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:

C. Costentin, M. Robert, J. Savéant, C. Tard
Inserting a Hydrogen Bond Relay between Proton Exchanging Sites in Proton–Coupled Electron Transfers

*Q. Liu, G. Li, J. He, J. Liu, P. Li, A. Lei**
Palladium–Catalyzed Aerobic Oxidation and Carbonylation of Arylboronate Esters under Mild Conditions

A. C. Filippou, O. Chernov, K. W. Stumpf, G. Schnakenburg*
Metal–Silicon Triple Bonds: The Molybdenum Silylidyne Complex [Cp(CO)$_2$Mo=SiR]

K. Meister, J. Niesel, U. Schatzschneider, N. Metzler-Nolte,* D. A. Schmidt, M. Havenith**
Metal–Carbonyl Complexes as a Method for Label-Free Live-Cell Imaging by Raman Microspectroscopy

*A. C. M. Ferreon, C. R. Moran, J. C. Ferreon, A. A. Deniz**
Parkinson's–Related Mutation Alters the α–Synuclein Folding Landscape

*A. Wilbuer, D. H. Vlecken, D. J. Schmitz, K. Kräling, K. Harms, C. P. Bagowski, E. Meggers**
Iridium Complex with Antiangiogenic Properties

*R. Rose, S. Erdmann, S. Bovens, A. Wolf, M. Rose, S. Hennig, H. Waldmann, C. Ottmann**
Identification and Structure of Small-Molecule Stabilizers of 14-3-3 Protein–Protein Interactions

*A. Schlossbauer, S. Warncke, P. E. Gramlich, J. Kecht, A. Manetto, T. Carell, T. Bein**
A Programmable DNA-Based Molecular Valve for Colloidal Mesoporous Silica

Author Profile

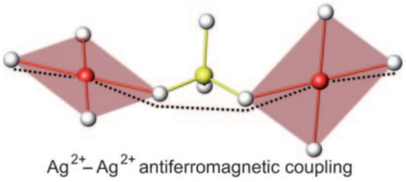
"I chose chemistry as a career because it is a nice combination of theory and practice.
I would have liked to have discovered football! ..."
This and more about Pier Giorgio Cozzi can be found on page 3110.

Books

Computational Inorganic and Bioinorganic Chemistry

Edward I. Solomon, Robert A. Scott, R. Bruce King

Highlights



The new complex silver(II) oxide AgSO$_4$ was synthesized by a methathetic reaction of Ag(SbF$_6$)$_2$ and K$_2$SO$_4$ in anhydrous HF at −80 °C or by the reaction of AgF$_2$ with H$_2$SO$_4$ at −35 °C. The magnetic moments of the rectangular planar coordinated Ag^{2+} ions in AgSO$_4$ are antiferromagnetically coupled to the chains through the O–O edges of the sulfate ions (see picture). The Ag^{2+}–Ag^{2+} super-superexchange interaction is unusually strong.

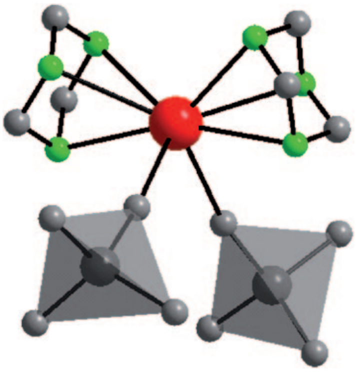
Silver(II)

Contents

Organolanthanides

G. Meyer* ______ **3116 – 3118**

Heteroleptic Samarium(II) Complexes by Base-Induced Reduction



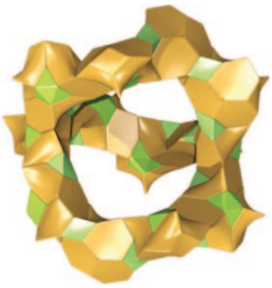
From SIR to BIR: Following the concept of the sterically induced reduction (SIR), the base-induced reaction (BIR) has now been discovered. [Sm(AlMe$_4$)$_3$] reacts with the bulky base 1,3,5-tricyclohexyl-1,3,5-triazacyclohexane (TCyTAC) in benzene to give [(TCyTAC)$_2$Sm^{II}(AlMe$_4$)$_2$] (see picture; Sm red, Al dark gray, N green, C light gray) and ethane, and is in competition with C–H activation yielding [TCyTAC)$_2$Sm{CH(AlMe$_3$)$_3$}] and methane.

Reviews

Zeolite Structures

J. Jiang, J. Yu, A. Corma* ___ **3120 – 3145**

Extra-Large-Pore Zeolites: Bridging the Gap between Micro and Mesoporous Structures



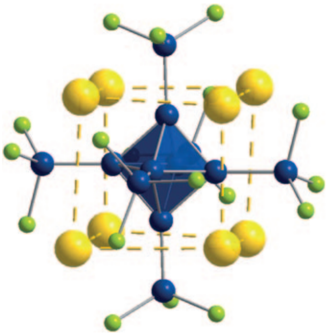
Zeolite XXL: Extra-large-pore zeolites (see structure) have been sought for a long time for their potential ability to support the reactions of bulkier molecules. This Review presents the role of synthesis parameters (effects of structure-directing agent, heteroatom, gel concentration, mineralization agents, etc) in producing extra-large-pore zeolites and includes the first mesoporous zeolites and their catalytic applications.

Communications

Solid-State Structures

P. Henke, N. Trapp, C. E. Anson,
H. Schnöckel* ______ **3146 – 3150**

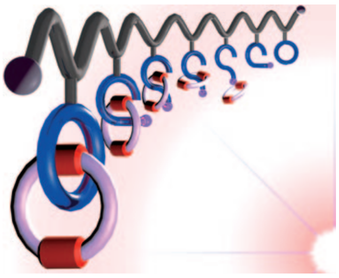
Al$_{12}$K$_8$[OC(CH$_3$)$_3$]$_{18}$: A Wade, Zintl, or Metalloid Cluster, or a Hybrid of All Three?



A molecular Zintl phase? Structural investigations and DFT calculations on the spectroscopic and thermodynamic properties of an Al$_{12}$K$_8$(O*t*Bu)$_{18}$ compound (see picture: Al blue, K yellow, O green) support the unusual bonding of this Al$_{12}$ cluster and its role in a unified cluster model.

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*, Journal Customer Services, John Wiley & Sons Inc., 350 Main St., Malden, MA 02148-5020. Annual subscription price for institutions: US$ 9442/8583 (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.

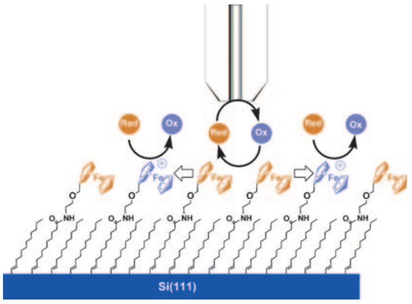
Thermodynamic cat attacks! Iodide-catalyzed reversible nucleophilic attacks have been exploited to access side-chain polycatenanes under thermodynamic control. Multiple catenations occurring all along the polymer chain are entirely driven to completion by the intra- and intermolecular side-chain $\pi\cdots\pi$ stacking interactions of contiguous catenanes.



Template-Directed Synthesis

M. A. Olson, A. Coskun,
L. Fang, A. N. Basuray,
J. F. Stoddart* ―――――― **3151 – 3156**

Polycatenation under Thermodynamic Control



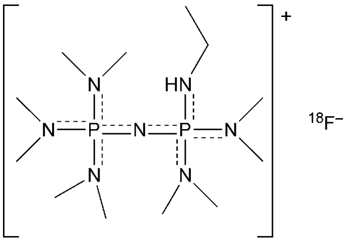
Controlling communication: The electronic communication between ferrocenyl centers bound to insulating silicon surfaces can be efficiently controlled; scanning electrochemical microscopy (SECM) shows that both the surface coverage of the electroactive units and the nature of the redox mediator allow for this control. The lateral charge propagation can be precisely tuned from an extremely slow to a very fast process.

Electron Transfer

D. Zigah, C. Herrier, L. Scheres,
M. Giesbers, B. Fabre,* P. Hapiot,
H. Zuilhof* ―――――― **3157 – 3160**

Tuning the Electronic Communication between Redox Centers Bound to Insulating Surfaces

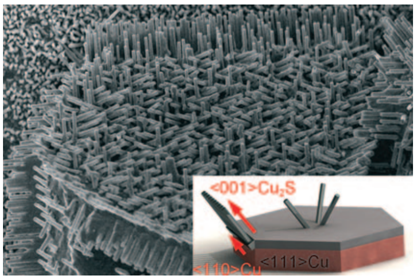
Doing without water: The ^{18}F labeling of radiopharmaceuticals requires nearly anhydrous solutions of [^{18}F]fluoride. Aqueous K_2CO_3 is generally used to elute [^{18}F]fluoride from an anion-exchange resin. Replacing aqueous K_2CO_3 with strong organic bases, such as the phosphazene base P_2Et (conjugate acid shown), enabled the recovery of highly reactive [^{18}F]fluoride and avoided the azeotropic evaporation of water, which is very difficult on a microchip device.



Radiofluorination

C. F. Lemaire,* J. J. Aerts, S. Voccia,
L. C. Libert, F. Mercier, D. Goblet,
A. R. Plenevaux, A. J. Luxen **3161 – 3164**

Fast Production of Highly Reactive No-Carrier-Added [^{18}F]Fluoride for the Labeling of Radiopharmaceuticals



Designer stubble: The growth of Cu_2S nanowires was found to be governed by the diffusion of copper ion vacancies. The resulting nanostructure morphologies depend on the defect density in the copper substrate. Balanced sulfur feeding produced uniform and aligned Cu_2S nanowires (see picture) that hold great promise in converting solar energy at high efficiencies.

Nanostructures

X. Liu, M. T. Mayer,
D. Wang* ―――――― **3165 – 3168**

Understanding Ionic Vacancy Diffusion Growth of Cuprous Sulfide Nanowires

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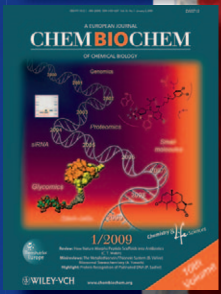

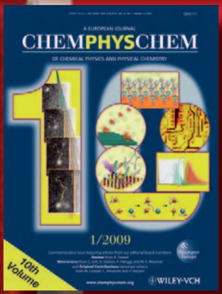

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Jean-Marie Lehn
Nobel Prize 1987


Roger Y. Tsien
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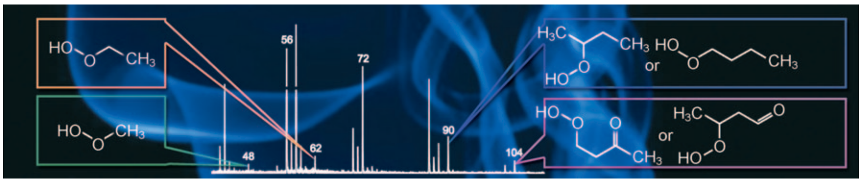
Hydroperoxides

F. Battin-Leclerc,* O. Herbinet,
P.-A. Glaude, R. Fournet, Z. Y. Zhou,
L. L. Deng, H. J. Guo, M. F. Xie,
F. Qi* ———— **3169 – 3172**

Experimental Confirmation of the Low-Temperature Oxidation Scheme of Alkanes

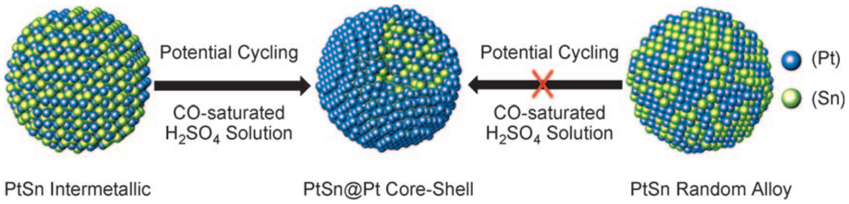


Intermediate detected: The design of internal combustion engines relies on a good understanding of the mechanism of the auto-ignition of hydrocarbons. A key assumption of this mechanism, which was commonly accepted but never proven, has now been experimentally demonstrated: the formation of ketohydroperoxides has been observed under conditions close to those actually observed before the auto-ignition.

Core–Shell Nanoparticles

Z. Liu, G. S. Jackson,
B. W. Eichhorn* ———— **3173 – 3176**

PtSn Intermetallic, Core–Shell, and Alloy Nanoparticles as CO-Tolerant Electrocatalysts for H_2 Oxidation

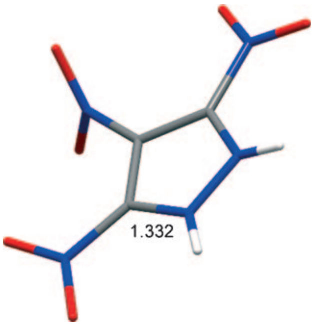


More order, more tolerance: PtSn intermetallic and alloy nanoparticles (NPs) were prepared by the co-reduction of $[Pt(acac)_2]$ (acac = acetylacetonate) and $SnCl_4$. The intermetallic NPs can convert to PtSn@Pt core–shell NPs after potential cycling in CO-saturated H_2SO_4 solution. Electrochemical studies demonstrated the core–shell and intermetallic electrocatalysts had substantially higher CO tolerance than PtSn alloy, PtRu alloy, and monometallic Pt.

Nitrated Heterocycles

G. Hervé, C. Roussel,
H. Graindorge* ———— **3177 – 3181**

Selective Preparation of 3,4,5-Trinitro-1*H*-Pyrazole: A Stable All-Carbon-Nitrated Arene

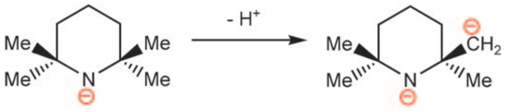


Lowering the boom: 3,4,5-trinitro-1*H*-pyrazole (TNP, see picture) has been prepared by the unexpected nitration of 3,5-dinitropyrazole with a super-electrophile generated from 20–30% sulfuric oleum mixed with nitric acid. The remarkable stability of TNP results from the preservation of the ring geometry and the specific conformation of the nitro group at C4 which confers low acidity on the material.

Organometallic Reagents

B. Conway, A. R. Kennedy,
R. E. Mulvey,* S. D. Robertson,
J. G. Álvarez ———— **3182 – 3184**

Structurally Stimulated Deprotonation/Alumination of the TMP Anion



Coerced conversion: Long utilized as a strong Brønsted base, the tetramethylpiperidine (TMP) anion is forced to convert to a Brønsted acid in the presence of a potassium–aluminate species. The new compound [(TMEDA)K(μ-TMP*)(μ-*i*Bu)Al(*i*Bu)] was obtained where TMP* represents a CH_3- and NH-deprotonated dianionic variant of TMP (see scheme).

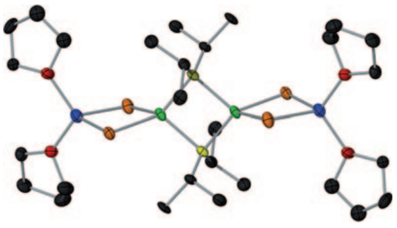
Contents

Turbo-Grignard Reagents

D. R. Armstrong, P. García-Álvarez,*
A. R. Kennedy, R. E. Mulvey,*
J. A. Parkinson ______ **3185–3188**

Diisopropylamide and TMP Turbo-Grignard Reagents: A Structural Rationale for their Contrasting Reactivities

Turbocharged! A neutral dimeric molecule in crystal form, the diisopropylamido turbo-Grignard reagent "(iPr$_2$N)MgCl·LiCl" (see structure; blue N, red O, green Mg, yellow Cl, black C) separates into several charged ate species in dynamic exchange with each other in THF solution as determined by a combination of EXSY and DOSY NMR studies.

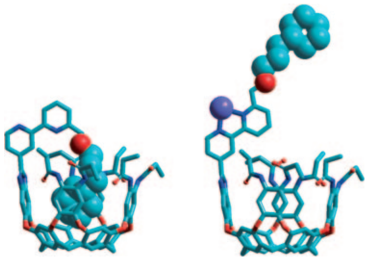


Self-Hosting Cavitand

F. Durola, J. Rebek, Jr.* ______ **3189–3191**

The Ouroborand: A Cavitand with a Coordination-Driven Switching Device

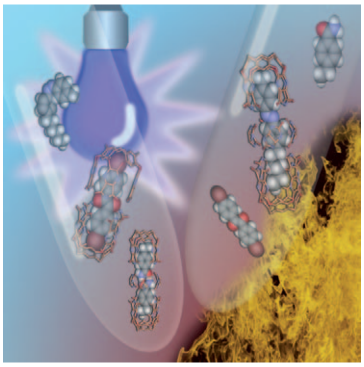
Molecular switch: The ouroborand coordinates an internal side chain in its cavity, just as it were swallowing its own tail. The presence or absence of zinc(II) in solution switches the cavity between open and closed states to external guests (see scheme: deep blue sphere: Zn).



Host–Guest Chemistry

H. Dube, D. Ajami,
J. Rebek, Jr.* ______ **3192–3195**

Photochemical Control of Reversible Encapsulation



Remote control: Molecules can be transferred in a chemical system between capsules and bulk solution by using light and heat. The principle is based on the isomerization of azobenzene, the *trans* isomer of which is encapsulated, but the *cis* isomer is not (see picture; C gray and brown, Br mauve; O red, N blue, H white). The photochemical control can also be used to switch between different capsular assemblies.

Synthetic Methods

K. Mohanan, A. R. Martin, L. Toupet,
M. Smietana,* J. J. Vasseur **3196–3199**

Three-Component Reaction Using the Bestmann–Ohira Reagent: A Regioselective Synthesis of Phosphonyl Pyrazole Rings

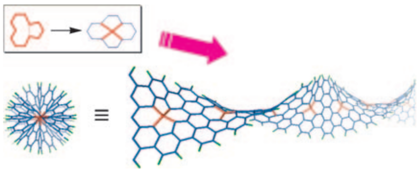
BOR-n to run: A new one-pot multicomponent reaction involving the use of an aldehyde, a cyanoacid derivative, and the Bestmann–Ohira reagent (BOR) has been developed for the synthesis of substituted phosphonyl pyrazoles. This process was also combined with a copper-catalyzed azide–alkyne 1,3-dipolar cycloaddition to generate five new bonds and two heterocyclic rings in a one-pot fashion.

Graphene Defects

X. Gao, L. Liu, S. Irle,* S. Nagase* ______ **3200 – 3202**

Carbon Spiral Helix: A Nanoarchitecture Derived from Monovacancy Defects in Graphene

The planar, magnetic isomer is the most stable form of interior graphene monovacancies, whereas the nonplanar, nonmagnetic spiro isomer is more stable for those closer to the edge of graphene sheets. On thermal annealing, interior monovacancies migrate towards the outermost periphery of graphene flakes. The spiro isomer is a suitable structural building block for the synthesis of carbon spiral helices (see picture).

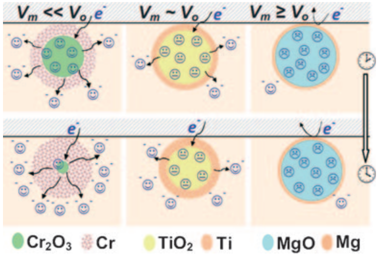


Solid-State Electroreduction

W. Li, X. B. Jin,* F. L. Huang, G. Z. Chen* ______ **3203 – 3206**

Metal-to-Oxide Molar Volume Ratio: The Overlooked Barrier to Solid-State Electroreduction and a "Green" Bypass through Recyclable NH_4HCO_3

Beating the barrier: The metal-to-oxide molar volume ratio V_m/V_o determines whether electroreduction of a metal oxide forms a porous metal shell that allows reduction to proceed ($V_m/V_o \ll 1$), or nonporous one that causes it to cease ($V_m/V_o \geq 1$; see picture). In the case of TiO_2 ($V_m/V_o \approx 1$), this barrier to reduction to Ti can be circumvented by recyclable use of NH_4HCO_3 as a fugitive porogenic agent.

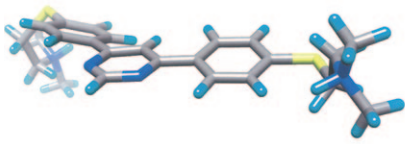


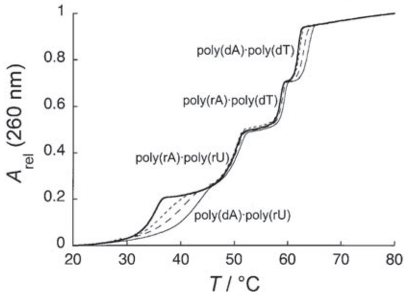
Targeting DNA·RNA Hybrids

R. T. Wheelhouse,* N. C. Garbett, N. J. Buurma, J. B. Chaires _ **3207 – 3210**

Probing the Molecular Recognition of a DNA·RNA Hybrid Duplex

Curiouser and curiouser! A biarylpyrimidine ligand (see picture: N blue, H cyan, S yellow) shows a marked structure and sequence selectivity for the poly(dA)·poly(rU) hybrid duplex. An intercalative binding site was discovered where the ligand occupies a surprising ten base pairs. A strong correlation between hybrid duplex and DNA triplex binding indicates new directions for ligand design.





Genetic Code Expansion

W. Wan, Y. Huang, Z. Wang, W. K. Russell, P.-J. Pai, D. H. Russell, W. R. Liu* ______ **3211 – 3214**

A Facile System for Genetic Incorporation of Two Different Noncanonical Amino Acids into One Protein in *Escherichia coli*

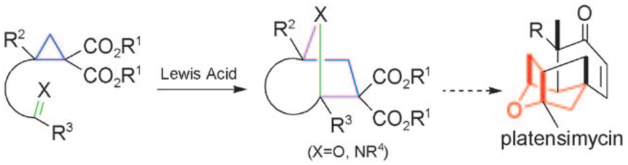
Two's company: Using a wild-type or evolved PylRS-pylT$_{UUA}$ pair to suppress ochre mutation and an evolved *Mj*TyrRS-*Mj*tRNA$^{Tyr}_{CUA}$ pair to suppress amber mutation, two different noncanonical amino acids (NAAs) have been concomitantly incorporated into one protein in *E. coli* with high efficiency (see picture, with NAAs **1**–**4**; GFP = green-fluorescent protein).

Contents

Cycloaddition

S. Xing, W. Pan, C. Liu, J. Ren,
Z. Wang* ________ **3215 – 3218**

Efficient Construction of Oxa- and Aza-[*n*.2.1] Skeletons: Lewis Acid Catalyzed Intramolecular [3+2] Cycloaddition of Cyclopropane 1,1-Diesters with Carbonyls and Imines

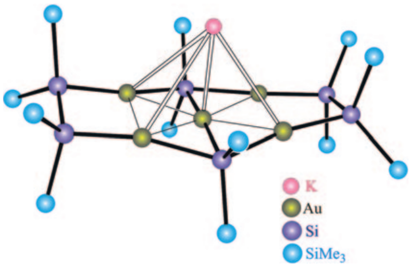


Building bridges: A Lewis acid promoted intramolecular [3+2] cycloaddition of cyclopropane 1,1-diesters with aldehydes, ketones, and imines (see scheme) has been developed to provide a general and efficient strategy for construction of bridged oxa- and aza-[*n*.2.1] ($n = 2,3,4$) skeletons. To highlight this method, the core of platensimycin was also constructed.

Si–Si Metathesis

M. Wilfling,
K. W. Klinkhammer* ________ **3219 – 3223**

Gold(I)-Mediated Silicon–Silicon Bond Metathesis at Room Temperature



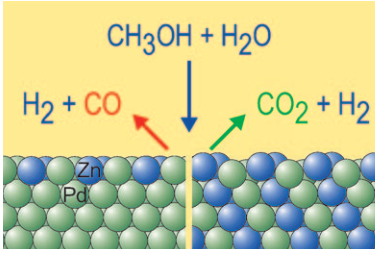
Digging for gold: Treatment of K[Au{Si(SiMe$_3$)$_3$}$_2$] with Me$_3$SiCl at room temperature leads to redox processes and Si–Si bond metathesis reactions. Numerous very unusual gold complexes are formed, such as the aurate shown.

Heterogeneous Catalysis

C. Rameshan, W. Stadlmayr, C. Weilach,
S. Penner, H. Lorenz, M. Hävecker,
R. Blume, T. Rocha, D. Teschner,
A. Knop-Gericke, R. Schlögl, N. Memmel,
D. Zemlyanov, G. Rupprechter,
B. Klötzer* ________ **3224 – 3227**

Subsurface-Controlled CO$_2$ Selectivity of PdZn Near-Surface Alloys in H$_2$ Generation by Methanol Steam Reforming

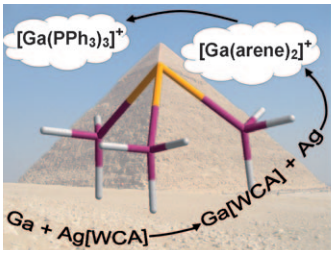
More than skin deep: In spite of their identical 1:1 surface composition, the geometric and electronic structures of a multilayer and monolayer PdZn surface alloy are different, as are their catalytic selectivities. The CO$_2$ selective multilayer alloy features surface ensembles of PdZn exhibiting a "Zn-up/Pd-down" corrugation (see picture). These act as "bifunctional" active sites both for water activation and for the conversion of methanol into CO$_2$. On the monolayer alloy CO and not CO$_2$ is produced.



Low-Valent Gallium

J. M. Slattery,* A. Higelin, T. Bayer,
I. Krossing* ________ **3228 – 3231**

A Simple Route to Univalent Gallium Salts of Weakly Coordinating Anions



Pyramidal [Ga(PPh$_3$)$_3$]$^+$ (see picture) is the first structurally characterized homoleptic gallium–phosphine complex. The synthesis of this ion was aided by the development of a facile route to gallium(I) salts with weakly coordinating anions (WCAs). These salts are an outstanding source of gallium in the oxidation state +1 for the generation of previously unknown low-valent gallium compounds.

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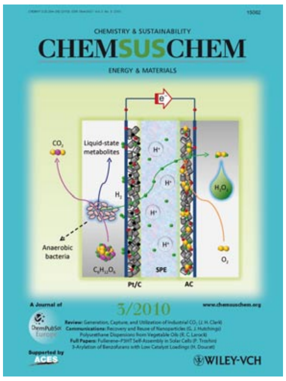

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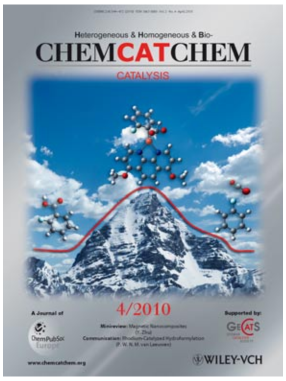

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