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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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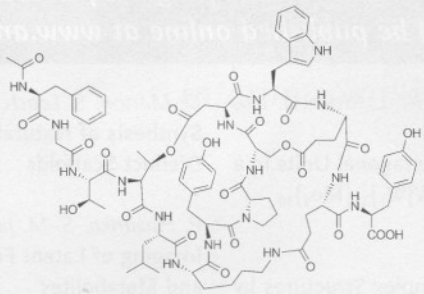
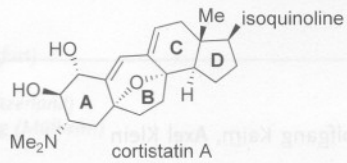
Highlights

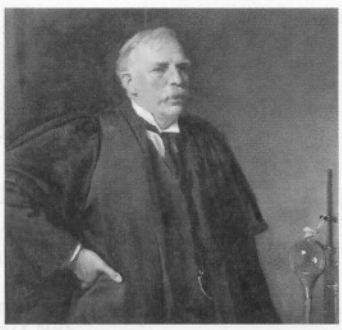


An extended family: The addition of microviridin B (see structure) and trunkamide to the ribosomal peptide biosynthetic family extends the molecular basis of posttranslational modifying reactions to include ω-ester/ω-amide linkage by ATP-grasp ligases (red) and prenylation. The discovery of these novel secondary metabolic reactions may presage the bioengineering of new antimicrobial peptide libraries.



Many routes to the destination: Cortistatins are steroids of marine origin of which cortistatin A has the highest antiangiogenetic action. Several total syntheses of this natural product have recently been achieved, based on biosynthesis, biomimetic synthesis, semisynthesis, and de novo synthesis, which are compared in this Highlight.

Essays



On the shoulders of giants: Lord Rutherford, who developed the theory of nuclear disintegration and a model of the nuclear atom, was lauded as one of the greatest scientists of all time. His research career witnessed the beginning of the atomic age, and his research group was a hotbed of talented, young scientists.

For the USA and Canada:
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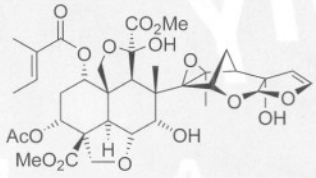
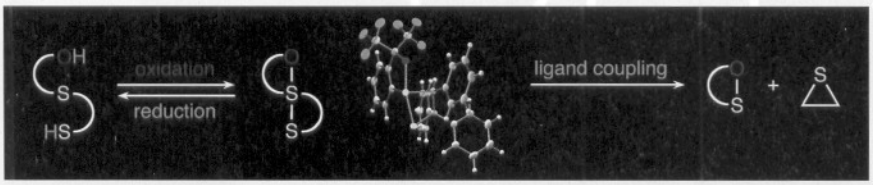
Reviews

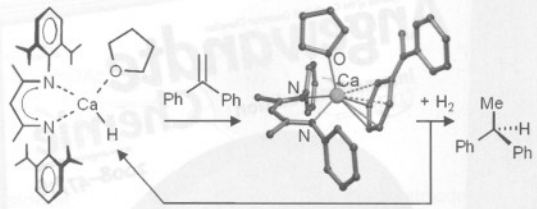


Long and winding road: The natural product azadirachtin (see figure) was first isolated in 1968 from the neem tree, and has been the focus of intense research efforts ever since. With numerous obstacles now overcome, the international efforts towards the total synthesis of this fascinating molecule have now achieved their long-standing goal.

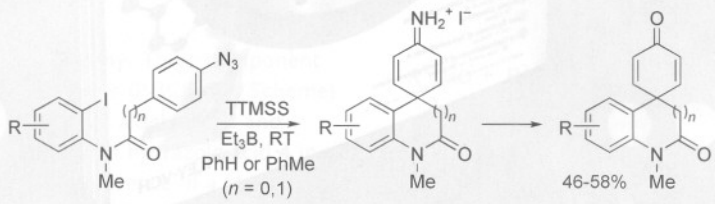
Communications



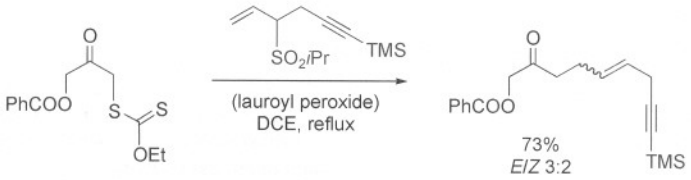
A highly polar hypervalent S^{IV}–S^{II} bond was formed in the synthesis of a sulfur-substituted sulfurane (see scheme), which was crystallographically characterized. Reduction of the 1,2-dithietane gives the corresponding thiol, and reoxidation gives the sulfurane by S–S bond reformation. Thermal decomposition leads to a cyclic sulfenate and a thiirane.



Transition-metal-free hydrogenation of alkenes can be carried out with simple organocalcium catalysts (20 bar H_2, 20 °C). Both steps in the proposed catalytic cycle, hydride addition to the double bond and σ-bond metathesis with H_2, have been confirmed. Alkenes sensitive to polymerization are also hydrogenated in good yields.



***Ipso* easy**: Cyclization of aryl radicals at the *ipso*-position of *p*-azido-substituted benzamides or 2-phenylacetamides results in effective production of spirocyclohexadieniminyl radicals through prompt elimination of molecular nitrogen by transient azidocyclohexadienyl radicals. The resultant iminyl radicals can be exploited for the synthesis of oxindoles or quinolones bearing spiro-cyclohexadienimine/cyclohexadienone rings (see picture, TTMSS = tris(trimethylsilyl)silane).

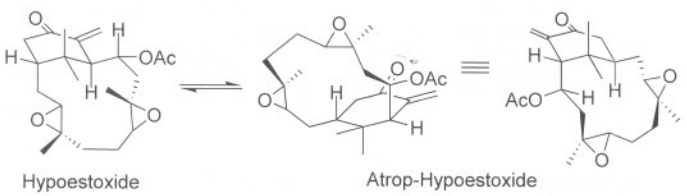


Branching out with sulfones: The use of allyl isopropyl sulfones solves the problem of premature isomerization and allows the radical addition of xanthates to α-branched allyl sulfones (see scheme; DCE = 1,2-dichloroethane, TMS = trimethylsilyl). Highly functionalized structures can thus be rapidly assembled under mild reaction conditions by using cheap and readily available substrates and reagents.

Radical Reactions

In contrast to icosahedral carboranes, instead of deboration, 13-vertex carboranes undergo cage-carbon extrusion and cluster contraction to give icosahedral monocarborane anions on reaction with nucleophiles. In the proposed mechanism, nucleophilic attack on a cage carbon atom cleaves the C_{cage}–C_{cage} bond, new C_{cage}–B bonds form to preserve cluster integrity, and hydrogen migration generates the final icosahedral product (see scheme).

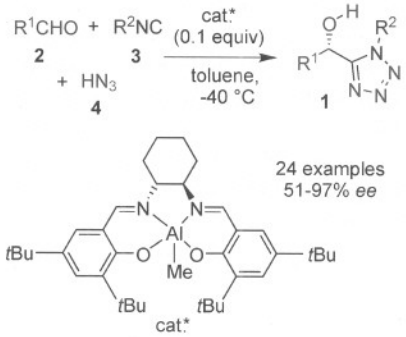
Carboranes



The bicycle works: A versatile route to the verticillane family of natural products has been devised, utilizing a strategically rigidified relay ring-closing metathesis reaction. The shape of the bicyclic product was used to stereoselectively control the bisepoxidation reaction towards hypoestoxide, a member of this natural product family.

Natural Products

Three-part harmony: Three-component Passerini reactions (P-3CR, see Scheme) of a wide range of aldehydes **2** and isocyanides **3**, with hydrazoic acid **4** in toluene, in the presence of a [(salen)-AlMe]-complex catalyst afford 5-(1-hydroxyalkyl)tetrazoles **1** in good-to-excellent yields and enantiomeric excess. A tandem Michael addition/enantioselective P-3CR, using an acrolein substrate, affords highly functionalized tetrazoles.



Asymmetric Synthesis

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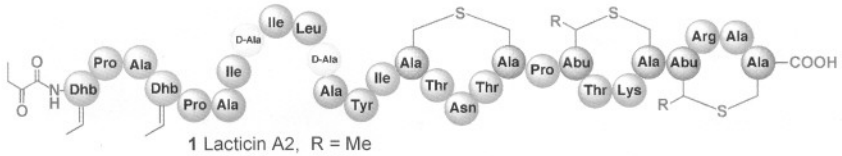
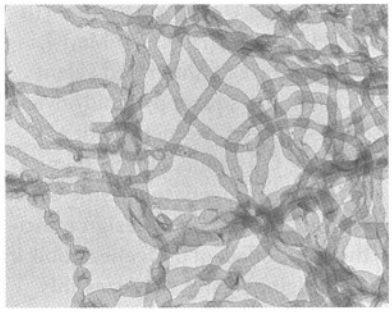


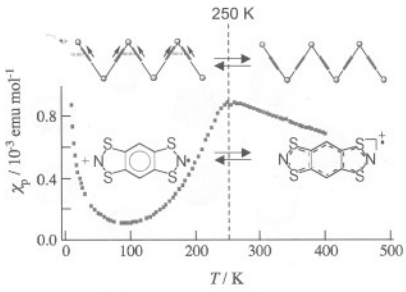
1 Lacticin A2, R = Me
2 Lan A2, R = H

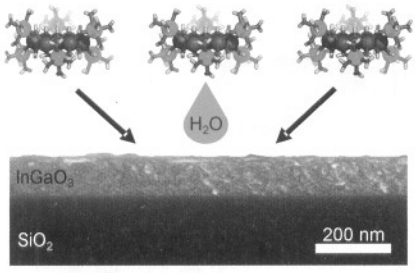
Lan-tastic! A lanthionine analogue of lacticin 3147 A2 (Lan-A2, **2**) containing multiple thioether bridges (see picture) has been successfully synthesized by a combination of solid- and solution-phase peptide synthesis. Chemically synthesized Lan-A2 (**2**) exhibits synergistic biological activity similar to natural lacticin A2 (**1**) in the presence of natural lacticin A1 against Gram-positive bacteria.

Catching the worm: Long myelin-like tubules of a polyethylene oxide-polybutylene oxide block copolymer are kinetically unstable but can be trapped by silica incorporation to produce hybrid nanostructures with high shape anisotropy (see TEM image). Sequestration of mixtures of organosilanes and metal alkoxides or drug molecules in the polymer mesophase gives rise to a range of novel functional nanomaterials.



A magnetic coordination polymer, BBDTA·$InBr_4$, undergoes a spin-Peierls-like phase transition at 250 K. X-ray crystal analysis illustrates that the lattice dimerization accompanies elongation and contraction of the In–N coordination bonds. Inhomogeneity of the spin and charge distribution on the organic radical increases progressively as the temperature decreases below the transition temperature.





Cluster's last stand: The hydrated gallium/indium nanocluster $[Ga_7In_6(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}(NO_3)_{15}]$ was prepared in a facile, high-yielding synthesis. The use of a key nitroso-containing organic compound as an additive allows for the isolation of multiple grams of the cluster. This larger-scale synthesis facilitates use of the cluster as a single-source precursor for effective thin-film transistors.

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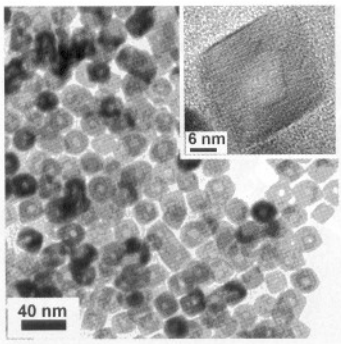
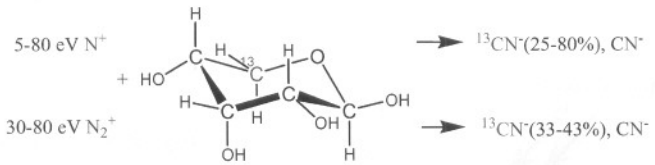


Hollow nan': Hollow face-centered cubic (fcc) Co nanoparallelepipeds were prepared by thermolysis of solid fcc CoO nanoparallelepipeds in oleylamine (see TEM image). The solid fcc CoO nanoparallelepipeds are reduced by the oleylamine surfactant to form hollow fcc Co nanoparallelepipeds. Voids and fcc Co are generated on the surface of the solid fcc CoO nanoparallelepipeds by the removal of oxide as carbon monoxide.

Hollow Nanoparticles

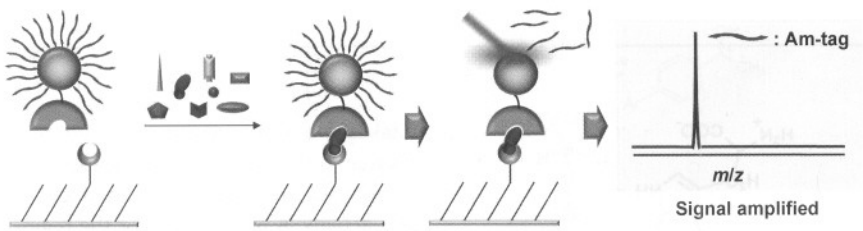


Stealing C: Scattering of hyperthermal nitrogen ions from a D-ribose film efficiently abstracts carbon from the molecule to form CN (see scheme). The reaction is strongly bond and energy selective for C5 of D-ribose in its pyranose form. The sugar moiety of the DNA/RNA backbone will thus be a vulnerable point for damage caused by reactive scattering of secondary atomic nitrogen ions produced by energetic heavy ions.

DNA Damage

Pure and porous: Several hundreds of square meters of enantiopure surface per gram of material were generated by introducing amino acids into periodically ordered mesoporous organosilica materials. The stereochemical nature of the surfaces was probed by measuring adsorption isotherms with chiral gases.

Porous Materials



Small but more than enough: Proteins are detected in solution without additional amplification or labeling steps by using a small molecule as a reporter of the protein (see picture, Am-tag = amplification tag). The combination of self-assembled monolayers on gold with matrix-free laser desorption/ionization time-of-flight mass spectrometry offers ultrahigh sensitivity with a detection limit of several attomoles.

Signal Amplification

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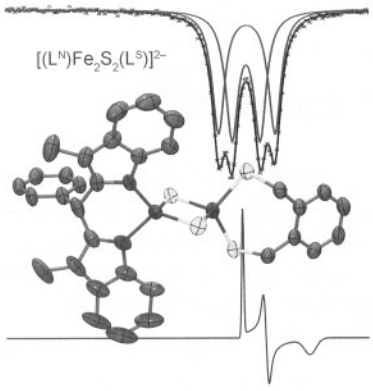
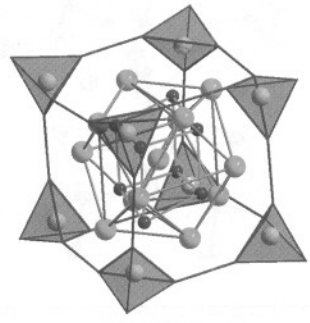


Copycat: An accurate synthetic model for Rieske type [2Fe-2S] cluster has been prepared that emulates structural and spectroscopic features of the natural protein sites, including the characteristic low g_{av} value in the EPR spectra of the reduced $[2Fe\text{-}2S]^+$ species. The picture shows the crystal structure of the molecule (C gray, Fe red, N blue, S yellow), its EPR spectrum after reduction (bottom) and its Mössbauer spectrum (top).

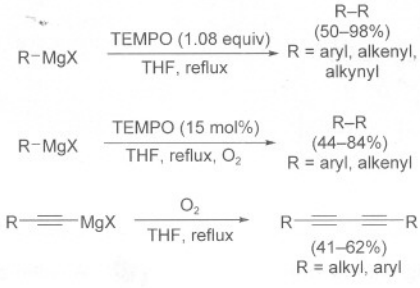
Bioinorganic Chemistry

Not like the others: A molecular palladium oxide cluster was formed by self-assembly of palladium(II) and arsenic(V) using mild reaction conditions. The resulting heteropolypalladate $[Pd^{II}_{13}As^{V}_{8}O_{34}(OH)_6]^{8-}$ has a distorted cubic shape and edge lengths of about 1 nm. The thirteen Pd^{II} ions retain four-coordinate square-planar geometry, in marked contrast to all other known discrete polyoxometalates.

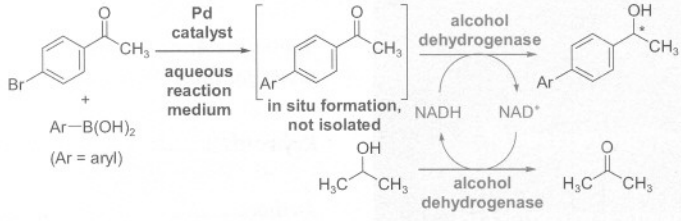


Polyoxometalates

Without a transition metal, unsaturated organomagnesium compounds undergo homocoupling in the presence of a substoichiometric amount of the oxidant 2,2,6,6-tertramethylpiperidine-*N*-oxyl radical (TEMPO) and oxygen. Alkynyl Grignard reagents can even be coupled to give the corresponding diynes with dioxygen in the absence of a catalyst (see scheme).



Synthetic Methods



Two breeds of cat: A palladium-catalyzed Suzuki cross-coupling and an enzymatic reduction with an alcohol dehydrogenase from *Rhodococcus* sp. together enable the efficient and highly enantioselective synthesis of chiral biaryl alcohols in a one-pot process (see scheme).

Aqueous Catalysis

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