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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:***

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Author Profile

"Science is fun because it provides a life-long satisfaction of curiosity.
My favorite time of day is dinner (for several reasons) …"
This and more about Jurriaan Huskens can be found on page 10282.

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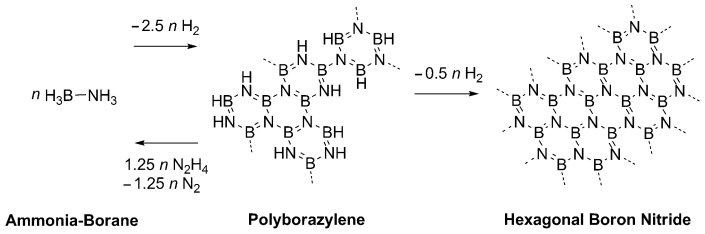
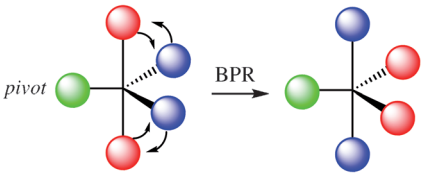
Highlights

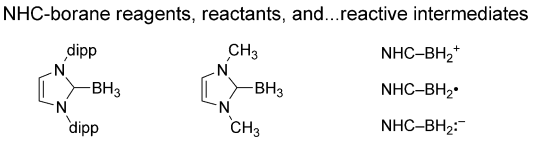


BN working: Under ambient conditions, ammonia-borane (AB) dehydrogenates to polyborazylene, which, in a recent advance, can be readily regenerated in a key step for hydrogen-storage applications (see scheme). In contrast, recent reports show that dehydrogenation of AB under chemical vapor deposition conditions yields atomically thin films of hexagonal BN and their hybrids with graphene.

Same difference: Berry pseutorotation (BPR) and Ugi turnstile rotation, which are generally treated as two distinctly different mechanisms for rearrangement of trigonal-bipyramidal structures, have been shown to be equivalent. Alternative mechanisms consist of sequences of pseudorotations proceeding in a single step.



Reviews



Forget everything you know about boron chemistry ... NHC-boranes (see picture) are different. Functionalities that are not usually present in organoboron compounds can be easily introduced. New classes of rare boron-based reactive intermediates (cations, radicals, and anions) have emerged. And NHC-boranes are promising as reagents and catalysts in organic synthesis and as co-initiators in radical polymerization.

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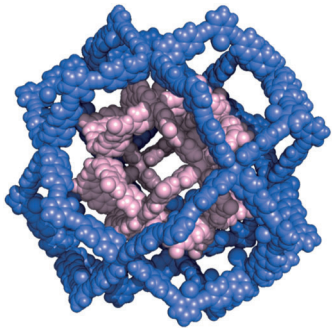
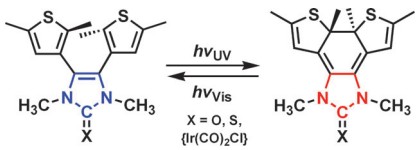
Communications



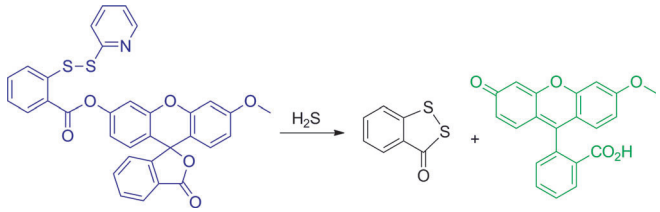
Russian dolls: Two covalently tethered, curved bispyridinyl ligands and Pd^{II} ions have been shown to self-assemble into a sphere-in-sphere complex (6.3 nm in diameter; see X-ray structure). The two ligands did not form heteroleptic mixed complexes, but instead assembled into two distinct homogeneous $[M_{12}L_{24}]$ cuboctahedra, reminiscent of a double-shell viral capsid.

Self-Assembly



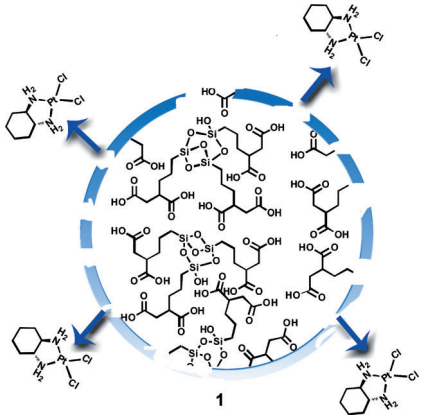
Ligands in the limelight: Light was used to change the electron-donating properties of an N-heterocyclic carbene (NHC) moiety within chalcogen and metal adducts. Photoinduced electrocyclic ring closure of a photochromic 4,5-dithienylimidazolone increased its ν_{CO} frequency. Likewise, UV irradiation of an analogous photochromic [(NHC)Ir(CO)$_2$Cl] complex decreased the carbene's electron-donating ability. Subsequent exposure to visible light reversed both photocyclization reactions.

Photoswitches



Reaction-based sensing: A fluorescent probe for the detection of hydrogen sulfide was prepared and evaluated on the basis of H_2S-mediated benzodithiolone formation. The probe showed good selectivity and sensitivity for hydrogen sulfide.

Sensors



Trigger happy: Polysilsesquioxane (PSQ) nanoparticles that contain a Pt^{IV}-based active agent (**1**; see picture) can be used for the triggered delivery of chemotherapeutics. The cytotoxicity of **1** was superior to that of oxaliplatin against four cancer cell lines in vitro, and targeting further enhanced the cytotoxicity. PEGylated and anisamide-targeted **1** showed drastically superior efficacy to oxaliplatin in inhibiting tumor growth.

Antitumor Agents

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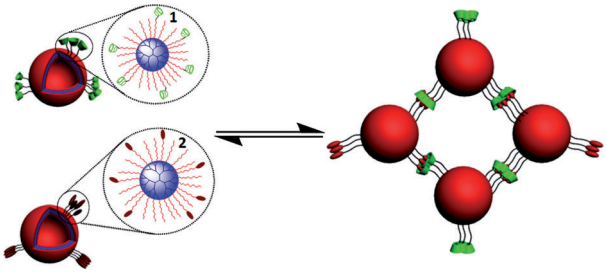
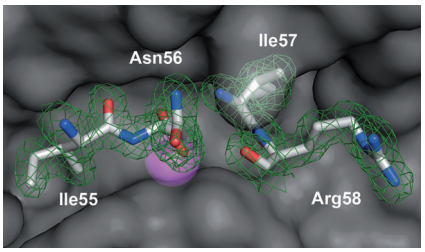


Sleeping giants: As a mimic of cell agglomeration to form tissues, a novel vesicle aggregation process with the characteristic advantages of being highly efficient, light-responsive, reversible, large-scale, and stable is reported. Giant hyperbranched polymer vesicles (5–10 μm) are used as the building blocks (see scheme), and the vesicle aggregates can assemble and disassemble with alternating UV and Vis irradiation.

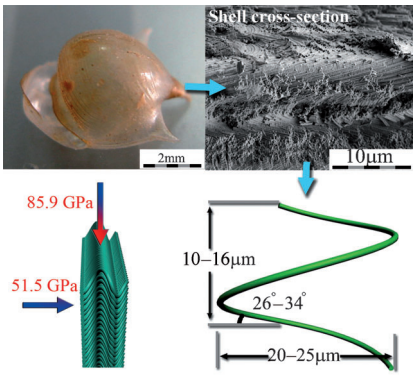
Vesicles



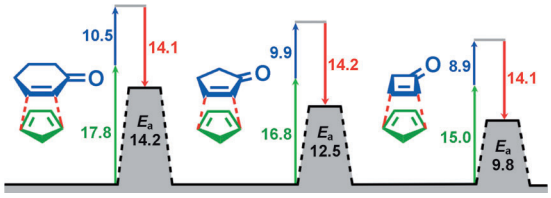
It goes both ways: An unprecedented mechanism of metalloendopeptidase inhibition has been identified for the insect metalloproteinase inhibitor, which is both cleaved and rejoined at bond Asn56–Ile57 by thermolysin under appropriate conditions. A two-product complex is formed after hydrolysis and, simultaneously, a Michaelis complex is poised for synthesis of a peptide bond (see crystal structure).

Peptide-Bond Synthesis

Natural ultrathin flexible armor: Novel hierarchical microstructures composed of densely packed helical aragonite nanofibers were observed in an ultrathin pteropod shell by a combination of techniques. The helical nanofibers are interlocked and crystallographically aligned with a misorientation of up to 10°. These structural features may contribute to its advanced anisotropic mechanical properties.



Biomineralization



Quantum chemical calculations are used to investigate the experimentally measured reactivities of cyclic dienes and cycloalkenones in the Diels–Alder reaction. The interaction energies (red) are nearly constant; differences arise in changes in distortion energies of both dienophile (blue) and diene (green; see picture, E_a = activation energy; values in kcal mol^{-1}).

Cycloaddition

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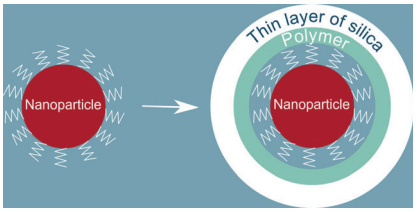
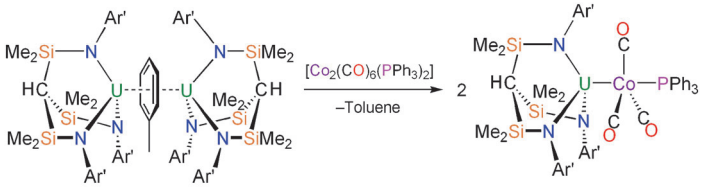


Doubly capped nanocrystals: A new technique was developed for coating of colloidal inorganic nanoparticles with different surface properties with a thin, cross-linked, and functionalized shell containing organic and inorganic layers (see picture). The underlying amphiphilic polymer foundation arranges on the particle surface as predicted in past reports.

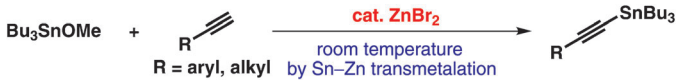
Organic–Inorganic Hybrid Composites



2 3

U–Co bond: Reduction of $[U(Ts^{Xy})(Cl)(thf)]$ [**1**; $Ts^{Xy} = HC(SiMe_2NAr)_3$; $Ar = 3,5\text{-}Me_2C_6H_3$] with KC_8 in toluene afforded the new arene-bridged diuranium complex **2**, whereas reduction of **1** in aliphatic hydrocarbons resulted in C–N bond activation and formation of an imido-aryl complex, which exhibits an unusual ferromagnetic interaction between the two uranium centers. The synthetic utility of **2** was demonstrated by the first synthesis of a U–Co complex, $[U(Ts^{Xy})Co(CO)_3(PPh_3)]$ (**3**).

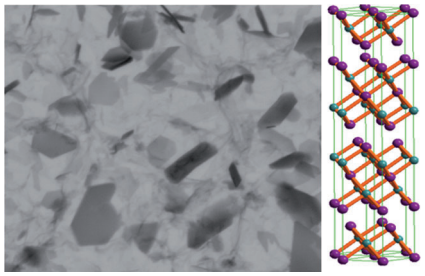
Uranium Arenes



Metal hopping: Various alkynylstannanes were synthesized by the direct reaction of Bu_3SnOMe with terminal alkynes at room temperature in the presence of a $ZnBr_2$ catalyst. Rather than acting as a Lewis acid, $ZnBr_2$ was transmetalated with Bu_3SnOMe to give $Zn(OMe)_2$, which is key to the catalytic reaction.

Stannanes

Bi_2Te_3 nanosheets have been synthesized on Si substrates by surface-assisted chemical vapor transport. The crumpled Bi_2Te_3 sheets grow in the basal plane of the hexagonal structure and are typically ≤ 3 nm in thickness (see picture; Te purple, Bi green). Raman studies found that modes involving atom displacement along the *c* axis that are inactive in the bulk material become Raman-active in the Bi_2Te_3 nanosheets.



Nanosheets

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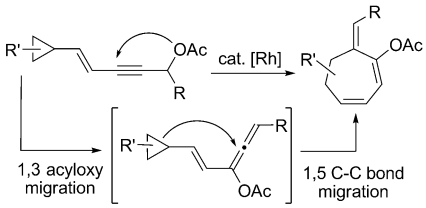
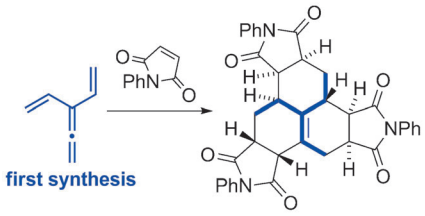
The golden side of rhodium: Highly functionalized seven-membered rings were prepared from substituted cyclopropanes by a Rh^{I}-catalyzed tandem isomerization reaction. The π-acidic Rh^{I} catalyst promoted the formation of an allene intermediate by a 1,3 acyloxy migration of a propargyl ester and a subsequent net 1,5 migration of a cyclopropane C–C bond.



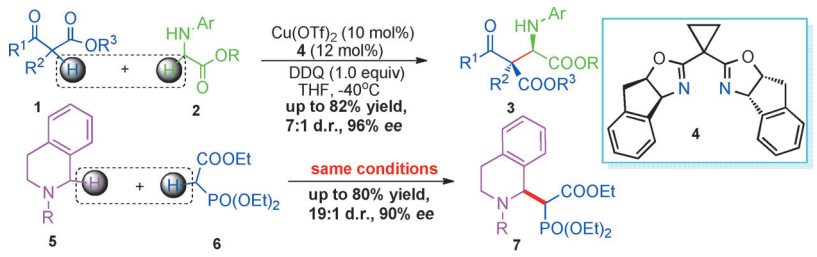
Ring Expansion



- unprecedented triple cycloaddition sequence
- six C–C bonds
- three rings
- eight stereocenters
- high diastereoselectivity

How to hit a triple: The title hydrocarbon, one of the most π-bond-rich small molecules, has been synthesized and characterized for the first time. This highly reactive hydrocarbon undergoes a new diene-transmissive, triple Diels–Alder cycloaddition sequence to form six new C–C bonds and the fused tricyclic phenalene ring system in one step. Controlled single additions have also been achieved.

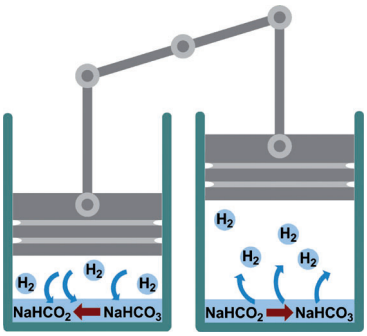
π-Bond-Rich Hydrocarbons



Simple and efficient: A one-pot oxidative and catalytic enantioselective alkylation of α-C_{sp^3}–H bonds adjacent to a nitrogen atom was realized for the first time. This novel strategy provides a simple, efficient, and environmentally friendly access to diverse optically active α-alkyl α-amino acid and C1-alkylated tetrahydroisoquinoline derivatives.

C–H Activation

Soda stream: Sodium bicarbonate was cyclically hydrogenated in aqueous solution to sodium formate at 100 bar H_2 in the presence of a Ru^{II}–sulfonated phosphine catalyst. The system functions as a true charge/discharge device for storage and delivery of hydrogen without the need for isolation of either formate or bicarbonate.



Hydrogen Storage

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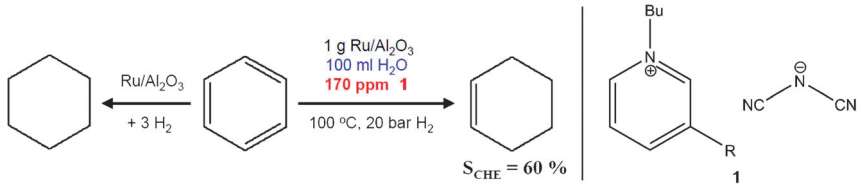
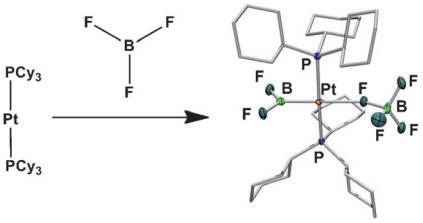


Reducing circumstances: The hydrogenation of benzene in organic phase leads rapidly to cyclohexane. A very simple catalyst system comprising only supported ruthenium in water with the addition of the ionic liquid **1** (R = Me) in the ppm range catalyzes the extremely difficult selective hydrogenation of benzene to cyclohexene. It is not necessary to add large amounts of salt ($ZnSO_4$) or other metals, which is otherwise done to control selectivity.

Heterogeneous Catalysis



A difficult break-up: Boron trifluoride was activated by oxidative addition to the transition-metal complex $[(Cy_3P)_2Pt]$. The product of this addition, *trans*-$[(Cy_3P)_2Pt(BF_2)(FBF_3)]$, was characterized by NMR spectroscopy and crystal structure determination. Furthermore, the degradation product *trans*-$[(Cy_3P)_2Pt(H)(FBF_3)]$ and the stable derivative *trans*-$[(Cy_3P)_2Pt(BF_2)(Cl)]$ were fully characterized.

B–F Activation

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

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

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Service

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Corrigendum

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The authors of this Communication wish to add a second affiliation for Hongwei Huang, Ran He, Wenjiao Yao, and Naixia Zhai as shown below.

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