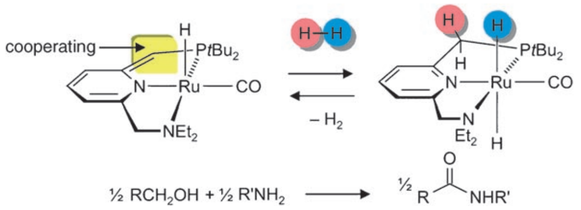
VIP The following Communications have been judged by at least two referees to be "very important papers" and will be published online at www.angewandte.org soon:

News

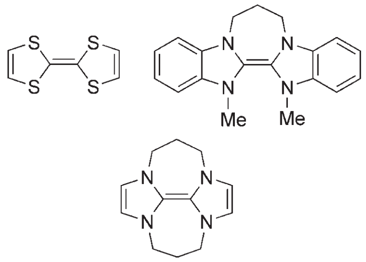
Books

Highlights



Let's stick together: Cooperating ligands participate directly in bond activation and thereby undergo a reversible chemical transformation. The interplay between metal center and ligand may facilitate a chemical process. In transition-metal-catalyzed reactions, this concept allows the discovery of new chemical reactions, such as the dehydrogenative coupling of primary alcohols and primary amines to amides and molecular hydrogen (see scheme).

A new generation of organic compounds (see examples) have been developed and used as single- and double-electron donors. Aryl halides and sulfones can be reduced, and using one particular electron donor, aryl anions can be formed. Up until now these reactions were mainly carried out by metals.



Contents

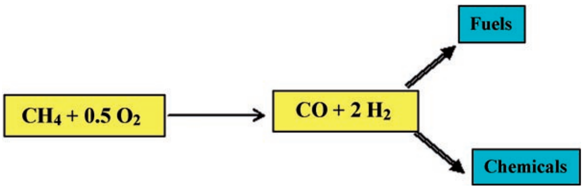
Essays

History of Science

Close, but no cigar. Why didn't Karl Lohmann, the discoverer of ATP, receive the Nobel Prize? This essay describes the life of the prominent biochemist, teacher, and administrator, who wasn't honored with this highest scientific distinction.

Reviews

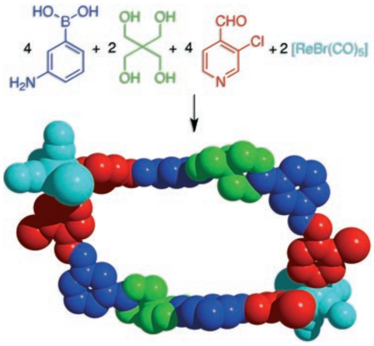
Syngas Production



The commercial catalytic reforming of methane into synthesis gas (syngas), an extremely versatile intermediate, requires the development of efficient heterogeneous catalysts. As long-term performance of the catalyst is crucial for wide-scale commercialization of the oxy reforming process, catalyst-related studies are abundant and are summarized in this Review.

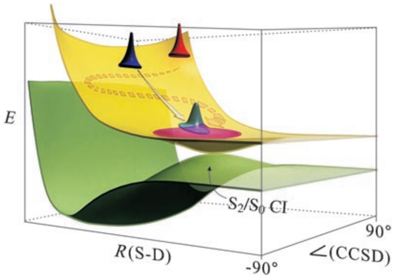
Communications

Supramolecular Chemistry



Simple one-pot reactions: Boronate ester condensation reactions can be combined with imine condensations and metal–ligand interactions to build nanometer-sized macrocycles and cages in one step from small building blocks (see scheme).

For the USA and Canada:
ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals postage paid at Jamaica, NY 11431. US POSTMASTER: send address changes to *Angewandte Chemie*, Wiley-VCH, 111 River Street, Hoboken, NJ 07030. Annual subscription price for institutions: US$ 7225/6568 (valid for print and electronic / print or electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.



Intramolecular orbital alignment can be controlled by conformational tuning of the initial wavepacket location on the two-dimensional potential-energy surfaces of thiophenol (see picture; CI = conical intersection). Chemical substitution induces conformational preference, leading to a dramatic change of the branching ratio between $\tilde{X}$ and $\tilde{A}$ states of the phenylthiyl radical.

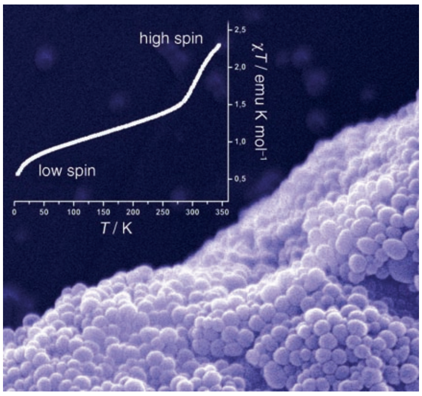
Chemical Dynamics

J. S. Lim, Y. S. Lee,
S. K. Kim* ______ **1853 – 1856**

Control of Intramolecular Orbital Alignment in the Photodissociation of Thiophenol: Conformational Manipulation by Chemical Substitution

---

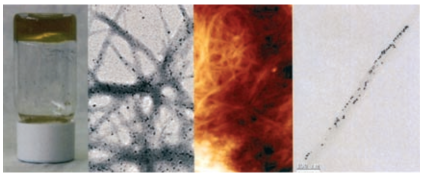
Metal–organic nanoparticles (see SEM image) showing valence-tautomeric behavior have been obtained by a versatile approach involving precipitation and coordination polymerization. They undergo reversible temperature-dependent interconversion between low- and high-spin forms, as revealed by plotting the magnetic moment χ as a function of temperature.



Functional Nanoparticles

I. Imaz, D. Maspoch, C. Rodríguez-Blanco, J. M. Pérez-Falcón, J. Campo,
D. Ruiz-Molina* ______ **1857 – 1860**

Valence-Tautomeric Metal–Organic Nanoparticles



Functionalized gold nanoparticles with complementary H-bonding groups can control the secondary structure of xerogel fibers formed by a molecular conductor thanks to their incorporation into the nanowires, which show metal-like conductivity once doped without the need for annealing. The picture shows a photograph of the xerogel, TEM images of Au particles in the gel and a single fiber, and an AFM image revealing the texture of the gel.

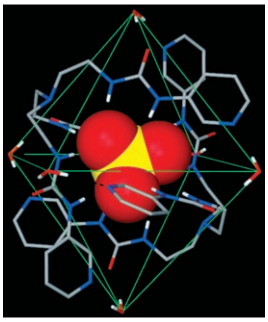
Supramolecular Nanocomposites

J. Puigmartí-Luis, A. Pérez del Pino,
E. Laukhina, J. Esquena, V. Laukhin,
C. Rovira, J. Vidal-Gancedo, A. G. Kanaras,
R. J. Nichols, M. Brust,
D. B. Amabilino* ______ **1861 – 1865**

Shaping Supramolecular Nanofibers with Nanoparticles Forming Complementary Hydrogen Bonds

---

Locked up: The sulfate anion is selectively encapsulated into rigid hydrogen-bonded capsules upon crystallization of a simple and flexible urea-functionalized ligand in the presence of Mg^{2+} ions and water (see structure; sulfate: space-filling). The resulting framework persists in the presence of different-shaped anions, allowing the shape selectivity of hydrogen-bonding hosts to be evaluated, and providing a simple way to separate the environmentally relevant sulfate from highly competitive mixtures of aqueous anions.



Anion Recognition

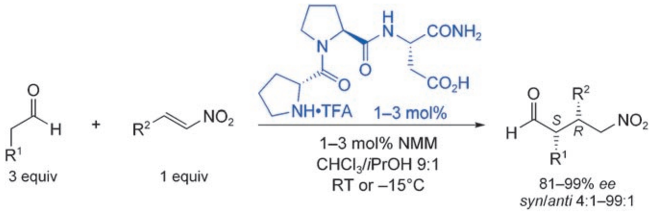
R. Custelcean,* P. Remy, P. V. Bonnesen,
D. Jiang, B. A. Moyer ______ **1866 – 1870**

Sulfate Recognition by Persistent Crystalline Capsules with Rigidified Hydrogen-Bonding Cavities

Peptidic Catalysts

M. Wiesner, J. D. Revell,
H. Wennemers* ——— **1871 – 1874**

Tripeptides as Efficient Asymmetric Catalysts for 1,4-Addition Reactions of Aldehydes to Nitroolefins–A Rational Approach

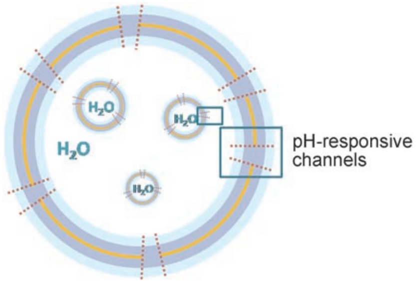


Bridging the gap: Conformational analysis of a peptidic catalyst for aldol reactions led to the development of H-D-Pro-Pro-Asp-NH$_2$ as a highly efficient catalyst for conjugate addition reactions between aldehydes and nitroolefins (see scheme). Only 1 mol% of catalyst suffices to obtain γ-nitroaldehydes in excellent yields and stereoselectivities.

Polymer Vesicles

H.-C. Chiu,* Y.-W. Lin, Y.-F. Huang,
C.-K. Chuang, C.-S. Chern ——— **1875 – 1878**

Polymer Vesicles Containing Small Vesicles within Interior Aqueous Compartments and pH-Responsive Transmembrane Channels



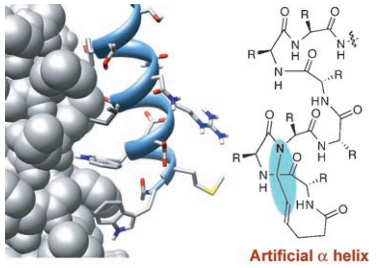
Multivesicle assemblies with pH-responsive transmembrane channels in the vesicle walls (see picture) were made by two-step double emulsion of copolymers comprising acrylic acid and acrylate of 1,2-distearoyl-*rac*-glycerol. These assemblies mimic eukaryotic cells, which contain functional organelles within the cell walls.

α-Helix Mimetics

D. Wang, M. Lu,
P. S. Arora* ——— **1879 – 1882**

Inhibition of HIV-1 Fusion by Hydrogen-Bond-Surrogate-Based α Helices

Inhibition with a twist: An artificial α helix obtained by replacing an N-terminal main-chain *i* and *i*+4 hydrogen bond with a carbon–carbon bond (see structure) inhibits gp41-mediated cell fusion. This work suggests that hydrogen-bond-surrogate-derived helices may provide a general class of scaffolds for the generation of leads against viral entry.



Allyl–Allyl Coupling

S. Porcel, V. López-Carrillo, C. García-Yebra, A. M. Echavarren* ——— **1883 – 1886**

Gold-Catalyzed Allyl–Allyl Coupling

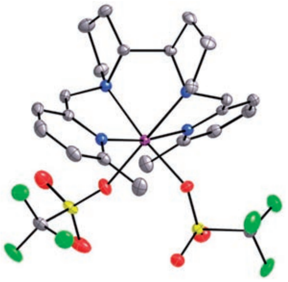
Gold rings: Cationic gold(I) complexes efficiently catalyze the intramolecular allyl–allyl coupling of allyl acetates with allylstannanes with excellent stereoselectivity (see scheme). This reaction is mechanistically very different from that catalyzed by palladium.

Asymmetric Catalysis

K. Suzuki, P. D. Oldenburg,
L. Que, Jr.* ——— **1887 – 1889**

Iron-Catalyzed Asymmetric Olefin *cis*-Dihydroxylation with 97% Enantiomeric Excess

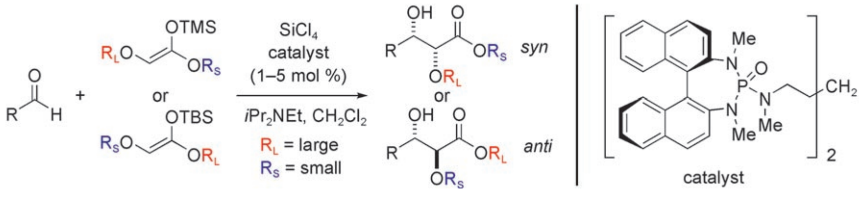
Big *cis*-ster: The use of an (*R*,*R*)-bipyrrolidine backbone with two α-methylpyridine pendant arms affords a tetradentate N$_4$ ligand that coordinates an iron center with *cis*-α topology (see picture; Fe purple, C gray, N blue, O red, S yellow, F green). This complex catalyzes the reaction between H$_2$O$_2$ and *cis*-2-heptene to afford a *cis*-diol product in very high enantioselectivity.



Asymmetric Catalysis

S. E. Denmark,*
W.-j. Chung 1890 – 1892

Lewis Base Activation of Lewis Acids: Catalytic Enantioselective Glycolate Aldol Reactions

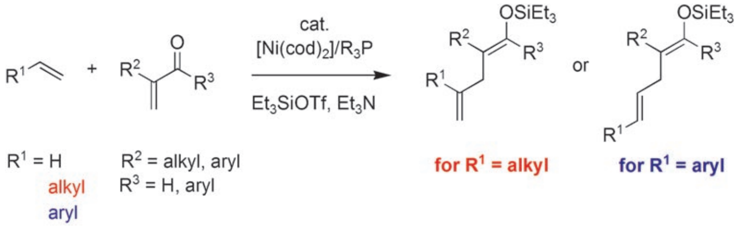


Both *syn*- and *anti*-1,2-diols can be obtained with high diastereoselectivity and enantioselectivity from the properly substituted glycolate-derived silyl ketene acetals in the presence of $SiCl_4$ and a chiral bisphosphoramide catalyst (see scheme; TMS = trimethylsilyl, TBS = *tert*-butyldimethylsilyl). The sense of diastereoselectivity can be reversed by changing the size of the substituents on the silyl ketene acetals.

Catalytic Coupling Reactions

C.-Y. Ho, H. Ohmiya,
T. F. Jamison* 1893 – 1895

α-Olefins as Alkenylmetal Equivalents in Catalytic Conjugate Addition Reactions

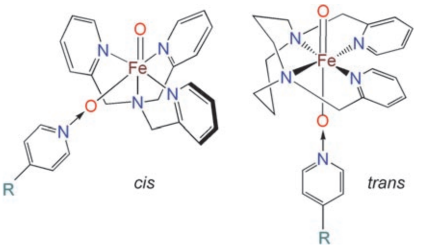


In the presence of a silyl triflate and an amine base, a nickel–phosphine complex catalyzes the direct conjugate addition of ethylene, α-olefins, and aryl alkenes to unsaturated aldehydes and ketones. The enolsilane products are isolated in good to very high yield, and in very high stereoselectivity for some cases. The alkene is a functional equivalent of an alkenylmetal reagent in the transformation.

Iron–Oxo Complexes

Y. Zhou, X. Shan, R. Mas-Ballesté,
M. R. Bukowski, A. Stubna,
M. Chakrabarti, L. Slominski, J. A. Halfen,
E. Münck, L. Que, Jr.* 1896 – 1899

Contrasting *cis* and *trans* Effects on the Reactivity of Nonheme Oxoiron(IV) Complexes



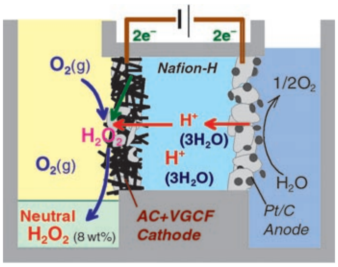
Position determines properties: The oxidative properties of $[Fe^{IV}(O)(L)(X)]$ species (L = tetradentate N_4 ligand, X = monodentate ligand) depend on the position of the X ligand. The Fe=O unit is a poorer oxidant with an electron-donating *cis* ligand but becomes a much better oxidant when this ligand is *trans* to the oxo group. This difference in reactivity reflects perturbations to the electronic structure of the highly covalent Fe=O moiety.

Hydrogen Peroxide Production

I. Yamanaka,* T. Murayama 1900 – 1902

Neutral H_2O_2 Synthesis by Electrolysis of Water and O_2

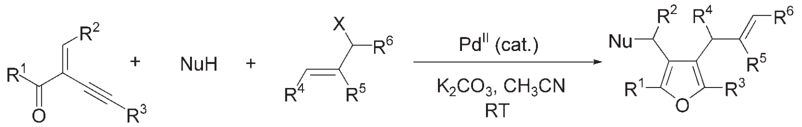
Direct, safe, and continuous synthesis of neutral H_2O_2 solutions with concentrations of up to 8 wt% from O_2 and water has been accomplished by an improved electrolysis method involving a solid-polymer electrolyte (SPE). The formation and accumulation of neutral H_2O_2 were strongly enhanced by exposing the cathode to a stream of O_2.



Furan Synthesis

Y. Xiao, J. Zhang* ________ **1903 – 1906**

Tetrasubstituted Furans by a Pd^{II}-Catalyzed Three-Component Michael Addition/Cyclization/Cross-Coupling Reaction

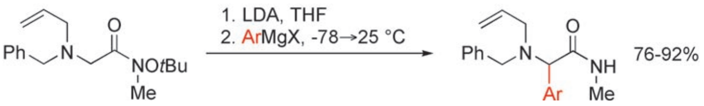


Dual personalities: Pd^{II}-catalyzed three-component Michael addition/cyclization/cross-coupling reaction provides an efficient route to functionalized tetraubstituted furans (see scheme). The [$PdCl_2(CH_3CN)_2$] catalyst plays a dual role in this transformation as both a Lewis acid and a transition-metal center.

Synthetic Methods

S. Hirner, O. Panknin, M. Edefuhr, P. Somfai* ________ **1907 – 1909**

Synthesis of Aryl Glycines by the α Arylation of Weinreb Amides

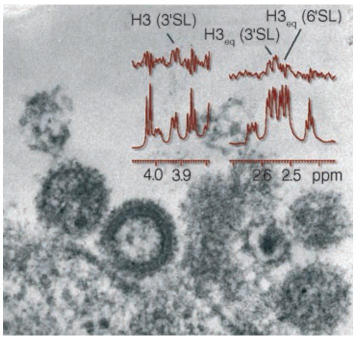


A rare example of the umpolung of an enolate forms the basis of the title reaction. In this procedure, a Grignard reagent is added to the iminium ion formed from the Weinreb amide upon treatment with a base (see scheme). When a chiral amide was used as the starting material, the nucleophilic addition proceeded with high diastereoselectivity. LDA = lithium diisopropylamide.

Avian Influenza

T. Haselhorst, J.-M. Garcia, T. Islam, J. C. C. Lai, F. J. Rose, J. M. Nicholls, J. S. M. Peiris, M. von Itzstein* ________ **1910 – 1912**

Avian Influenza H5-Containing Virus-Like Particles (VLPs): Host-Cell Receptor Specificity by STD NMR Spectroscopy

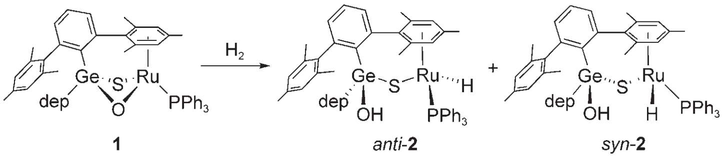


Gripped by the flu: The emergence of a human pandemic influenza virus from an avian progenitor involves a switch in preferential binding of the influenza virus hemagglutinin (HA). Saturation transfer difference NMR spectroscopy of avian H5 chimeric virus-like particles (VLPs) encoding viral HA in a complex with α(2,3)-and α(2,6)-linked *N*-acetylneuraminides (3′SL and 6′SL, respectively) has shown that avian influenza H5-containing VLPs clearly discriminate between α(2,3)- and α(2,6)-linkages.

Dihydrogen Activation

T. Matsumoto, Y. Nakaya, K. Tatsumi* ________ **1913 – 1915**

Heterolytic Dihydrogen Activation by a Sulfido- and Oxo-Bridged Dinuclear Germanium–Ruthenium Complex

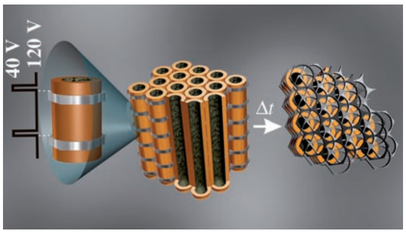


Cooperation of soft and hard bridging ligands (μ-S and μ-O, respectively) is crucial to the mechanism of heterolytic dihydrogen activation by germanium–ruthenium complex **1** to give *syn* and *anti* isomers of the corresponding hydroxogermanium–hydridoruthenium complex **2** (see scheme; dep = 2,6-diethylphenyl).

Electrochemical Nanotechnology

S. P. Albu, D. Kim, P. Schmuki* ________ **1916 – 1919**

Growth of Aligned TiO_2 Bamboo-Type Nanotubes and Highly Ordered Nanolace

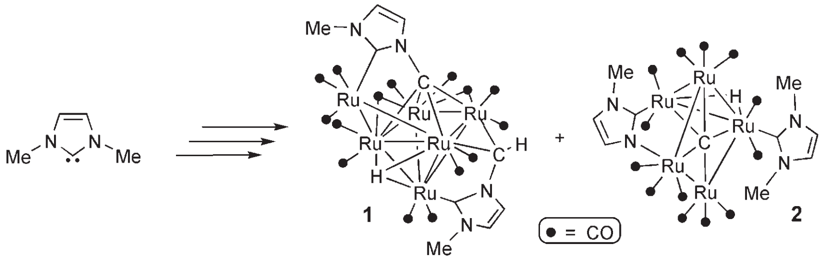


Alternating-voltage anodization of titanium foil in a fluoride-containing electrolyte allowed novel, self-organized nanoscale morphologies of TiO_2 to be grown, such as reinforced nanotubes (nanobamboo) and laterally extended two-dimensional networks (nanolace).

Carbene Heterocycles

J. A. Cabeza,* I. del Río, D. Miguel,
M. G. Sánchez-Vega ______ **1920 – 1922**

From an *N*-Methyl N-Heterocyclic Carbene to Carbyne and Carbide Ligands via Multiple C—H and C—N Bond Activations



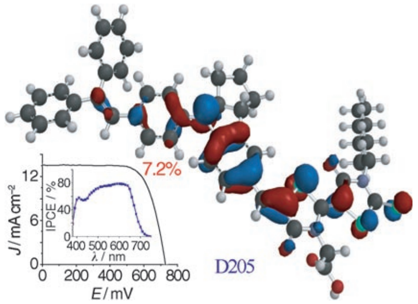
Multiple choices: The carbyne C atom of **1** and the carbide of **2** arise from an *N*-methyl group of 1,3-dimethylimidazol-2-ylidene. The synthesis of complex **1**, which involves activation of the three C—H bonds of an *N*-methyl group, and that of complex **2**, which requires additional activation of the C—N bond, provide new examples of metal-mediated degradation of N-heterocyclic carbenes.

Dye-Sensitized Solar Cells

D. Kuang, S. Uchida, R. Humphry-Baker,
S. M. Zakeeruddin,*
M. Grätzel* ______ **1923 – 1927**

Organic Dye-Sensitized Ionic Liquid Based Solar Cells: Remarkable Enhancement in Performance through Molecular Design of Indoline Sensitizers

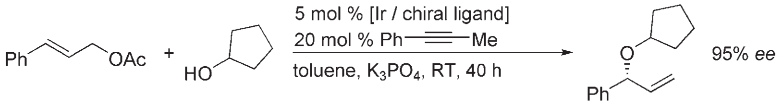
A power conversion efficiency of more than 7.2% under AM 1.5 sunlight (100 mW cm^{-2}) is reported for the first time for an organic-dye-sensitized solar cell used in conjunction with a newly developed binary ionic-liquid (solvent-free) electrolyte (see current–voltage plot and photocurrent action spectrum for the sensitizer D205, the highest occupied molecular orbital of which is shown).



Allylic Etherification

S. Ueno, J. F. Hartwig* ______ **1928 – 1931**

Direct, Iridium-Catalyzed Enantioselective and Regioselective Allylic Etherification with Aliphatic Alcohols

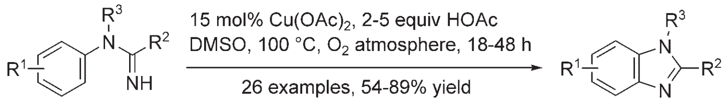


From alcohol to ether: Iridium-catalyzed allylations yield α chiral ether derivatives directly from aliphatic alcohols with a simple alkali metal base (see equation). These reactions form ethers from primary, secondary, and tertiary alkoxides with high enantioselectivity. By-products from isomerization were suppressed by the use of an alkyne additive.

C—H Functionalization

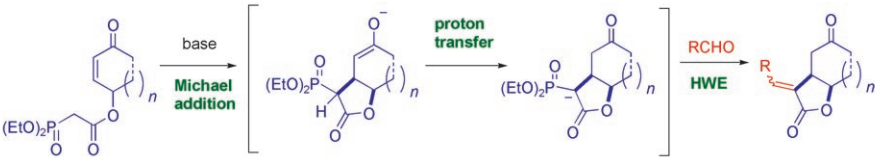
G. Brasche, S. L. Buchwald* **1932 – 1934**

C—H Functionalization/C—N Bond Formation: Copper-Catalyzed Synthesis of Benzimidazoles from Amidines



R^1 = H, Me, CO$_2$*t*Bu, OMe, Hal
R^2 = *ortho* substituted phenyl, *t*Bu
R^3 = H, Me

Copper closes the ring: Benzimidazoles are synthesized from amidines through a copper-catalyzed C—H functionalization/C—N bond-forming process. The method tolerates a broad range of functional groups and provides the benzimidazoles in up to 89% yield. Best results are obtained by using 15 mol% Cu(OAc)$_2$, 2–5 equivalents of HOAc as additive, and oxygen as the stoichiometric reoxidant (see scheme).

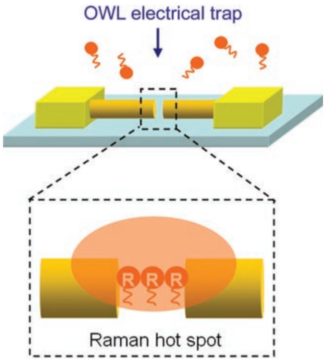


Scoping out TIMO: A telescoped intramolecular Michael addition/proton transfer/Horner–Wadsworth–Emmons olefination sequence was developed to provide rapid access to α-alkylidene-γ-butyrolactones (see scheme). The method was applied to prepare a range of tetrahydrobenzofuran-2,5-diones and related systems, and it was utilized in a short synthesis of enantiomerically pure (+)-paeonilactone B.

Tandem Reactions

M. G. Edwards, M. N. Kenworthy,
R. R. A. Kitson, M. S. Scott,
R. J. K. Taylor* ——— **1935 – 1937**

The Telescoped Intramolecular Michael/Olefination (TIMO) Approach to α-Alkylidene-γ-butyrolactones: Synthesis of (+)-Paeonilactone B

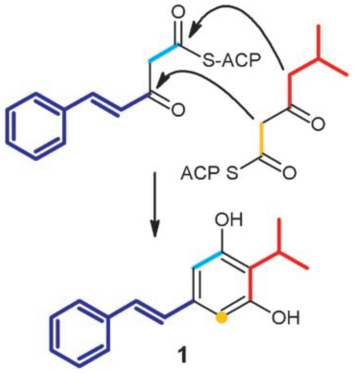


Electrical traps with Raman hot spots: On-wire-lithography (OWL) nanotraps electrically localize DNA in a nanometer-scale gap (see picture, red oligonucleotides with Raman dyes), which allows for the identification of the localized material by surface-enhanced Raman spectroscopy. With microfluidic delivery, sample volumes as small as 1 μL with target concentrations as low as 230 fM can be studied without secondary amplification.

Nanotraps

G. Zheng, L. Qin,
C. A. Mirkin* ——— **1938 – 1941**

Spectroscopically Enhancing Electrical Nanotraps



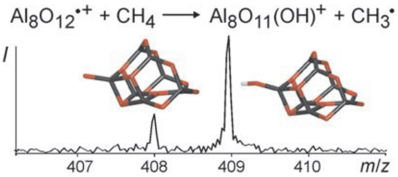
1

Commuting between kingdoms: The biosynthesis of the only nonplant stilbene **1** from *Photorhabdus* bacteria has been solved by identification of all the genes involved in its biosynthesis and by feeding experiments. Stilbene **1** is derived from the condensation of two β-ketoacyl thioesters and is required for the normal development of *Heterorhabditis* nematodes, the natural host of *Photorhabdus*.

Biosynthesis

S. A. Joyce, A. O. Brachmann, I. Glazer,
L. Lango, G. Schwär, D. J. Clarke,*
H. B. Bode* ——— **1942 – 1945**

Bacterial Biosynthesis of a Multipotent Stilbene



A matter of radical sites and bond energies: Experimental and theoretical studies show that the cationic polynuclear aluminum oxide clusters, which are oligomeric systems of $(Al_2O_3)_x^+$ ($x=3$, 4, 5), activate methane at room temperature (see picture). In contrast, clusters with an odd number of aluminum atoms are unreactive.

Methane Activation

S. Feyel, J. Döbler, R. Höckendorf,
M. K. Beyer, J. Sauer,*
H. Schwarz* ——— **1946 – 1950**

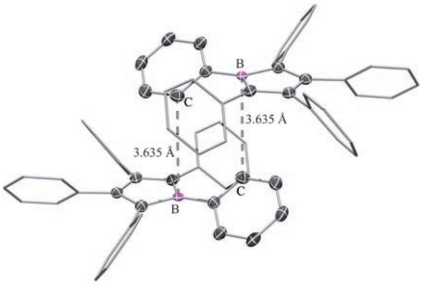
Activation of Methane by Oligomeric $(Al_2O_3)_x^+$ ($x=3,4,5$): The Role of Oxygen-Centered Radicals in Thermal Hydrogen-Atom Abstraction

Boron Heterocycles

H. Braunschweig,* I. Fernández,
G. Frenking,* T. Kupfer ____ **1951 – 1954**

Structural Evidence for Antiaromaticity in Free Boroles

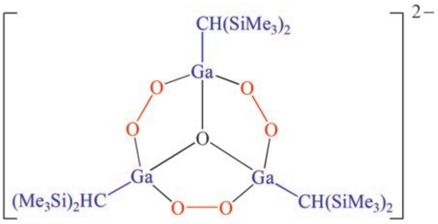
Pentaphenylborole and a ferrocenylborole were synthesized and structurally characterized. Both experimental and theoretical data reveal that rather weak intermolecular interactions are able to significantly alter the bond lengths in the borole ring of pentaphenylborole (see picture). Moreover, the high Lewis acidity of boroles is demonstrated by a significant Fe···B interaction in the ferrocenylborole in the solid state.



Peroxides

W. Uhl,* M. Reza Halvagar _ **1955 – 1957**

Strongly Oxidizing and Reducing Functions Combined in a Single Compound: An Alkyl Gallium Peroxide Possessing a Nine-Membered $(GaR)_3(O_2)_3$ Heterocycle

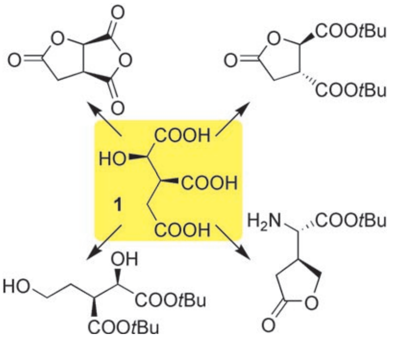


Organoelement peroxides of the heavier Group 13 elements form a class of extraordinarily reactive compounds, which decompose spontaneously by intramolecular redox processes as a result of the close contact of oxidizing peroxo groups and reducing E–C bonds. The synthesis of a unique compound is presented, in which three peroxo ligands bridge three alkyl gallium groups by the formation of a nine-membered heterocycle (see structural formula).

Isocitric Acid

P. Heretsch, F. Thomas, A. Aurich,
H. Krautscheid, D. Sicker,
A. Giannis* ____________ **1958 – 1960**

Syntheses with a Chiral Building Block from the Citric Acid Cycle: (2*R*,3*S*)-Isocitric Acid by Fermentation of Sunflower Oil

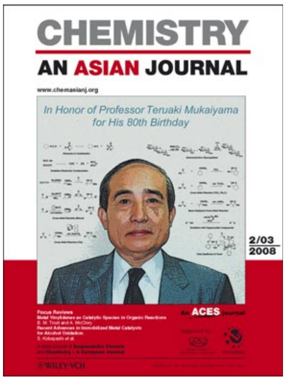


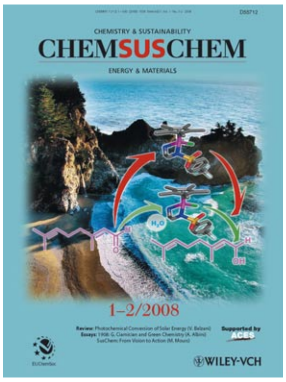
No longer just analytical: Previously, (2*R*,3*S*)-isocitric acid (**1**), a component of the citric acid cycle, had not been available on a preparative scale. A new route to this acid on a kilogram scale combines a biotechnological formation through fermentation from sunflower oil with a chemical separation process. In a variety of transformations into further chiral derivatives, **1** is established as a valuable new member of the chiral pool (see scheme).

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





RSS Feed

Journal content prior to publication in an issue can be found online on our **Early View** page at www.angewandte.org. Stay updated on the latest journal content by registering for our **free e-mail alerts** at http://interscience.wiley.com/alerts.

Keep up with the latest research with our **RSS feed**, which provides the titles, authors, and the Digital Object Identifiers (DOIs) of Early View articles, including links to the full texts. RSS (“Really Simple Syndication”) is an XML-based format for sharing and distributing web content. To receive the RSS feed, just click on the orange feed icon at www.angewandte.org, and visit http://interscience.wiley.com/rss for more information.