of a tetranuclear complex; larger substituents lead to planarization in dinuclear $cyclo-P_4$ complexes.

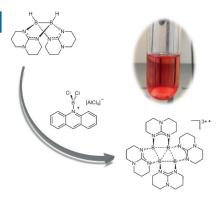
Boron Compounds

S. Litters, E. Kaifer, H.-J. Himmel*

___ 4345 – 4347



A Radical Tricationic Rhomboid Tetraborane(4) with Four-Center, Five-Electron Bonding

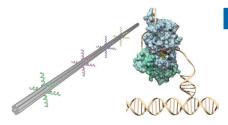


Share and share alike: Reaction of the doubly base-stabilized diborane(4) [HB-(hpp)]₂ with the strong hydride abstraction reagent [(acridine)BCl₂][AlCl₄] leads to the unprecedented red-colored tetraborane(4) $[B_4(hpp)_4]^{3+*}$ with a rhomboid B_4 skeleton and four-center, five-electron bonding.





In nature, relaxase proteins are involved in the conjugative transfer of plasmids between bacteria. Here it is shown that their specificity for a single-stranded DNA target, their good orthogonality, and their binding properties can also be utilized for the functionalization of DNA nanostructures with proteins.



DNA Nanotechnology

S. Sagredo, T. Pirzer, A. Aghebat Rafat, M. A. Goetzfried, G. Moncalian,

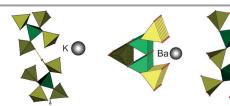


F. de la Cruz* _ 4348-4352

Orthogonal Protein Assembly on DNA Nanostructures Using Relaxases



Q



Extension of structural variability is the feature of the first borosulfates of a divalent and a trivalent cation showing bandsilicate (see picture; middle: borate tetrahedra green, sulfate tetrahedra yellow)

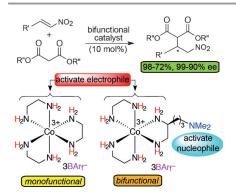
and cyclosilicate topologies (right), which were obtained by a new synthetic approach. Moreover, the first hydrogenborosulfate is presented (left; small spheres: H).

Borosulfates

P. Gross, A. Kirchhain, H. A. Höppe* _____ 4353 - 4355

The Borosulfates $K_4[BS_4O_{15}(OH)]$, $Ba[B_2S_3O_{13}]$, and $Gd_2[B_2S_6O_{24}]$





Two are better than one: Unlike the catalyst Λ -[Co(en)₃]³⁺ 3 BAr_f⁻, the bifunctional tertiary-amine-containing analogue Λ -3 c^{3+} 3 BAr_f effects highly enantioselective additions of alkyl malonates to βaryl- and β-alkylnitroethenes. The efficacy diminishes as the $(CH_2)_3$ tether is shortened or lengthened.

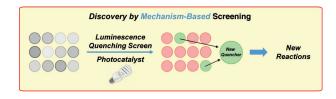
Bifunctional Catalysts

S. K. Ghosh, C. Ganzmann, N. Bhuvanesh,

_ 4356-4360 J. A. Gladysz* .

Werner Complexes with ω-Dimethylaminoalkyl Substituted Ethylenediamine Ligands: Bifunctional Hydrogen-Bond-Donor Catalysts for Highly **Enantioselective Michael Additions**





Enlightened! A mechanism-based screening approach can accelerate discovery in photocatalysis. It focuses on a single mechanistic step of a reaction class: the quenching step central to photocatalytic transformations. Luminescence spectroscopy was used to screen 100 compounds, identifying two promising substrate classes. A second, more-focused screen provided mechanistic insights for developing proof-of-concept reactions.

Screening Methods

M. N. Hopkinson, A. Gómez-Suárez, M. Teders, B. Sahoo,

F. Glorius* ___ _ 4361 - 4366

Accelerated Discovery in Photocatalysis using a Mechanism-Based Screening Method



Front Cover





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