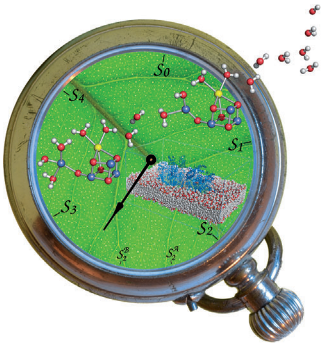
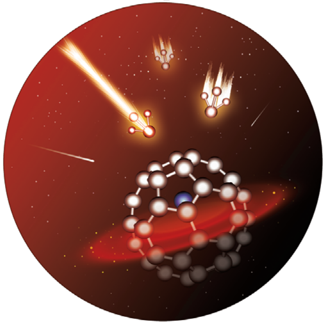
A catalytic method …

… to synthesize a diverse array of phosphorus-bridged biaryls from readily available tertiary phosphines is described by K. Baba, M. Tobisu, and N. Chatani in their Communication on page 11892 ff. The substrate must surmount two barriers, namely the cleavage of C–H and C–P bonds, to be transformed into the product. This process is facilitated by a palladium catalyst to afford various phosphorus-based π systems, some of which exhibit intense solid-state fluorescence.



Photosynthesis
In their Communication on page 11744 ff. L. Guidoni and co-workers find theoretical studies on the {Mn_4CaO_5} clusters of the S_2 state of photosystem II explain the contradictory results of earlier EPR studies on this system.

Masking
The apta-caging method exploits aptamers for the masking and light-induced release of large protein domains. As A. Heckel, G. Mayer et al. show in their Communication on page 11912 ff. no knowledge of the protein structure is required.



Fullerenes
In their Communication on page 11770 ff., H. Shinohara et al. describe how unstable metallofullerenes can be stabilized and readily extracted. This study gives access to a wide variety of missing unconventional metallofullerenes.

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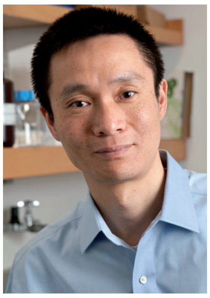


"In a spare hour, I go swimming and watch sports. If I had one year of paid leave I would become an American football coach. …"
This and more about Chuan He can be found on page 11692.

News

B. L. Feringa

N. Chatani

P. S. Baran

R. Kniep

D. G. Lynn

V. Gotor

M. Alcarazo

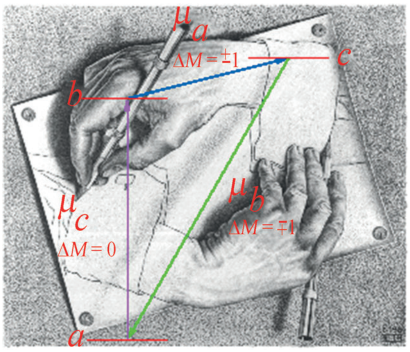
K. Matyjaszewski

Books

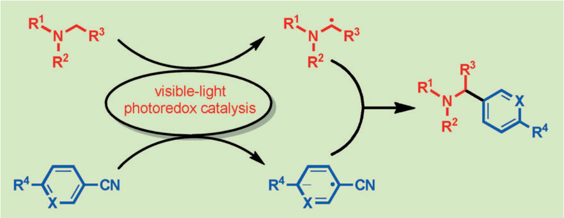
Highlights

Rotating Enantiomers

Optical activity can be positive or negative depending on whether the electric and magnetic dipole transition moments point into the same or opposite halves of a sphere centered on the molecule. A new technique takes a different route: Radiation emitted by molecules of opposite chirality associated with a loop of three dipole-allowed transitions between rotational states is exactly out of phase, thus providing a direct signal of molecular chirality.



Photochemistry



Two birds with one stone: Recent advances in activating two reactants simultaneously using homogeneous visible-light photoredox catalysis have been described. The conceptually new catalytic mode will aid in the design of some green and sustainable reactions.

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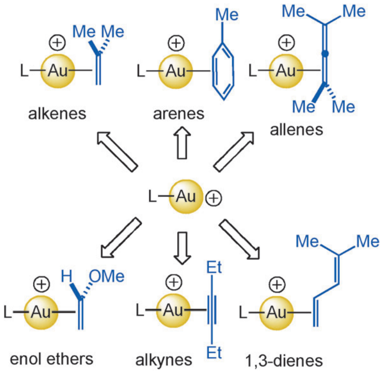
Essays

History of Chemistry

More than hydrazones: In 1901, Kizhner became the inaugural Professor of Organic Chemistry at the newly founded Imperial Tomsk Technological Institute in Siberia. In the first decade of his career, Kizhner had built a laboratory; contracted gangrene of the extremities that ultimately led to the amputation of both legs below the knee; fomented revolt and organized student strikes; been dismissed and exiled from Tomsk, then reinstated; and had discovered the reactions that bear his name.

Minireviews

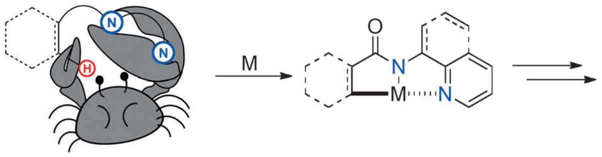
Ligand Effects



Unraveling gold: The title complexes have been widely invoked as intermediates in the gold-catalyzed functionalization of C—C multiple bonds and yet remained unknown until recently. This Minireview summarizes the recent efforts directed toward the synthesis and such intermediates, which have provided insight into the nature, bonding, and ligand exchange behavior of these complexes.

Reviews

C—H Functionalization



Caught in the act: The regiochemical functionalization of C—H bonds is a reliable strategy in synthetic chemistry. The regiocontrol can be achieved by using a directing group in the substrate which brings the catalyst into proximity with the target C—H bond. Bidentate directing groups in particular have proven to be extremely effective.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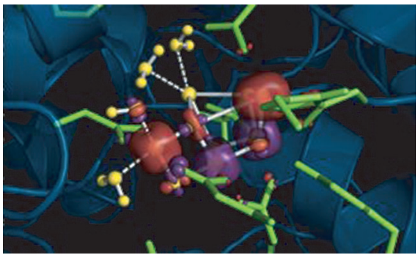
Communications

Photosynthesis

D. Bovi, D. Narzi,
L. Guidoni* ________ 11744 – 11749

The S_2 State of the Oxygen-Evolving Complex of Photosystem II Explored by QM/MM Dynamics: Spin Surfaces and Metastable States Suggest a Reaction Path Towards the S_3 State



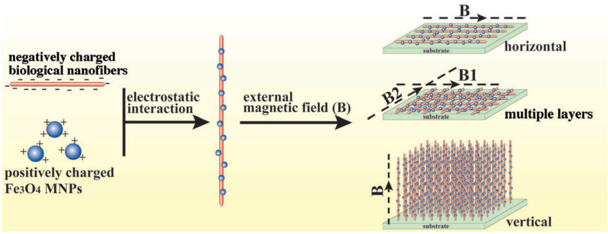
Split and polish: Quantum mechanics/molecular mechanics simulations reveal the role of spin surfaces, kinetics, and thermodynamics on the interconversion between two structural models of the $\{Mn_4CaO_5\}$ cluster (see picture) in the S_2 state of the water-splitting Kok's cycle in photosystem II. The results account for the temperature, illumination, and procedure dependence of historical EPR experiments and suggest a detailed pathway for the S_2 to S_3 transition.

Frontispiece

Biomolecular Assembly

B. R. Cao, Y. Zhu, L. Wang,
C. B. Mao* ________ 11750 – 11754

Controlled Alignment of Filamentous Supramolecular Assemblies of Biomolecules into Centimeter-Scale Highly Ordered Patterns by Using Nature-Inspired Magnetic Guidance

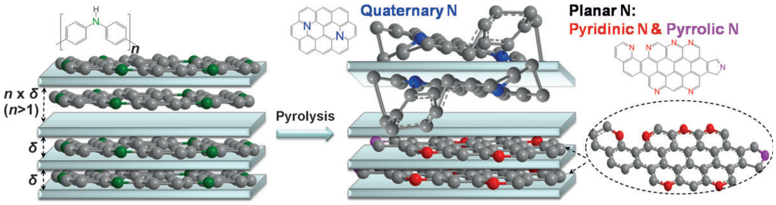


Magnetic nanoparticles (MNPs), which can be aligned along a magnetic field, were applied to generate large-scale assemblies of biological nanofibers with the orientation of the constituent nanofibers defined by the applied magnetic field. When decorated with MNPs, these nanofibers could be guided by the external magnetic field to become oriented either horizontally or vertically.

Electrocatalysis

W. Ding, Z.-D. Wei,* S.-G. Chen, X.-Q. Qi,
T. Yang, J.-S. Hu, D. Wang L.-J. Wan,*
S. F. Alvi, L. Li ________ 11755 – 11759

Space-Confinement-Induced Synthesis of Pyridinic- and Pyrrolic-Nitrogen-Doped Graphene for the Catalysis of Oxygen Reduction



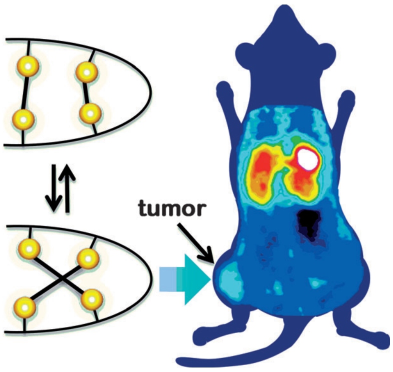
Forced obedience: Layer-structured montmorillonite (MMT) was used as a nanoreactor for the generation of planar pyridinic and pyrrolic N sites in nitrogen-doped graphene (NG; see picture). The selectivity for the formation of planar N sites was inversely proportional to the interspace width (δ) of the MMT and reached a maximum of 90.27%. The NG catalyst exhibited low electrical resistance, high electrocatalytic activity, and good stability.

Miniproteins

F. Zoller, A. Markert, P. Barthe, U. Hebling, A. Altmann, T. Lindner, W. Mier, U. Haberkorn* ___ **11760 – 11764**

A Disulfide-Constrained Miniprotein with Striking Tumor-Binding Specificity Developed by Ribosome Display

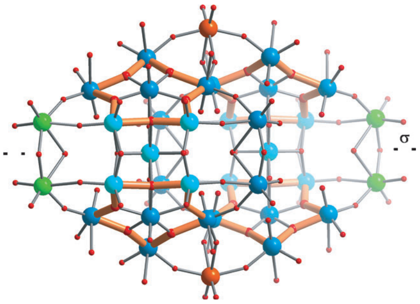
Fold me to hold me: A specific binding agent against the delta-like ligand 4 protein, which is expressed in angiogenesis, was identified by ribosome display. Specific tumor binding of this molecular imaging agent depends on the appropriate disulfide connectivity of its scaffold.



Trapping Intermediates

A. Merca, S. Garai, H. Bögge, E. T. K. Haupt, A. Ghosh, X. López, J. M. Poblet, F. Averseng, M. Che, A. Müller* ___ **11765 – 11769**

An Unstable Paramagnetic Isopolyoxomolybdate Intermediate Non-Homogeneously Reduced at Different Sites and Trapped in a Host Based on Chemical Adaptability



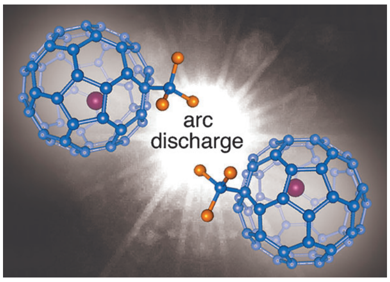
Stabilize me: A metal oxide host with a trapped unstable {Mo_{36}}-type polyoxomolybdate guest exhibits independent reduced diamagnetic building blocks and paramagnetic centers (both types with colors other than the dark blue of the Mo centers). The guest in such systems is stabilized especially by a hydrogen-bond network between the core and the shell.

Fullerenes

Z. Wang, Y. Nakanishi, S. Noda, H. Niwa, J. Zhang, R. Kitaura, H. Shinohara* ___ **11770 – 11774**

Missing Small-Bandgap Metallofullerenes: Their Isolation and Electronic Properties

Lost and found: In situ exohedral trifluoromethylation of endohedral fullerenes using an arc-discharge method (see picture) gives access to a wide variety of missing unconventional metallofullerenes. Such otherwise insoluble and unstable metallofullerenes become soluble and stable in organic solvents after an exterior functionalization.

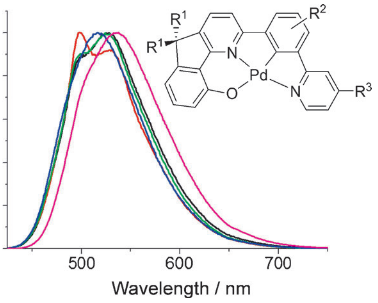


Back Cover

Functional Materials

P. K. Chow, C. Ma, W.-P. To, G. S. M. Tong, S.-L. Lai, S. C. F. Kui, W.-M. Kwok, C.-M. Che* ___ **11775 – 11779**

Strongly Phosphorescent Palladium(II) Complexes of Tetradentate Ligands with Mixed Oxygen, Carbon, and Nitrogen Donor Atoms: Photophysics, Photochemistry, and Applications

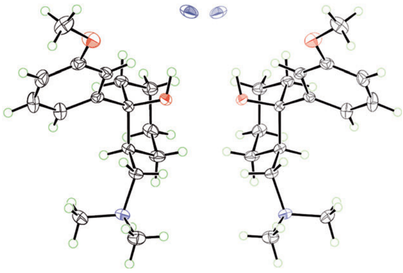


A healthy glow: A series of palladium(II) complexes with tetradentate O^N^C^N ligands (see structure) exhibit intense green phosphorescence and long-lived excited states with emission quantum yields and lifetimes up to 22% and 122 μs, respectively. The complexes show potential as novel functional materials, with promising results in a variety of applications, such as oxygen sensing, photocatalysis, and organic light-emitting diodes.

Natural Products

A. Boumendjel, G. Sotoing Taïwe,*
E. Ngo Bum, T. Chabrol, C. Beney,
V. Sinniger, R. Haudecoeur, L. Marcourt,
S. Challal, E. Ferreira Queiroz, F. Souard,
M. Le Borgne, T. Lomberget, A. Depaulis,
C. Lavaud, R. Robins, J.-L. Wolfender,
B. Bonaz, M. De Waard* **11780 – 11784**

Occurrence of the Synthetic Analgesic Tramadol in an African Medicinal Plant

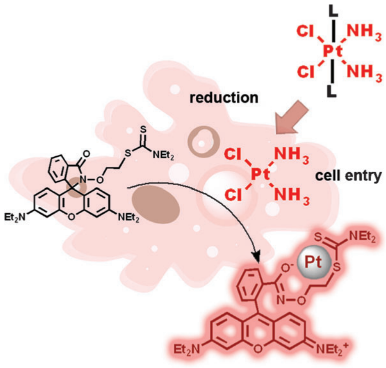


The root of the matter: The analgesic tramadol has been isolated from the root bark of *N. latifolia*, an African medical plant. This finding is a rare example of a common synthetic drug that occurs at considerable concentrations in nature. Cl purple, N blue, O red.

Cellular Imaging

D. Montagner, S. Q. Yap,
W. H. Ang* **11785 – 11789**

A Fluorescent Probe for Investigating the Activation of Anticancer Platinum(IV) Prodrugs Based on the Cisplatin Scaffold

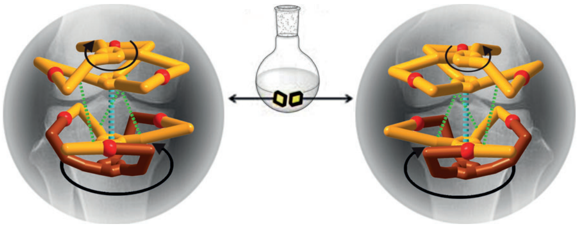


Watching closely: A fluorescent probe was engineered to detect the clinically relevant platinum drug cisplatin within a complex cellular environment, thus providing a direct means for visualizing its cell entry and the activation of platinum(IV) prodrugs in cancer cells.

Helical Metallacyclophanes

H. Lee, T. H. Noh,
O.-S. Jung* **11790 – 11795**

A Ball-Joint-Type Host–Guest System that Consists of Conglomerate Helical Metallacyclophanes

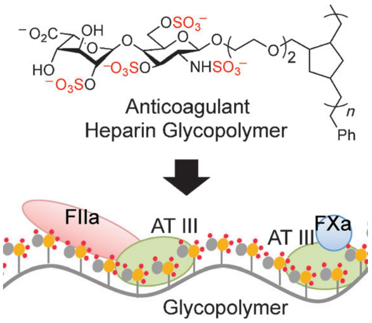


Flexible joint: The synthesis and characterization of a nanoscale ball-joint-type host–guest system are described. The system consists of unprecedented conglomerates of two distinct helical metallacyclophanes. Its structure features one π⋯π interaction and three NH⋯O=C hydrogen bonds.

Biomimetic Polymers

Y. I. Oh, G. J. Sheng, S.-K. Chang,
L. C. Hsieh-Wilson* **11796 – 11799**

Tailored Glycopolymers as Anticoagulant Heparin Mimetics



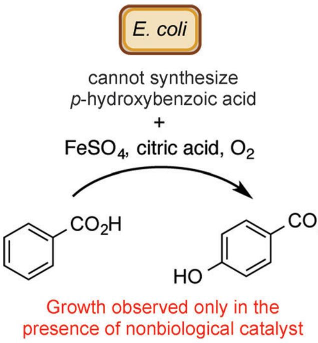
Not to clot: Heparin and its low-molecular-weight derivatives are clinical therapeutics used to treat and prevent blood clots. The synthesis of heparin-based glycopolymers that are potent and potentially safer mimetics of heparin is described. The mimetics exhibited activity against proteases (FXa and FIIa) in the coagulation cascade and prolonged blood clot times in human plasma with efficacies similar to those of clinical anticoagulants. ATIII = antithrombin III.

Biocompatible Chemistry

Y. Lee, A. Umeano,
E. P. Balskus* ———— **11800 – 11803**

Rescuing Auxotrophic Microorganisms with Nonenzymatic Chemistry

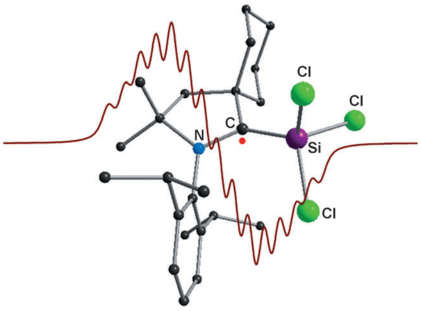
Organic chemistry to the rescue: Two unrelated nonenzymatic chemical reactions can support the growth of auxotrophic *E. coli* strains by generating essential nutrients in situ. These biocompatible reactions, which take place in the presence of the organisms and are designed to interface with cellular metabolic processes, provide a means of linking the growth of an organism to the success of a nonbiological chemical transformation.



Carbon-Centered Radicals

K. C. Mondal, H. W. Roesky,* A. C. Stückl, F. Ehret, W. Kaim,* B. Dittrich,* B. Maity, D. Koley* ———— **11804 – 11807**

Formation of Trichlorosilyl-Substituted Carbon-Centered Stable Radicals through the Use of π-Accepting Carbenes

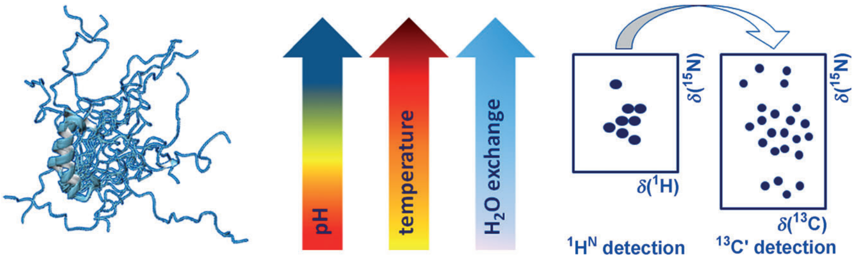


A radical change: Cyclic alkyl(amino) carbenes formed zwitterionic adducts with $SiCl_4$, which were further converted into carbon-centered stable radicals by changing the donor-acceptor C→Si coordinate bond into a C−Si covalent bond through a KC_8 reduction. As the carbon radical site was directly bonded to a $SiCl_3$ unit, a radical center that is right next to an acceptor has been generated.

NMR Spectroscopy of Proteins

S. Gil, T. Hošek, Z. Solyom, R. Kümmerle, B. Brutscher, R. Pierattelli, I. C. Felli* ———— **11808 – 11812**

NMR Spectroscopic Studies of Intrinsically Disordered Proteins at Near-Physiological Conditions



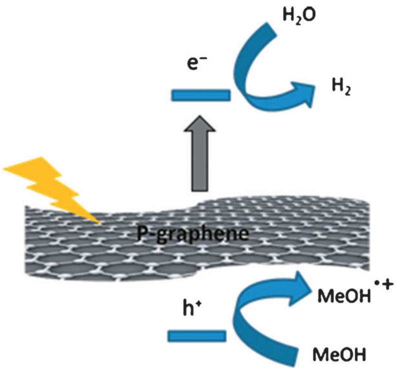
When approaching physiological conditions, solvent exchange of amide protons in intrinsically disordered proteins (IDPs) is so pronounced that it becomes a key feature to be considered in NMR experiment design. ^{13}C NMR experiments recover information that is not accessible through amide proton detection, and solvent exchange can be used to increase sensitivity.

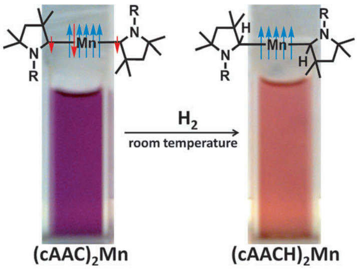
Graphene for Hydrogen Generation

M. Latorre-Sánchez, A. Primo,*
H. García* ———— **11813 – 11816**

P-Doped Graphene Obtained by Pyrolysis of Modified Alginate as a Photocatalyst for Hydrogen Generation from Water–Methanol Mixtures

The right dope: Phosphorus-doped graphene was obtained by the pyrolysis of natural alginate that contained $H_2PO_4^-$ at 900 °C. This material catalyzes the generation of H_2 from a water/methanol mixture upon irradiation with UV or visible light. An increase in the amount of $H_2PO_4^-$ leads to a higher photocatalytic activity.



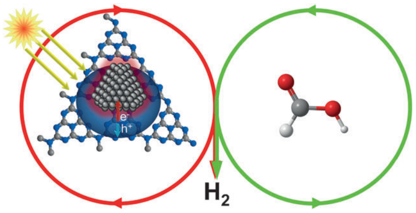


The (cAAC)$_2$Mn complex (cAAC = cyclic alkyl(amino)carbene) features a linear two-coordinate Mn center. The antiferromagnetic coupling of a radical electron, delocalized on two carbene C atoms, with the central Mn^I having d^6 electronic configuration, mainly contributes to the $S_T = {}^3/_2$ ground state. Treatment of (cAAC)$_2$Mn with H$_2$ at RT resulted in the addition of H atoms at both "carbene" C atoms, leaving the central Mn atom in the $S_T = {}^5/_2$ spin ground state.

Dihydrogen Splitting

P. P. Samuel, K. C. Mondal,
H. W. Roesky,* M. Hermann,
G. Frenking,* S. Demeshko, F. Meyer,
A. C. Stückl, J. H. Christian, N. S. Dalal,
L. Ungur, L. F. Chibotaru, K. Pröpper,
A. Meents, B. Dittrich* ____ **11817–11821**

Synthesis and Characterization of a Two-Coordinate Manganese Complex and its Reaction with Molecular Hydrogen at Room Temperature

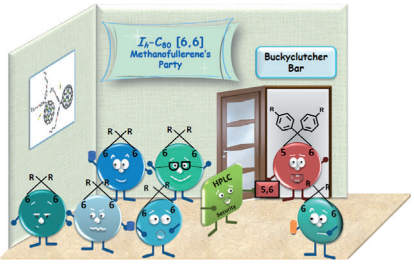


Exploiting useful contacts: The exceptional catalytic performance of a photocatalyst composed of Pd nanoparticles and mesoporous carbon nitride for the dehydrogenation of formic acid in water at room temperature to produce H$_2$ gas (see picture) is due to enhanced electron enrichment of the Pd nanoparticles through charge transfer at the interface of the Mott–Schottky contact.

Hydrogen Generation

Y. Y. Cai, X. H. Li,* Y. N. Zhang, X. Wei,
K. X. Wang, J. S. Chen* ____ **11822–11825**

Highly Efficient Dehydrogenation of Formic Acid over a Palladium-Nanoparticle-Based Mott–Schottky Photocatalyst

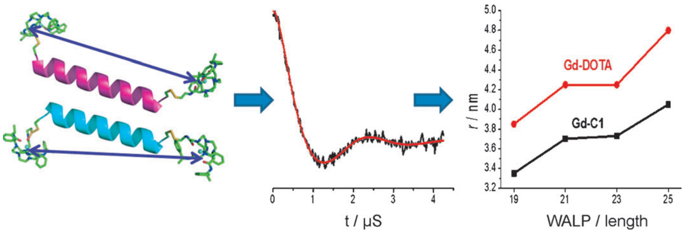


Newcomers on the scene: The modification of endohedral metallofullerenes with an I_h-C$_{80}$ cage by cyclopropanation-type addition reactions generally yields the [6,6] methanofullerene adducts. Now [5,6]-open methanofullerenes with an I_h-C$_{80}$-derived cage have been synthesized, as confirmed by X-ray crystallography, under relatively mild, stoichiometric conditions along with the corresponding [6,6]-open derivatives in good yields.

Derivatization of Fullerenes

M. Izquierdo, M. R. Cerón,
M. M. Olmstead, A. L. Balch,*
L. Echegoyen* ____________ **11826–11830**

[5,6]-Open Methanofullerene Derivatives of I_h-C$_{80}$



High-frequency double electron-electron resonance (DEER) distance measurements using different Gd^{3+} tags (Gd-DOTA and Gd-C1) were carried out on transmembrane helical peptides (ca. 0.15 nmol; WALP peptides) in a model membrane. The ability to pick up small distance variations, the chemical flexibility of the tags, and the remarkable absolute sensitivity, make this approach attractive for studies of membrane proteins.

EPR Spectroscopy

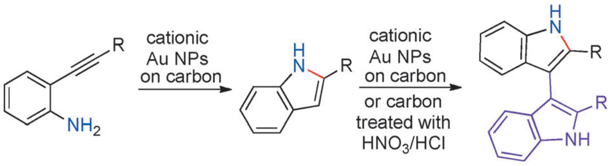
E. Matalon, T. Huber, G. Hagelueken,
B. Graham, V. Frydman, A. Feintuch,
G. Otting, D. Goldfarb* __ **11831–11834**

Gadolinium(III) Spin Labels for High-Sensitivity Distance Measurements in Transmembrane Helices

Heterogeneous Catalysis

J. E. Perea-Buceta, T. Wirtanen,
O.-V. Laukkanen, M. K. Mäkelä, M. Nieger,
M. Melchionna, N. Huittinen,
J. A. Lopez-Sanchez,*
J. Helaja* ______________ **11835 – 11839**

Cycloisomerization of 2-Alkynylanilines to Indoles Catalyzed by Carbon-Supported Gold Nanoparticles and Subsequent Homocoupling to 3,3′-Biindoles

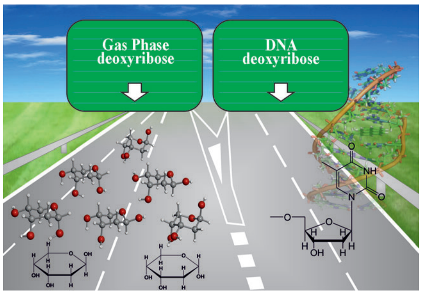


Elevated by the support: 2-Alkynyl aniline cycloisomerization to indole is catalyzed by cationic Au NPs on a carbon support. Electroneutral and rich 2-aryl indoles are further converted into 3,3′-biindoles by oxidative homocoupling that is readily catalyzed by the Au NPs on carbon, and exclusively but also somewhat sluggishly by the carbon support.

Microwave Spectroscopy

I. Peña, E. J. Cocinero,* C. Cabezas,
A. Lesarri, S. Mata, P. Écija, A. M. Daly,
Á. Cimas, C. Bermúdez, F. J. Basterretxea,
S. Blanco, J. A. Fernández, J. C. López,
F. Castaño, J. L. Alonso* **11840 – 11845**

Six Pyranoside Forms of Free 2-Deoxy-D-ribose

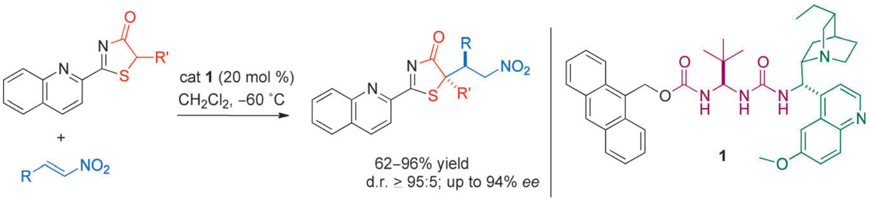


A clear picture of the conformations of isolated 2-deoxy-D-ribose was obtained using chirped pulse and Balle–Flygare Fourier-transform microwave spectrometers, both coupled with laser ablation sources. Two conformers of α-D-deoxyribopyranose and four of β-D-deoxyribopyranose were found on the basis of the spectroscopic rotational parameters and ab initio predictions. The substitution and effective structures of the most abundant conformer have been determined.

Organocatalysis

S. Diosdado, J. Etxabe, J. Izquierdo,
A. Landa, A. Mielgo, I. Olaizola, R. López,
C. Palomo* ______________ **11846 – 11851**

Catalytic Enantioselective Synthesis of Tertiary Thiols From 5*H*-Thiazol-4-ones and Nitroolefins: Bifunctional Ureidopeptide-Based Brønsted Base Catalysis

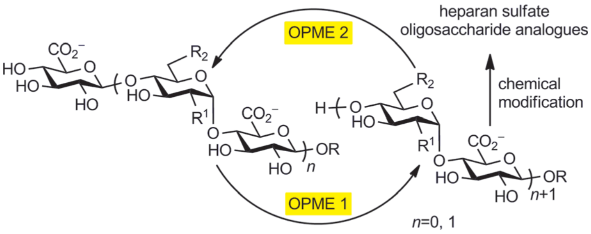


Fully loaded: The ureidopeptide-based bifunctional Brønsted base **1** efficiently promotes the first direct catalytic Michael reaction of α-mercapto carboxylate surrogates with nitroolefins involving a fully substituted α-carbon atom construction.

Enzymatic Synthesis

Y. Chen, Y. Li, H. Yu, G. Sugiarto, V. Thon,
J. Hwang, L. Ding, L. Hie,
X. Chen* ______________ **11852 – 11856**

Tailored Design and Synthesis of Heparan Sulfate Oligosaccharide Analogues Using Sequential One-Pot Multienzyme Systems

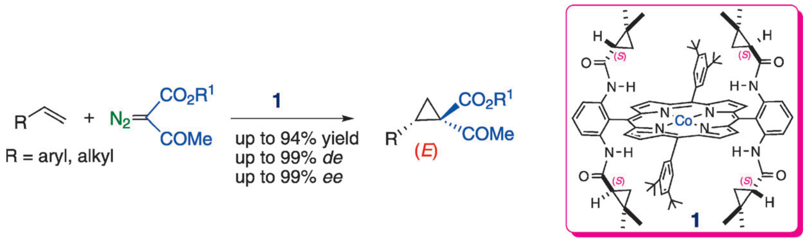


Heparan sulfate analogues: Highly efficient one-pot multienzyme (OPME) chemoenzymatic systems for the activation and transfer of *N*-acetylglucosamine (GlcNAc) and glucuronic acid (GlcA) have been developed. They were applied to the sequential tailored synthesis of *N*-sulfated analogues of heparan sulfate oligosaccharides, which could be potential therapeutics.

Synthetic Methods

X. Xu, S. Zhu, X. Cui, L. Wojtas,
X. P. Zhang* ——— **11857 – 11861**

Cobalt(II)-Catalyzed Asymmetric Olefin Cyclopropanation with α-Ketodiazoacetates

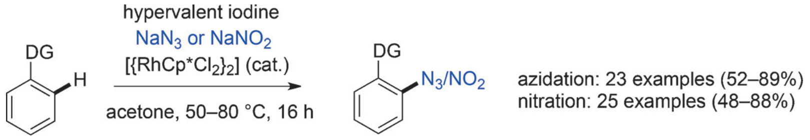


Porphyrin and Co.: The cobalt(II) complex **1** is an effective metalloradical catalyst for cyclopropanation of alkenes with α-acetodiazoacetates at room temperature to yield *E*-1,1-cyclopropaneketoesters in high yields with both high diastereo- and enantioselectivities. Epimerization of the resulting enantioenriched *E* diastereoisomers into the corresponding *Z* isomers with retention of the enantiopurity is promoted by iodide.

Synthetic Methods

F. Xie, Z. Qi, X. Li* ——— **11862 – 11866**

Rhodium(III)-Catalyzed Azidation and Nitration of Arenes by C–H Activation

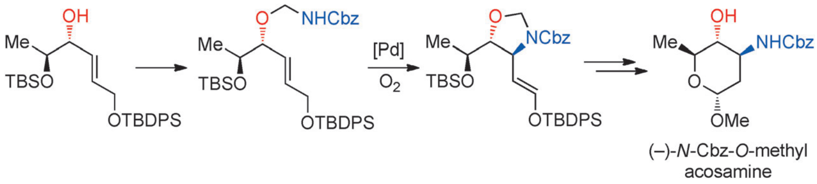


Getting a handle on it: In the chelation-assisted title reactions in the presence of a hypervalent iodine oxidant, sodium azide and sodium nitrite served as readily available nitrogen sources, and pyridine, pyrimidine, and pyrazole substituents were efficient directing groups (DGs; see scheme; Cp* = C_5Me_5). The synthetic utility of the azidation products was demonstrated in subsequent functional-group transformations.

Synthetic Methods

A. B. Weinstein, D. P. Schuman, Z. X. Tan,
S. S. Stahl* ——— **11867 – 11870**

Synthesis of Vicinal Aminoalcohols by Stereoselective Aza-Wacker Cyclizations: Access to (−)-Acosamine by Redox Relay



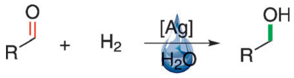
Diastereoselective aza-Wacker cyclization of *O*-allyl hemiaminals under aerobic conditions enables efficient access to 1,2-aminoalcohol derivatives from allylic alcohols. The scope of this method is presented and its utility is highlighted in a streamlined synthesis of the biologically important aminosugar (−)-acosamine. Cbz = benzyloxycarbonyl, TBDPS = *tert*-butyldiphenylsilyl, TBS = *tert*-butyldimethylsilyl.

Homogeneous Catalysis

Z.-H. Jia, F. Zhou, M. Liu, X.-S. Li,
A. S. C. Chan, C.-J. Li* ——— **11871 – 11874**

Silver-Catalyzed Hydrogenation of Aldehydes in Water

Inside Cover

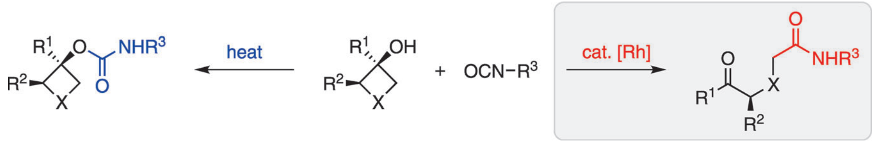


Silver bullet: The first silver-catalyzed hydrogenation in water was developed. A silver complex containing a bulky monodentate phosphine ligand was used to generate alcohols from a broad range of aldehydes, including aliphatic, aromatic, and heterocyclic aldehydes. This method provides a direct and efficient route to alcohols from aldehydes and opens a new avenue in silver catalysis.

Selective Catalysis

N. Ishida, Y. Nakanishi,
M. Murakami* ________ **11875 – 11878**

Reactivity Change of Cyclobutanols towards Isocyanates: Rhodium Favors *C*-Carbamoylation over *O*-Carbamoylation

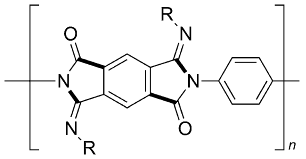


The other way around: Contrasting reaction pathways were observed in the addition reaction of cyclobutanols to isocyanates in the presence or absence of a rhodium catalyst. Simple heating prompted a direct *O*-carbamoylation reaction to afford cyclobutyl carbamates. In contrast, upon addition of a rhodium catalyst, the reaction pathway was directed to *C*-carbamoylation through a ring-opening process.

Heterocycles

S. Sueki, Y. Guo, M. Kanai,
Y. Kuninobu* ________ **11879 – 11883**

Rhenium-Catalyzed Synthesis of 3-Imino-1-isoindolinones by C–H Bond Activation: Application to the Synthesis of Polyimide Derivatives



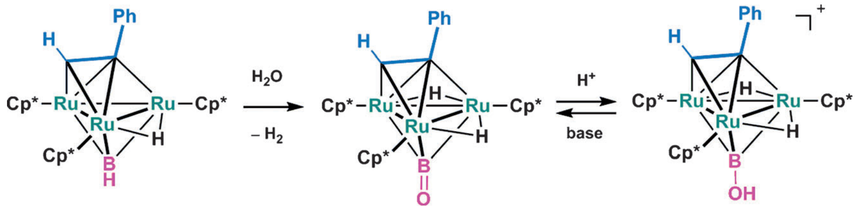
by C–H bond activation
highly soluble polyimide analogue

Polyimide solution: Synthesis of the title compounds from aromatic imidates and isocyanates in good to excellent yields by a rhenium-catalyzed C–H bond transformation is described. The reaction also proceeded in high yield on gram scale and could be applied to the synthesis of polyimide derivatives (see figure), which are highly soluble in organic solvents.

Cluster Compounds

T. Kaneko, T. Takao,*
H. Suzuki* ________ **11884 – 11887**

A Triruthenium Complex Capped by a Triply Bridging Oxoboryl Ligand



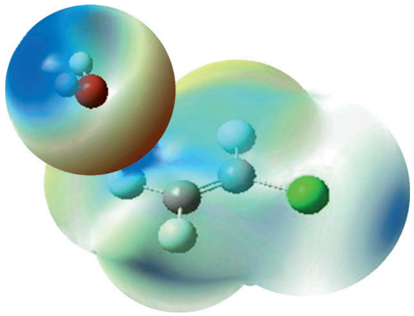
Building new bridges: A triply bridging oxoboryl ligand was formed by treatment of the μ_3-borylene complex [{Cp*Ru(μ-H)}$_3$(μ_3-PhCCH)(μ_3-BH)] (Cp* = η^5-C_5Me_5) with H_2O (see scheme). The multiple-bond character of the B–O bond was revealed by X-ray diffraction, spectroscopy, and a DFT calculation. Protonation of the μ_3-BO complex to give a cationic μ_3-hydroxyborylene complex clearly showed the highly polarized nature of the B^+–O^- bond.

Microwave Spectroscopy

Q. Gou, G. Feng, L. Evangelisti,
W. Caminati* ________ **11888 – 11891**

Lone-Pair···π Interaction: A Rotational Study of the Chlorotrifluoroethylene–Water Adduct

The rotational spectra of several isotopologues of the chlorotrifluoroethylene–water adduct show that the two subunits are linked together through a lone-pair···π interaction (see picture). This structure is also predicted by calculations.

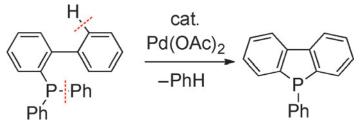


Heterocycle Synthesis

K. Baba, M. Tobisu,*
N. Chatani* ———— **11892 – 11895**

Palladium-Catalyzed Direct Synthesis of Phosphole Derivatives from Triarylphosphines through Cleavage of Carbon–Hydrogen and Carbon–Phosphorus Bonds

Front Cover

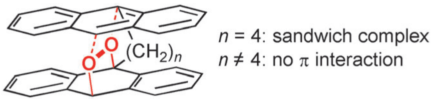


(Phosp)hole in one: A palladium-catalyzed synthesis for directly assembling phosphole skeletons from triarylphosphines through C–H and C–P bond cleavage was developed. This approach overcomes several of the limitations of the so far reported methods. Phospholes bearing a range of functionalities (including Br, F, CO$_2$Me, Ac, and CN) and an array of fused rings (naphthalenes, anthracenes, furans, and pyrroles) can be easily synthesized.

Sandwich Complexes

M. Klaper, T. Linker* ———— **11896 – 11899**

Evidence for an Oxygen Anthracene Sandwich Complex

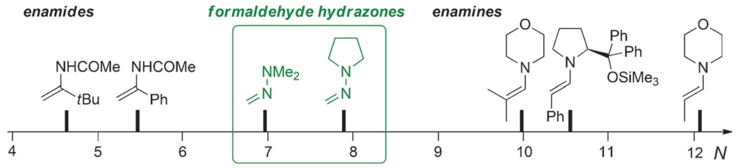


Oxygen sticks in between acenes: The rate of the photooxygenation of bis(anthryl)alkanes with singlet oxygen shows a maximum for a defined chain length ($n = 4$). In combination with calculations, a bathochromic shift of the UV/Vis absorption for only one endoperoxide and a CT absorption band, this gives considerable evidence for an oxygen anthracene sandwich complex.

Ambident Reactivity

B. Maji,* K. Troshin,
H. Mayr* ———— **11900 – 11904**

Ambident Reactivities of Formaldehyde *N*,*N*-Dialkylhydrazones

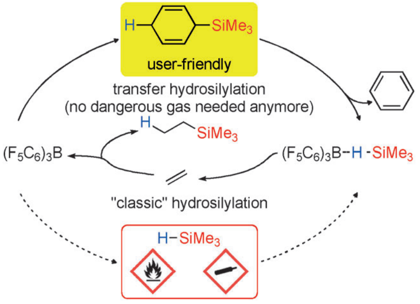


What can attack at carbon? With a nucleophilicity $N \approx 7$ for attack at the azomethine carbon, formaldehyde hydrazones can undergo noncatalyzed reactions at room temperature with electrophiles that have a reactivity parameter E that is greater than -12.

Transfer Hydrosilylation

A. Simonneau,
M. Oestreich* ———— **11905 – 11907**

3-Silylated Cyclohexa-1,4-dienes as Precursors for Gaseous Hydrosilanes: The B(C$_6$F$_5$)$_3$-Catalyzed Transfer Hydrosilylation of Alkenes

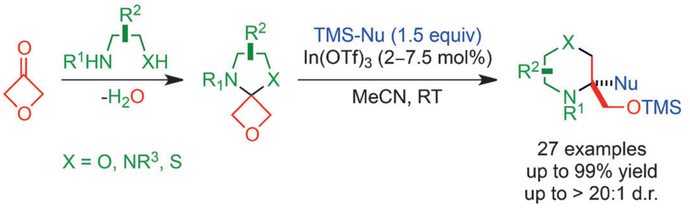


Set Me$_3$SiH free! The strong Lewis acid B(C$_6$F$_5$)$_3$ catalyzes the release of hydrosilanes from 3-silylated cyclohexa-1,4-dienes with concomitant formation of benzene. Subsequent B(C$_6$F$_5$)$_3$-catalyzed Si–H bond activation allows for alkene hydrosilylation (see scheme). The net reaction is an ionic transfer hydrosilylation. The new technique is particularly attractive in the case of otherwise gaseous, highly flammable hydrosilanes.

Synthetic Methods

S. A. Ruider, S. Müller,
E. M. Carreira* ________ **11908 – 11911**

Ring Expansion of 3-Oxetanone-Derived Spirocycles: Facile Synthesis of Saturated Nitrogen Heterocycles



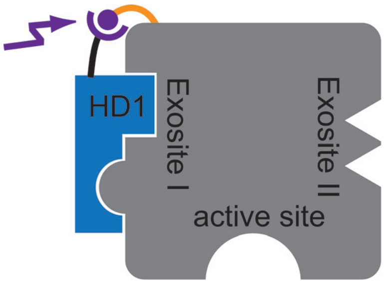
One ring to bring them all: 4,5-Spirocycles derived from 3-oxetanone and β-heteroatom-substituted amino compounds undergo a Lewis acid mediated reaction cascade to form saturated nitrogen heterocycles. The unique reactivity of 3-oxetanone facilitates access to biologically important morpholines, piperazines, and thiomorpholines with an otherwise difficult-to-access substitution pattern from readily available starting materials.

Caged Compounds

F. Rohrbach, F. Schäfer, M. A. H. Fichte,
F. Pfeiffer, J. Müller, B. Pötzsch,
A. Heckel,* G. Mayer* __ **11912 – 11915**

Aptamer-Guided Caging for Selective Masking of Protein Domains

Inside Back Cover

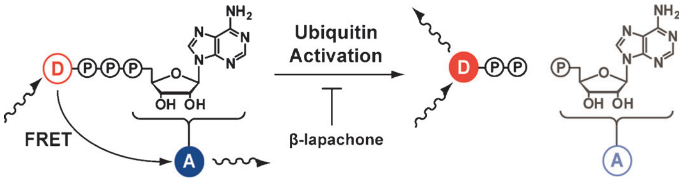


Lightly unmasked: Large protein subdomains can be masked and photolytically released using aptamers with a suitable photocleavable linker. No structural knowledge of the protein site is needed. Thrombin Exosite I activity can be efficiently regulated with this approach (see scheme), allowing light-controlled activation of blood clotting.

ATP FRET Probes

S. M. Hacker, D. Pagliarini, T. Tischer,
N. Hardt, D. Schneider, M. Mex,
T. U. Mayer, M. Scheffner,*
A. Marx* ____________ **11916 – 11919**

Fluorogenic ATP Analogues for Online Monitoring of ATP Consumption: Observing Ubiquitin Activation in Real Time



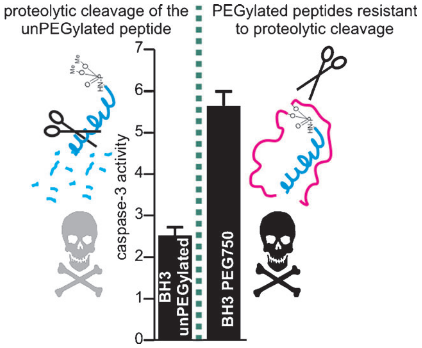
Many enzymes use ATP in signal-transducing processes or as an energy source. New fluorogenic ATP analogues signal ATP consumption by ubiquitin-like protein-activating enzymes in real time. Thus the inhibition and stimulation of these ATP-processing enzymes can be studied without auxiliary enzymes and reagents. β-Lapachone was identified as an inhibitor of the ubiquitin-activating enzyme UBA1 (see scheme; A = acceptor, D = donor).

Bioactive PEG-Peptides

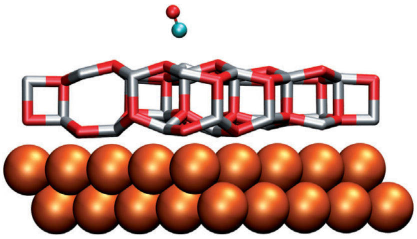
N. Nischan, A. Chakrabarti, R. A. Serwa,
P. H. M. Bovee-Geurts, R. Brock,
C. P. R. Hackenberger* __ **11920 – 11924**

Stabilization of Peptides for Intracellular Applications by Phosphoramidate-Linked Polyethylene Glycol Chains

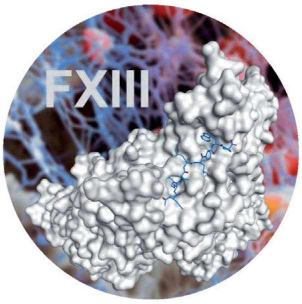
PEG intracellularly! Although long known to enhance residence half-life of peptides in serum and lysates, the effect of PEGylation on biological probes in cells has received only limited attention. Here it is shown that phosphoramidate-linked PEGylated proapoptotic peptides display a dramatically increased stability in Jurkat cell lysate and a homogenous intracellular distribution as well as high apoptotic activity after introduction into cells.



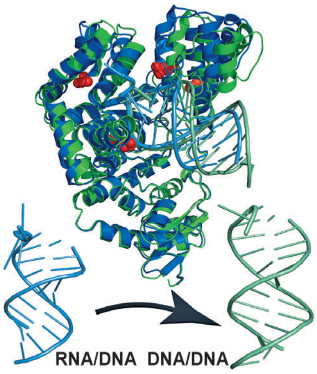
Influential support: Metal substrates affect the chemical properties of ZnO layers, which are important catalyst materials for the industrial production of methanol through the oxidation of CO. Interactions with the substrate lead to the formation of a new, planar ZnO thin-film phase, in which less highly oxidized Zn atoms bind CO more strongly than the Zn atoms in the normal wurtzite modification.



On active duty: The available drugs for cardiovascular diseases can promote blood clotting but can also lead to life-threatening bleeding episodes. A promising target for the development of safer alternatives is the transglutaminase Factor XIII (FXIII), the active structure of which is presented. The binding and coordination of three calcium ions induce major domain movements in the enzyme upon activation.



Unfaithful: The structure of a DNA-dependent DNA polymerase, whose parental ancestor has no significant reverse transcriptase activity, was obtained for the first time incorporating a nucleotide against an RNA template and then structurally characterized. The DNA polymerase variant has significant reverse transcriptase activity that allows its application in PCR-based molecular diagnostics.



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

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The Hot Papers are articles that the Editors have chosen on the basis of the referee reports to be of particular importance for an intensely studied area of research.

Angewandte Corrigendum

Direct Peptide Lipidation through Thiol–Ene Coupling Enables Rapid Synthesis and Evaluation of Self-Adjuvanting Vaccine Candidates

T. H. Wright, A. E. S. Brooks, A. J. Didsbury, G. M. Williams, P. W. R. Harris, P. R. Dunbar, M. A. Brimble* ________ **10616–10619**

Angew. Chem. Int. Ed. **2013**, *52*

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In the original manuscript, the name of a co-author, Dr. Julie D. MacIntosh, was inadvertedly omitted. The full and proper authorship should therefore be as follows:

*Tom H. Wright, Anna E. S. Brooks, Alicia J. Didsbury, Julie D. MacIntosh, Geoffrey M. Williams, Paul W. R. Harris, P. Rod Dunbar, and Margaret A. Brimble**

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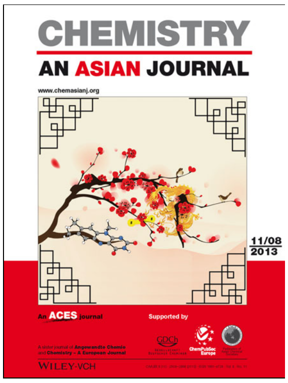

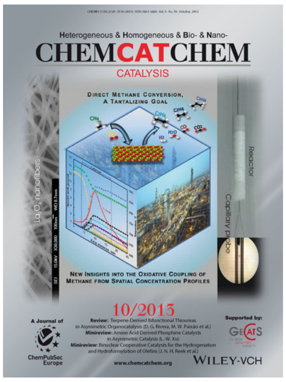

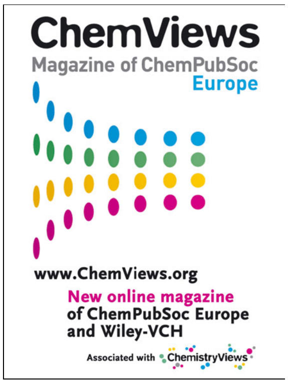

Abstracts for Communications

From January 2014 onwards, all Communications in *Angewandte Chemie* will contain an abstract as their first paragraph. We therefore request that every new Communication be submitted with such an abstract. When you write the abstract, please keep the following aspects in mind (they can be found in more detail in the Author Guidelines on the journal's homepage in Section 3.1):

In the abstract, the **motivation** for the work, the **methods** applied, the **results**, and the **conclusions** drawn should be presented (maximum 1000 characters). The abstract should contain several keywords to aid finding the paper online, and it should not mention graphical elements, tables, or references within the paper.