VIP *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:*

Author Profile

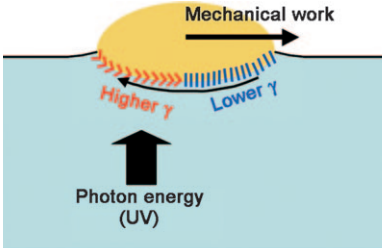
"If I could be anyone for a day, I would be an orchestra conductor.
A good work day begins with a strong espresso and an unexpected crystal structure of significant interest …"
This and more about Didier Bourissou can be found on page 3258.

Books

Highlights

Droplet Motion

Do the locomotion: Direct conversion of light energy into mechanical work is possible using photoresponsive compounds. A new report by Baigl and co-workers shows how photoresponsive surfactant molecules (red and blue in the picture; γ is the surface tension) can be harnessed to move oil droplets resting on an aqueous solution, thus paving the way to exciting applications in microfluidics.

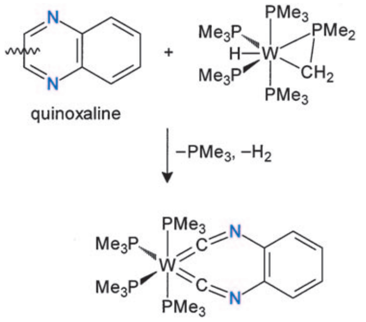


C–C Bond Activation

M. D. Walter,* M. Tamm* — **3264 – 3266**

Breaking News: Tungsten Cleaves Aromatic C–C Bonds

An amazing response: The unstrained, aromatic carbon–carbon bond in quinoxaline is cleaved upon reaction with $[W(\eta^2\text{-}CH_2PMe_2)(PMe_3)_4]$ to afford an unprecedented *o*-phenylene diisocyanide complex. The proposed mechanism proceeds via a benzyne intermediate, which is formed by a double C–H activation, elimination of H_2, and subsequent metal insertion into the C–C bond.

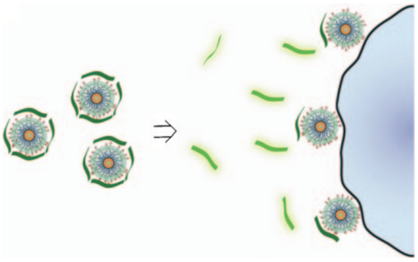


Minireviews

Biosensors

U. H. F. Bunz,*
V. M. Rotello* ———— **3268 – 3279**

Gold Nanoparticle–Fluorophore Complexes: Sensitive and Discerning “Noses” for Biosystems Sensing



Disruption desired: Different monolayer-protected nanoparticle–fluorophore constructs are used in indicator-displacement assays to spy on proteins, bacteria, cells, and ions (see picture). The modus operandi involves disruption of the preformed quencher–fluorophore complexes, leading to partial and analyte-dependent fluorescence turn-on. Small libraries of nanoparticle–fluorophore complexes get the sensing job for different biological analytes done.

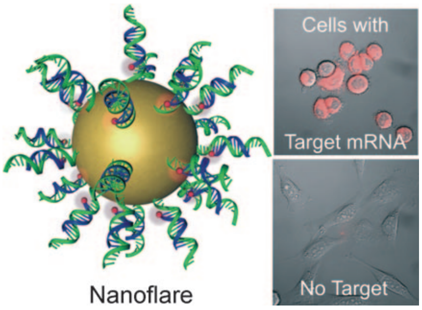
Reviews

Nanotechnology

D. A. Giljohann, D. S. Seferos,
W. L. Daniel, M. D. Massich, P. C. Patel,
C. A. Mirkin* ———— **3280 – 3294**

Gold Nanoparticles for Biology and Medicine

Sitting on a gold mine: Gold nanoparticles have been developed and studied as gene-regulating agents, drug carriers, photoresponsive therapeutics, and as imaging platforms (see the nanoflare, which allows detection of mRNA by fluorescence microscopy). These structures have new properties that are advantageous for biological applications. This Review highlights the synthesis of gold nanoparticles and their application from cell-based assays to therapeutic materials.



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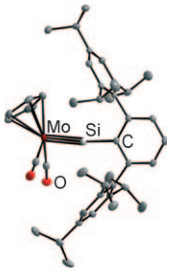
Communications

Silylidyne Complexes

A. C. Filippou,* O. Chernov, K. W. Stumpf, G. Schnakenburg ________ **3296 – 3300**

Metal–Silicon Triple Bonds: The Molybdenum Silylidyne Complex $[Cp(CO)_2Mo{\equiv}Si\text{-}R]$

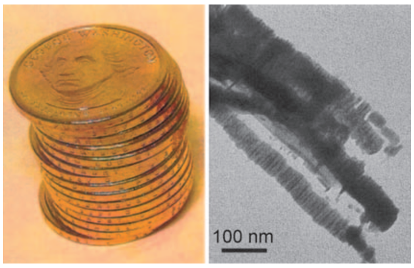


Carbene transfer from the silylidene complex $[Cp(CO)_2Mo{=}Si(C_6H_3\text{-}2,6\text{-}Trip_2)(Im\text{-}Me_4)]$ (Trip = 2,4,6-triisopropylphenyl, Im-Me_4 = tetramethylimidazol-2-ylidene) to a triarylborane leads to the silylidyne complex $[Cp(CO)_2Mo{\equiv}Si(C_6H_3\text{-}2,6\text{-}Trip_2)]$, which contains the first Mo–Si triple bond (see picture).

Nanostructures

A. Yella, E. Mugnaioli, M. Panthöfer, U. Kolb, W. Tremel* ________ **3301 – 3305**

Mismatch Strain versus Dangling Bonds: Formation of “Coin-Roll Nanowires” by Stacking Nanosheets

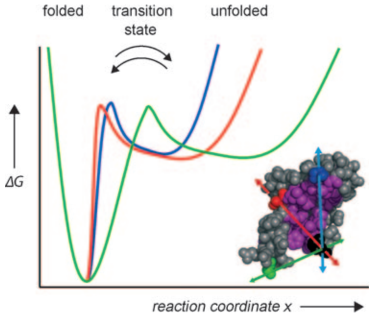


The third dimension comes to the rescue in the synthesis of laterally confined 2D crystals. Graphene-type sheets of layered metal(IV) chalcogenides are stabilized by stacking to form nano-objects that resemble a coin roll. Mismatch strain between NbS_2 and WS_2 lattices is important for the stabilization of the coin-roll structure as well as for preventing the formation of the intrinsically more stable scroll structures such as fullerenes or nanotubes.

Protein Folding

J. P. Junker, M. Rief* ________ **3306 – 3309**

Evidence for a Broad Transition-State Ensemble in Calmodulin Folding from Single-Molecule Force Spectroscopy

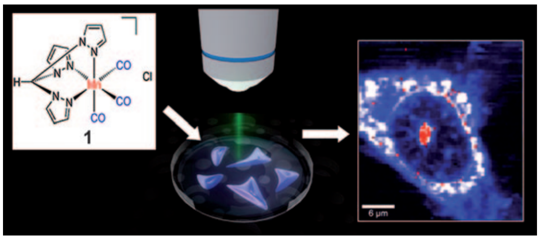


Same difference: Single-molecule force spectroscopy was used to study folding and unfolding pathways of calmodulin. Depending on the force application points, different pathways that are similar in energy can be populated. Such a broad transition-state ensemble has been postulated for ultrafast protein folding.

Bioorganometallic Chemistry

K. Meister, J. Niesel, U. Schatzschneider,* N. Metzler-Nolte,* D. A. Schmidt, M. Havenith* ________ **3310 – 3312**

Label-Free Imaging of Metal–Carbonyl Complexes in Live Cells by Raman Microspectroscopy



A new kid in town: 3D Raman intensity images of a HT29 colon cancer cell incubated with an aqueous solution of the CO-releasing metal–carbonyl complex **1** show that the compound penetrates the cellular membrane and is localized mainly in the nuclear membrane and the nucleolus. The C≡O vibration of **1** serves as an intrinsic spectroscopic label.

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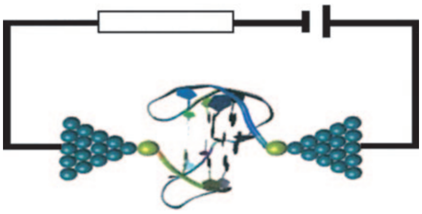

Totally wired: The folding of G-quadruplexes leads to a stacking of the G-bases, which provide a relatively large conductance. Stretching these complexes results in changes to the resistance that are only slightly over a broad range of molecular lengths. G-quadruplexes can thus be seen as molecular wires with adjustable length.

DNA Electronics

S.-P. Liu, S. H. Weisbrod, Z. Tang, A. Marx,
E. Scheer, A. Erbe* ________ **3313 – 3316**

Direct Measurement of Electrical Transport Through G-Quadruplex DNA with Mechanically Controllable Break Junction Electrodes

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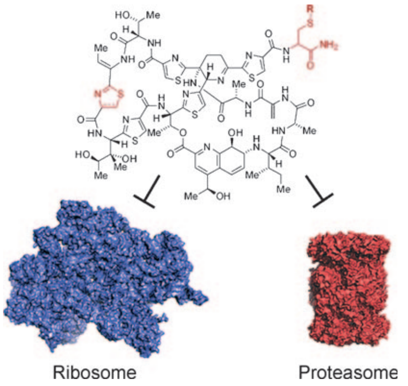

Two birds, one stone: Semisynthetic derivatives of the ribosomal inhibitor thiostrepton display up to ten times higher antiplasmodial activity than the natural product itself. This activity was correlated with selective functional inhibition of the 20S proteasome. Thiostrepton derivatives are now established as novel antimalarials with a dual mode of action and highly promising scaffolds for proteasome inhibitor development.

Natural Products

S. Schoof, G. Pradel,* M. N. Aminake,
B. Ellinger, S. Baumann, M. Potowski,
Y. Najajreh, M. Kirschner,
H.-D. Arndt* ________ **3317 – 3321**

Antiplasmodial Thiostrepton Derivatives: Proteasome Inhibitors with a Dual Mode of Action

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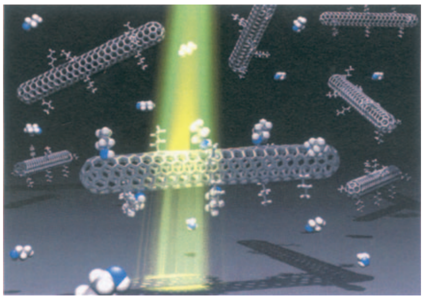
As if nothing had happened: A detailed mechanistic investigation of the nucleophilic addition of organolithium reagents onto single-walled carbon nanotubes (SWCNTs) revealed that the initial functionalization step is part of an equilibrium. Consequently, the functionalization of the sidewalls of SWCNTs is reversible, and the introduced substituents can be detached easily by reduction.



Nanotube Chemistry

Z. Syrgiannis, B. Gebhardt, C. Dotzer,
F. Hauke, R. Graupner,
A. Hirsch* ________ **3322 – 3325**

Reductive Retrofunctionalization of Single-Walled Carbon Nanotubes

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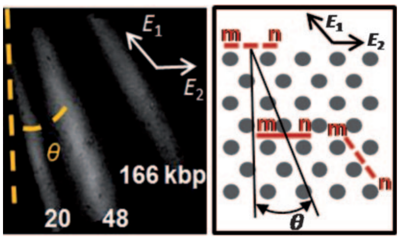
Unbending: Asymmetric pulsed field electrophoresis of DNA was conducted in a nanoporous array formed by colloidal self-assembly of nanoparticles inside a microfluidic system. In confinement smaller than the persistence length of DNA molecules, DNA is maintained in highly stretched conformation. A model correlating pulse frequency, electric field, and molecular size with the observed angular dispersion was developed and experimentally verified.



DNA Electrophoresis

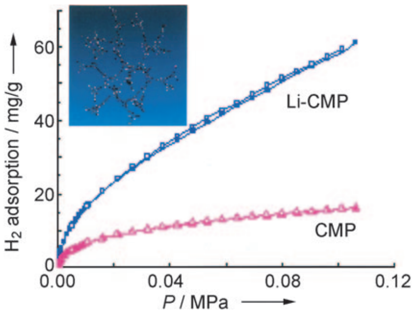
N. Nazemifard, S. Bhattacharjee,
J. H. Masliyah,
D. J. Harrison* ________ **3326 – 3329**

DNA Dynamics in Nanoscale Confinement under Asymmetric Pulsed Field Electrophoresis

Hydrogen Storage

A. Li, R. F. Lu, Y. Wang, X. Wang, K.-L. Han, W.-Q. Deng* ____ **3330 – 3333**

Lithium-Doped Conjugated Microporous Polymers for Reversible Hydrogen Storage

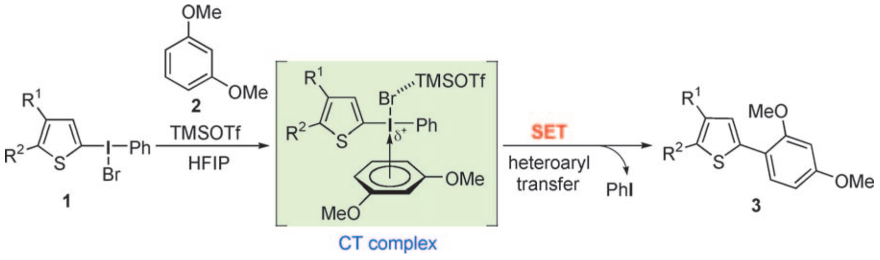


Hi de hi-drogen: An extremely large hydrogen storage capacity is shown by Li-doped conjugated microporous polymers (CMP). These materials have an isosteric enthalpy of hydrogen adsorption up to 8.1 kJ mol^{-1}, and an excellent hydrogen adsorption of 6.1 wt% was achieved at 77 K under an ambient pressure of 0.1 MPa (1 bar).

Aromatic Substitution

T. Dohi, M. Ito, N. Yamaoka, K. Morimoto, H. Fujioka, Y. Kita* ________ **3334 – 3337**

Unusual *ipso* Substitution of Diaryliodonium Bromides Initiated by a Single-Electron-Transfer Oxidizing Process

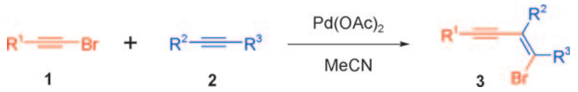


Aromatic substitution: The treatment of diaryliodonium bromides **1** with aromatic nucleophiles **2**, afforded a variety of heteroaryl-containing biaryls **3** in good yields. The *ipso*-substitution process at the heteroaryl ring in **1** occurs through the formation of aromatic cation radicals, which are initiated by the single-electron-transfer (SET) oxidation of **2**. (HFIP = hexafluoroisopropanol)

Synthetic Methods

Y. B. Li, X. H. Liu, H. F. Jiang,* Z. N. Feng ________________ **3338 – 3341**

Expedient Synthesis of Functionalized Conjugated Enynes: Palladium-Catalyzed Bromoalkynylation of Alkynes

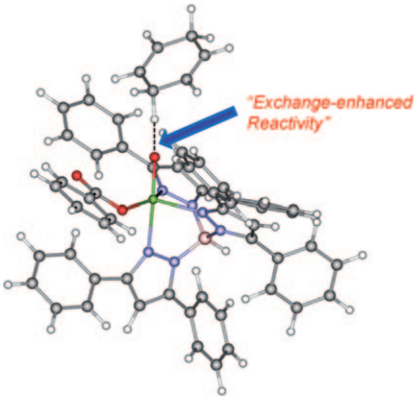


Side by side: Direct *cis* addition of bromoalkynes **1** to various alkynes **2** was found to proceed in the presence of a Pd$^{\mathrm{II}}$ catalyst to give difunctionalized enyne products **3**. The method is facile for the synthesis of bromo alkenynes. Furthermore, an unusual mechanism is proposed.

Nonheme Iron Complexes

D. Janardanan, Y. Wang, P. Schyman, L. Que, Jr.,* S. Shaik* ______ **3342 – 3345**

The Fundamental Role of Exchange-Enhanced Reactivity in C−H Activation by $S=2$ Oxo Iron(IV) Complexes

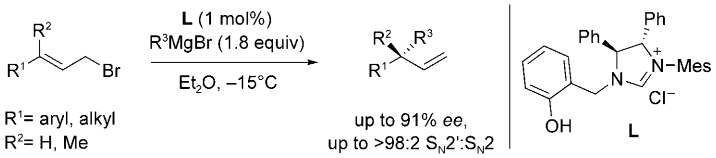


High five: H-abstraction reactivity by oxo iron(IV) complexes with a quintet ground state is greatly enhanced by exchange stabilization arising from the increased number of d–d exchange interactions near the transition state (see picture). It is postulated that nonheme enzymes evolved to make use of this fundamental mechanism in activation of strong C−H bonds.

Asymmetric Catalysis

O. Jackowski, A. Alexakis* ____ **3346–3350**

Copper-Free Asymmetric Allylic Alkylation with Grignard Reagents

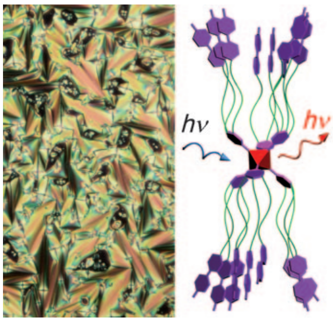


Open wide and say AAA: The copper-free asymmetric allylic alkylation reaction of Grignard reagents, catalyzed by N-heterocyclic carbenes, is reported for allyl bromide derivatives. This reaction offers good enantioselectivity and good to excellent γ regioselectivity, particularly for the formation of quaternary chiral centers (see scheme; Mes = mesityl).

Clustomesogens

Y. Molard,* F. Dorson, V. Cîrcu, T. Roisnel, F. Artzner, S. Cordier* ____ **3351–3355**

Clustomesogens: Liquid Crystal Materials Containing Transition-Metal Clusters

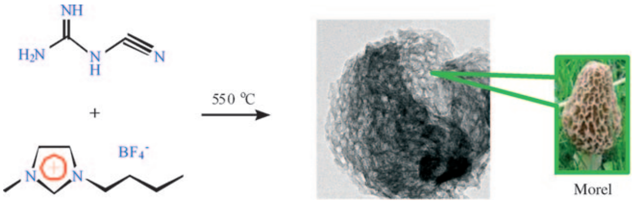


Shining red–NIR light: Bright red–NIR photoluminescent liquid crystals were obtained by grafting six promesogenic units onto an octahedral molybdenum cluster core (see picture). This hybrid self-arranges in a lamellar structure over a wide range of temperatures to give the first clustomesogen.

Mesoporous Materials

Y. Wang,* J. Zhang, X. Wang, M. Antonietti, H. Li* ____ **3356–3359**

Boron- and Fluorine-Containing Mesoporous Carbon Nitride Polymers: Metal-Free Catalysts for Cyclohexane Oxidation

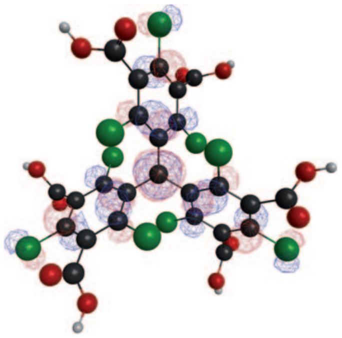


Beefed up with B,F: A boron- and fluorine-enriched carbon nitride polymeric semiconductor was synthesized by a facile one-step process using 1-butyl-3-methylimidazolium tetrafluoroborate as a soft template. The resulting materials show an advantageous “morel-like” mesopore structure (see picture) with narrow pore size distribution and good photoactivity under visible light. The materials are also good catalysts for the selective oxidation of cyclohexane.

Dynamic Nuclear Polarization

C. Gabellieri, V. Mugnaini, J. C. Paniagua, N. Roques, M. Oliveros, M. Feliz, J. Veciana,* M. Pons* ____ **3360–3362**

Dynamic Nuclear Polarization with Polychlorotriphenylmethyl Radicals: Supramolecular Polarization-Transfer Effects

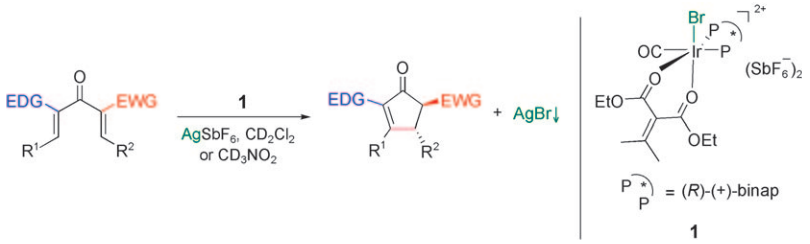


Ups and downs of DNP: Polychlorinated trityl radicals (see structure: C black, Cl green, Na gray, O red) used for dynamic nuclear polarization (DNP) showed a new transfer mechanism involving quadrupolar chlorine nuclei. The observation of positive or negative enhancements, depending on the substrate, highlights the supramolecular character of the initial polarization-transfer process.

Iridium Catalysis

T. Vaidya, A. C. Atesin, I. R. Herrick,
A. J. Frontier,*
R. Eisenberg* ______ **3363 – 3366**

A Highly Reactive Dicationic Iridium(III) Catalyst for the Polarized Nazarov Cyclization Reaction

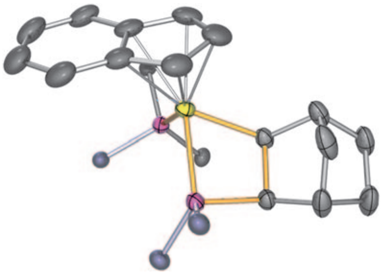


Pushing the Nazarov envelope: An electrophilic complex (**1**; see scheme; EDG = electron-donating group, EWG = electron-withdrawing group, binap = 2,2-bis(diphenylphosphanyl)-1,1-binaphthyl) exhibits unusual catalytic activity in the polarized Nazarov cyclization reaction. Aryl vinyl ketones that show poor reactivity with well-known catalysts can be readily cyclized with **1**/$AgSbF_6$ (1:1) under mild reaction conditions with concurrent AgBr precipitation.

Metallacycles

E. J. Derrah, D. A. Pantazis, R. McDonald,
L. Rosenberg* ______ **3367 – 3370**

Concerted [2+2] Cycloaddition of Alkenes to a Ruthenium–Phosphorus Double Bond

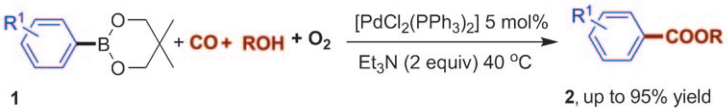


A square deal for Ru=PR$_2$: The Ru=PR$_2$ π bond in a terminal phosphido complex undergoes regio- and stereoselective [2+2] cycloaddition reactions of alkenes to yield metallaphosphacyclobutanes (see structure; P red, Ru yellow, C gray), which are analogous to olefin metathesis intermediates.

Oxidative Carbonylation

Q. Liu, G. Li, J. He, J. Liu, P. Li,
A. Lei* ______ **3371 – 3374**

Palladium-Catalyzed Aerobic Oxidative Carbonylation of Arylboronate Esters under Mild Conditions

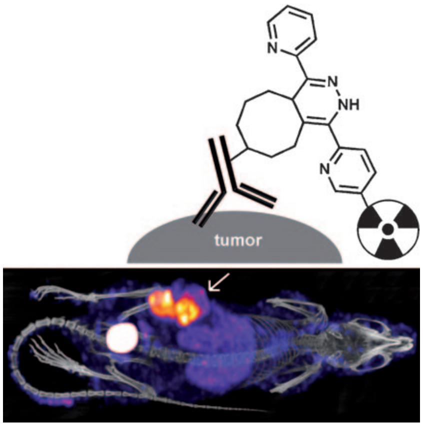


“CO”n Air: The title reaction was carried out using $[PdCl_2(PPh_3)_2]$ as the catalyst precursor under very mild conditions (balloon pressure of CO and air, at 40→50 °C), and produced a wide range of aryl carboxyl esters **2** in good to excellent yields. Remarkable selectivity between oxidative carbonylation and homocoupling of arylboronate esters **1** was also achieved.

Bioorganic Chemistry

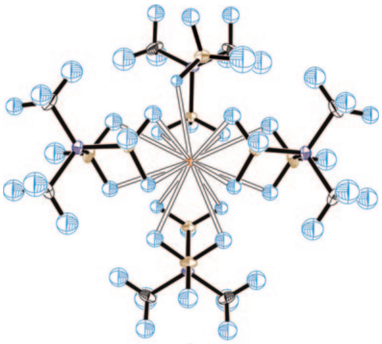
R. Rossin, P. Renart Verkerk,
S. M. van den Bosch, R. C. M. Vulders,
I. Verel, J. Lub,
M. S. Robillard* ______ **3375 – 3378**

In Vivo Chemistry for Pretargeted Tumor Imaging in Live Mice



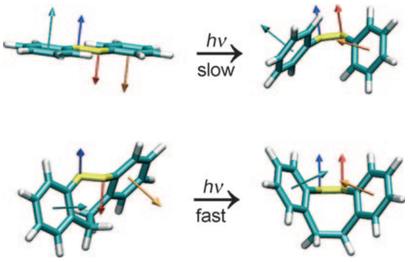
Mice and men: An antibody conjugate with *trans*-cyclooctene was administered to tumor-bearing mice, and the resulting chemically tagged tumors were subsequently treated with an ^{111}In-labeled tetrazine probe in an inverse-electron-demand Diels–Alder reaction. The adduct was formed in a remarkable 52–57 % yield in vivo and used for non-invasive pretargeted tumor imaging in mice (see picture).

Playing with a full deck: Single-crystal X-ray and neutron diffraction data show that the Th center in the title complex **1** (see structure; Th orange, B beige, N purple, C black, H blue) forms bonds with 15 H atoms, thus making **1** the first crystallographically characterized example of a complex with a Werner coordination number of fifteen. DFT calculations suggest that **1** adopts the fully symmetric 16-coordinate structure in the gas phase.



1

Counterintuitively improved photoswitching properties of bridged azobenzene compared to the unbridged counterpart (see picture) were demonstrated recently. Mechanistic insights obtained from non-adiabatic ab initio molecular dynamics reveal that the bridge suitably preorients the phenyl rings and thus enhances the *E*→*Z* quantum yield and shortens the lifetime of the first excited state.



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

A video clip is available as Supporting Information on www.angewandte.org (see article for access details).

Service

Corrigendum

Induced-Fit Binding of the Macrocyclic Noncovalent Inhibitor TMC435 to its HCV NS3/NS4A Protease Target

M. D. Cummings,* J. Lindberg, T.-I. Lin, H. de Kock, O. Lenz, E. Lilja, S. Felländer, V. Baraznenok, S. Nyström, M. Nilsson, L. Vrang, M. Edlund, Å. Rosenquist, B. Samuelsson, P. Raboisson K. Simmen ______________ **1652–1655**

Angew. Chem. Int. Ed. **2010**, *49*

DOI 10.1002/anie.200906696

In the Supporting Information of this Communication (DOI: 10.1002/anie.200906696) the Uniprot accession codes for genotypes **1a** and **1b** are incorrect. The correct codes are B1PBR5_9HEPC (**1a**) and P90191_9HEPC (**1b**).