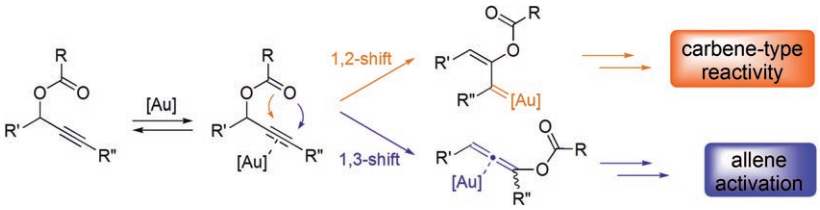
VIP *The following Communications have been judged by at least two referees to be "very important papers" and will be published online at www.angewandte.org soon:*

Obituary

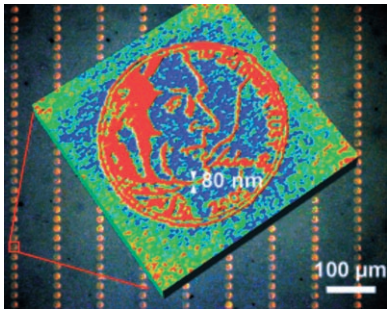
Books

Highlights

Gold Catalysis



Shifty business: The use of propargylic esters in Au-based catalysis results in the synthesis of an impressive variety of products as a function of the pendant groups' functionalities. Skeletal rearrangement by 1,2- and 1,3-migration results in gold–carbene and allene intermediates, respectively.



Neat styles of writing: Recent reports on massively parallel dip-pen nanolithography and further improvements in the resolution of microcontact printing signify that patterning self-assembled monolayers on the submicrometer scale over large areas has now reached a level of sophistication that allows it to rival "hard" lithographic techniques, while retaining the flexibility of using the patterned substrates as a platform for further chemical modification.

Soft Lithography

Contents

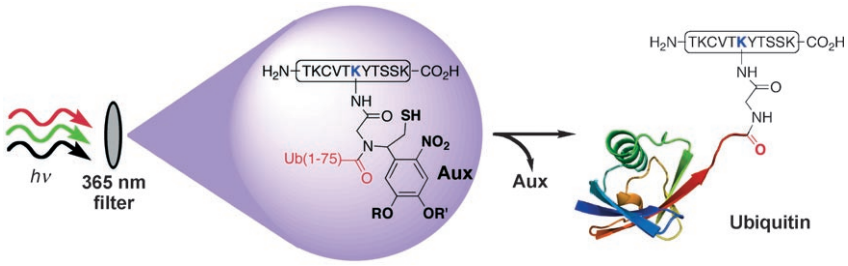
Essays

Periodic law and order: 2007 marks the 100th anniversary of the death of Dmitrii Ivanovich Mendeleev (1834–1907), the Russian chemist best known for formulating the Periodic Table. This Essay looks at Mendeleev in the context of the chemistry and the Russia of his own time and remembers him as the scientist, bureaucrat, and father who died believing that he had begun to put his affairs in order.

Reviews

Universal cross-coupling catalysts: Pd^0 complexes of bulky N-heterocyclic carbene (NHC) ligands show unprecedented substrate scope and high activity. The σ-electron donating NHCs renders the oxidative addition, even into highly functionalized and deactivated substrates, facile whereas the steric bulk expedites reductive elimination. At the same time, the strong Pd–NHC bonds ensure excellent catalyst longevity.

Communications



Lighting up ubiquitylation: A photolytically removable ligation auxiliary (Aux) was employed for the site-specific attachment of ubiquitin (Ub) to one of three lysine residues in a C-terminal peptide fragment of histone H2B (cH2B). Following photolysis, the ligation product was a viable substrate for the ubiquitin C-terminal hydrolase UCH-L3.

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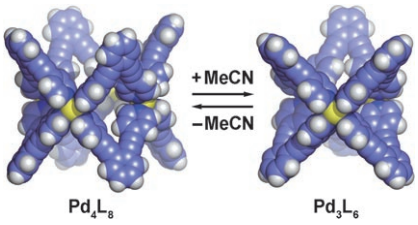
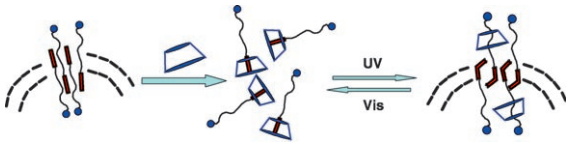


Living in a box: The dynamic self-assembly of Pd_4L_8 and Pd_3L_6 (L = 1,2-bis[2-(pyridin-4-yl)ethynyl]benzene) box-shaped structures is controlled by the solvent (see picture; Pd yellow, C, N blue, H gray). The two structures can be interconverted reversibly and repeatedly by simply switching the medium between DMSO (Pd_4L_8) and MeCN/DMSO (Pd_3L_6).

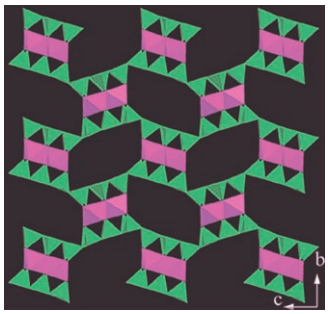
Coordination Compounds



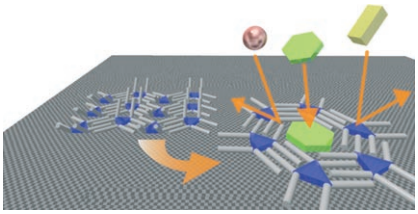
Inclusion and exclusion of an azobenzene-containing surfactant with α-cyclodextrin (α-CD) can be used to fabricate photostimulus-responsive vesicle-like aggregates that can undergo assembly and disassembly reversibly (see picture). The movement of α-CD is like that of a molecular shuttle.

Photoresponsive Vesicles

A microporous indate germanate, prepared under mild solvothermal conditions with an organic amine as structure-directing agent, has a structure in which germanate layers (green) are linked by *cis*-edge-sharing chains of In–O octahedra (pink) to form a framework with 1D 12-ring channels (see picture).

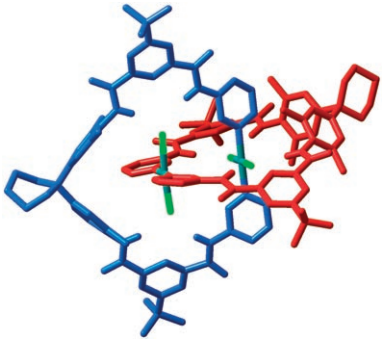


Microporous Materials



Making honeycomb: The addition of guest molecules to a linear nonporous two-dimensional network results in its transformation into a honeycomb porous network. The transformation shows guest selectivity (see picture).

Host–Guest Chemistry



Reversible catenation: A remarkably stable [2]catenane (see picture; Pd turquoise, Cl green) is formed in one step through a combination of first- and second-sphere coordination of a bidentate ligand and the $\{PdCl_2\}$ metal center. The catenated topology of the two rings can be reversibly converted to the non-interlocked macrocyclic products simply by changing the solvent polarity.

Catenanes

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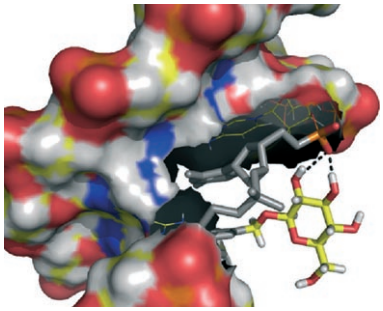
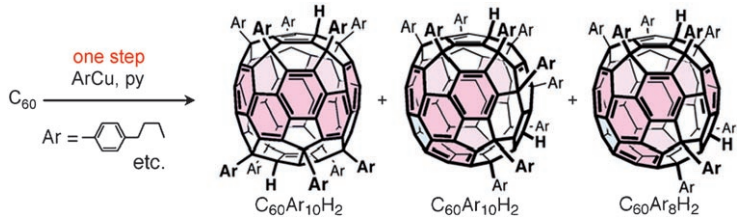


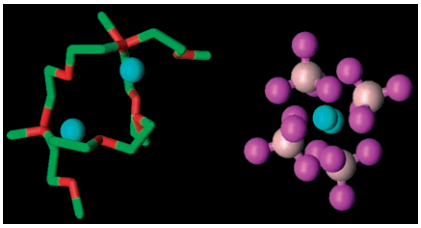
A binding edge? Comparison of dissociation constants and molecular-dynamics snapshots of a panel of synthetic telomeric double-stranded DNA sequences containing HMdU O-glycosides has revealed that the DNA-binding protein of kinetoplastids, such as *Leishmania* and *Trypanosoma*, JBP1, recognizes a critical edge-on conformation of the pyranosyl ring of base J. If this conformation is perturbed, JBP1 binding is dramatically reduced.

Molecular Recognition



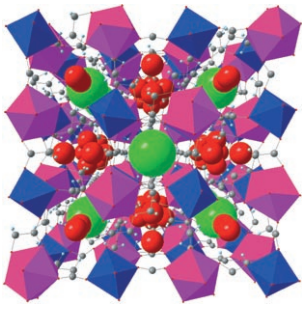
The amount of pyridine (py) is essential for the outcome of the efficient addition of aryl copper compounds to [60]fullerene on a 20-mg to 1-g scale (see scheme). It controls—in addition to the installation of an *ortho*-methyl group on the aryl reagent—the regioselectivity and the number of aryl groups introduced. The tenfold-addition adduct may be further converted into the corresponding double-decker metallocene.

Functionalization of Fullerene



Tunnel route: A new class of solid ionic conductors based on glymes and lithium salts is described. The structure of one example, $(CH_3O(CH_2CH_2O)_4CH_3)_{0.5}$:$LiBF_4$, contains two types of tunnels filled by Li^+ ions, which are lined by tetraglyme molecules or BF_4^- ions, respectively (see picture; Li blue, B pink, C green, O red, F purple).

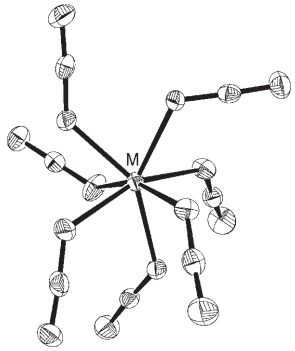
Conducting Materials



All aligned: A cubic $3d^5$–$4f^7$ network of Mn^{2+} and Gd^{3+} ions is assembled by oxydiacetate ($O(CH_2CO_2^-)_2$). The network, which is reminiscent of Prussian blue analogues (see picture; Gd coordination polyhedra: purple, Mn coordination polyhedra: blue, $[Mn(H_2O)_6]^{2+}$: green, H_2O: red), has a weak but definite ferromagnetic interaction.

Ferromagnetic Materials

Contents

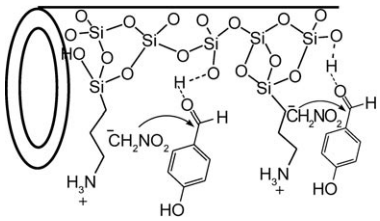


Structures with a bang: The title anions are the first examples of doubly charged heptaazido anions and structurally characterized transition-metal heptaazides. Contrary to the either monocapped octahedral or pentagonal-bipyramidal actinide trianion $[U(N_3)_7]^{3-}$, but in accord with the $[NbF_7]^{2-}$ anion, the title anions have monocapped trigonal-prismatic structures (see picture; M = Nb, Ta).

Group 5 Azides

Taking the tube: A silica-supported palladium catalyst packed into teflon tubing is a simple, low-cost, and effective method for carrying out carbonylative cross-coupling reactions of arylhalides with amines and radiolabeled carbon monoxide gas. In carbonylation reactions, the microtube reactor displays enhanced yields over a short time period (12 min) compared with batch methods.

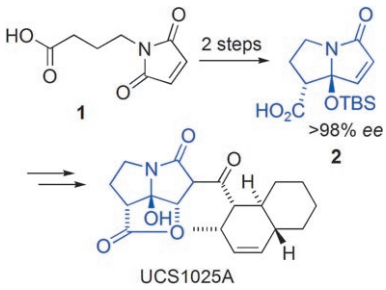
Microfluidic Reactors



Hard graft pays off for Henry: An efficient acid–base bifunctional mesoporous catalyst was prepared by one-step post-synthesis grafting of aminoorganoalkoxysilane groups on mesoporous silica (see picture). The catalyst led to yields of over 99% in the Henry reaction (nitroaldol condensation) of *p*-hydroxybenzaldehyde and nitromethane to form nitrostyrene.

Mesoporous Materials

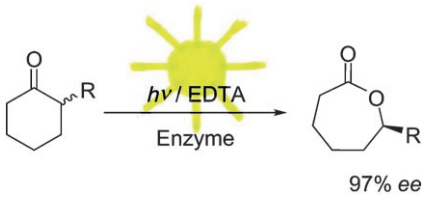
In only two steps the commercially available maleimide **1** is converted into the key pyrrolizidine carboxylic acid unit (**2**) of the telomerase inhibitor UCS1025A. A kinetic resolution through an enantioselective oxa-Michael lactonization and trituration of the resulting scalemic mixture allow for a virtually quantitative separation of a racemate into the enantiomers.



Asymmetric Synthesis

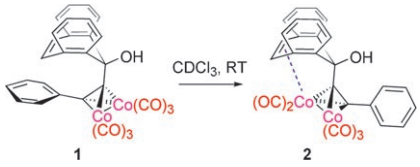
Contents

Let the sunshine in: Light can be used to drive enantioselective Baeyer–Villiger oxidations of cyclic ketones catalyzed by a flavin-dependent enzyme. Photochemical reduction of the flavin using ethylenediaminetetraacetate (EDTA) as the sacrificial electron donor closes the catalytic cycle, thus providing a means to directly regenerate reduced flavin cofactors without the need for costly nicotinamide cofactors as electron donors.

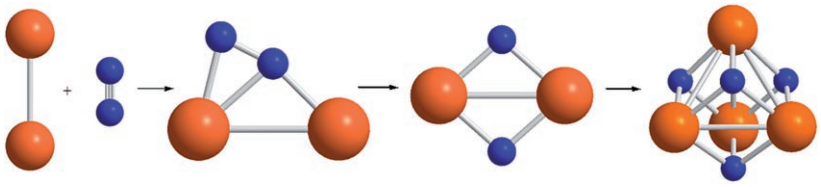


Biocatalysis

Caught in the act: The [(dibenzosuberenol)$Co_2(CO)_6$] cluster **1** (see scheme) loses a carbonyl ligand to yield **2**, the first structurally characterized alkyne–dicobaltpentacarbonyl–alkene complex. This finding provides experimental support for the first step of the proposed mechanism of the Pauson–Khand reaction and yields crucial structural data relevant to computational studies of the process.

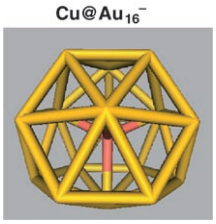


Cobalt–Alkyne Complexes



Building up from scratch: The Gd_2 molecule reacts with N_2 in solid argon to form a homoleptic dinuclear dinitrogen complex containing a drastically activated side-on and end-on bonded N_2 ligand (see scheme; Gd orange, N blue). The complex rearranges to a planar cyclic [Gd(μ-N)$_2$Gd] isomer with a completely cleaved N–N bond, which further dimerizes to form a cubic [Gd_4N_4] cluster, a building block for $(GdN)_x$ nanoparticles.

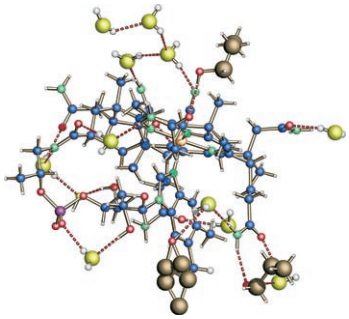
N_2 Activation



Golden cage: The two smallest anionic gold cages, Au_{16}^- and Au_{17}^-, are doped with a Cu atom to give the cluster anions $CuAu_{16}^-$ (see picture) and $CuAu_{17}^-$, respectively. The photoelectron spectra of $CuAu_{16}^-$ and $CuAu_{17}^-$ suggest that the doping does not alter the structures of the parent cages. Theoretical studies confirm that the Cu atom resides in the center of the gold cages, similar to the situation with endohedral fullerenes.

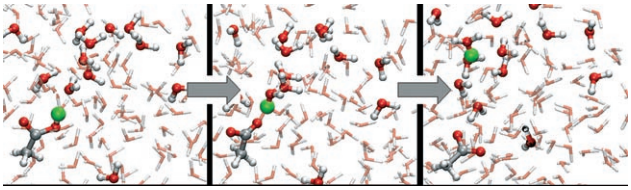
Gold Cages

Contents



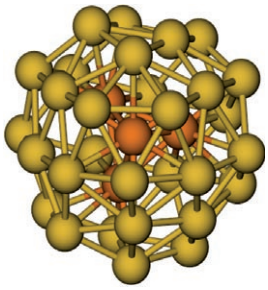
Crystal clear: The experimental charge density of a new solvate of vitamin B_{12} with more than 250 atoms in the asymmetric unit is determined by high-resolution X-ray diffraction. A data set of approximately 660 000 Bragg reflections is interpreted using a combination of the pseudoatom formalism and quantum-chemical models.

Structural Analysis of Biomolecules



Taking the long way home: The dynamic protonation equilibrium between acetic acid and a water box is studied by molecular dynamics simulations. Two types of motion are found: 1) the proton is swapped rapidly between acetic acid and a hydrogen-bonded water molecule (see picture); 2) the proton escapes into the bulk volume and rebinds to acetic acid only at a separation of roughly 5 Å.

Proton Transfer



Gold prospecting: Trapped-ion electron diffraction, photoelectron spectroscopy, and density functional theory are used to establish the structure of the free gold cluster ion Au_{34}^-. The results suggest a chiral cluster with an internal trigonal pyramid and C_3 point symmetry.

Gold Clusters

Supporting information is available on the WWW (see article for access details).

A video clip is available as Supporting Information on the WWW (see article for access details).

Service

