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:

*J. A. Teprovich Jr., M. N. Balili, T. Pintauer, R. A. Flowers II**
Mechanistic Studies of Proton-Donor Coordination to Samarium Diiodide

*E. B. Hadley, A. M. Witek, F. Freire, A. J. Peoples, S. H. Gellman**
Thermodynamic Analysis of a β-Sheet Secondary Structure By Backbone Thioester Exchange

*G. E. Veitch, E. Beckmann, B. J. Burke, A. Boyer, S. L. Maslen, S. V. Ley**
The Synthesis of Azadiractin: A Long But Successful Journey

*G. E. Veitch, E. Beckmann, B. J. Burke, A. Boyer, C. Ayats, S. V. Ley**
A New Relay Route for the Synthesis of Azadirachtin

I. Paterson, E. A. Anderson, A. D. Findlay*
Synthesis of an Advanced C10–C32 Spiroacetal Fragment and Assignment of the Absolute Stereochemistry of Spirangien A

*B. L. J. Kindler, P. Spiteller**
Chemical Defence of the Crust Fungus *Aleurodiscus amorphus* by a Tailor-Made Cyanogenic Cyanohydrin Ether

Obituary

Charles Mioskowski (1946–2007)

A. Wagner, B. Rousseau, V. Gouverneur ____ **6220**

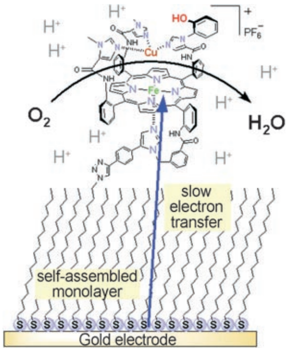
Books

Asymmetric Synthesis with Chemical and Biological Methods — Dieter Enders, Karl-Erich Jaeger

reviewed by R. Mahrwald ____ **6221**

Highlights

Bioinorganic Chemistry



Researchers came one step closer to understanding the mysterious complexity of the O$_2$-reducing site in cytochrome *c* oxidase. Realization of the individual tasks fulfilled by the components of this enzyme pocket became possible by electrocatalytic measurements on model-complex-modified gold electrodes under conditions of slow electron flux.

M. Bröring* ____ **6222 – 6224**

Supramolecular Bioinorganic Chemistry: Model Complexes of Cytochrome *c* Oxidase Meet Functional Surfaces

Minireviews

DNA Nanotechnology

Metallogenetic code: With the development of the metal–base pair concept it has recently become possible to selectively incorporate metal ions into the core of the DNA double helix. It is possible to stack up to ten metal ions in a double helix, and different metal ions can be incorporated in a programmable fashion. A wide range of applications are forseeable in nanotechnology.

G. H. Clever, C. Kaul, T. Carell* ____ **6226 – 6236**

DNA–Metal Base Pairs

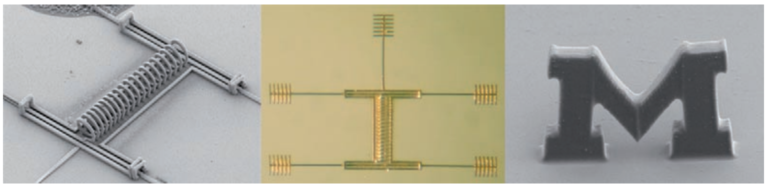
Contents

Reviews

Microstructures

C. N. LaFratta, J. T. Fourkas,*
T. Baldacchini, R. A. Farrer __ **6238–6258**

Multiphoton Fabrication



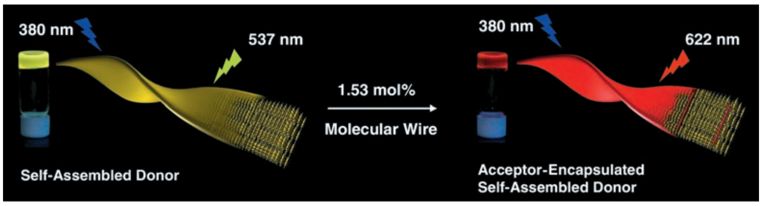
Now in 3D! Whereas conventional microfabrication techniques are essentially two dimensional, new schemes based on multiphoton absorption open up the third dimension, making it possible to create arbitrarily complex three-dimensional microstructures.

Communications

Energy Transfer

A. Ajayaghosh,* V. K. Praveen,
C. Vijayakumar, S. J. George **6260–6265**

Molecular Wire Encapsulated into π Organogels: Efficient Supramolecular Light-Harvesting Antennae with Color-Tunable Emission



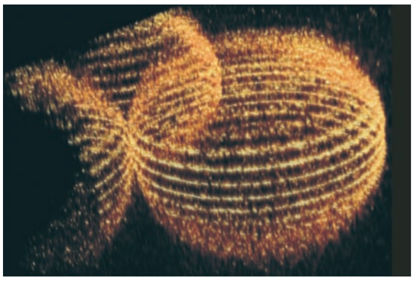
Reaping the benefit: A supramolecular light-harvesting antenna has been developed by encapsulating small amounts of a π-conjugated oligomer (molecular wire) within a self-assembled gel-forming donor scaffold. The supramolecular tapes of oligo(*p*-phenylenevinylene)s facilitate fast exciton migration and funneling of the excitation energy to the encapsulated molecular wire, thereby resulting in intense red emission (see picture).

Imaging Agents

J. Fölling, V. Belov, R. Kunetsky, R. Medda,
A. Schönle, A. Egner, C. Eggeling,
M. Bossi,* S. W. Hell* ____ **6266–6270**

Photochromic Rhodamines Provide Nanoscopy with Optical Sectioning

Exciting developments: Switching individual photochromic and fluorescent rhodamine amides enables 3D far-field optical microscopy with nanoscale resolution, excellent signal-to-noise ratio, and fast acquisition times. The rhodamine amides can be switched on using two photons, which enables 3D detailed imaging of thick and densely stained samples (such as 5-μm silica beads (see image) and living cells) to be constructed.



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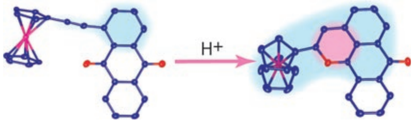


Just add a proton: The cyclocondensation of 1-aryl ethynylanthraquinones in the presence of a strong organic acid proceeds almost quantitatively to give oxodihydrodibenzochromenylium compounds (see scheme for a 1-ferrocenyl derivative; blue C, red O, purple Fe). Expansion of the π-conjugated system of the starting anthraquinones causes a lowering of the π* orbital and promotes intramolecular electron transfer.

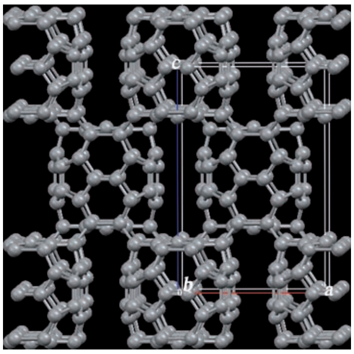
Valence Tautomerism

M. Kondo, M. Uchikawa, W.-W. Zhang, K. Namiki, S. Kume, M. Murata,* Y. Kobayashi, H. Nishihara* **6271 – 6274**

Protonation-Induced Cyclocondensation of 1-Aryl Ethynylanthraquinones: Expanding the π Conjugation

---

Endorsed doping: Calculations on the recently characterized cuboid C_{60} fullerene (see picture) confirm that it is metallic. Doping of Ba atoms into the cage and interstitial sites of cuboid C_{60} cages is shown theoretically to be energetically favorable. The changes in electronic properties that result from Ba doping suggest that cuboid C_{60} might be an important electronic material for technological applications.



Fullerene Networks

J. Yang,* J. S. Tse,* Y. Yao, T. Iitaka **6275 – 6277**

Structural and Electronic Properties of Pristine and Ba-Doped Clathrate-Like Carbon Fullerenes

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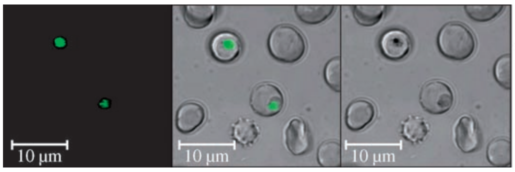

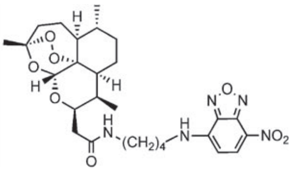

The iron-y of fate: Isobole analyses of fluorescently labeled antimalarial endoperoxides with chelators selective for non-heme iron, and laser confocal microscopy studies within living malaria parasites have shown that the semisynthetic analogues of artemisinin and synthetic endoperoxides (see example) share a common mechanism of action involving chelatable-iron-mediated bioactivation (see images) and irreversible alkylation of parasite targets.

Bioorganic Chemistry

P. A. Stocks, P. G. Bray,* V. E. Barton, M. Al-Helal, M. Jones, N. C. Araujo, P. Gibbons, S. A. Ward, R. H. Hughes, G. A. Biagini, J. Davies, R. Amewu, A. E. Mercer, G. Ellis, P. M. O'Neill* **6278 – 6283**

Evidence for a Common Non-Heme Chelatable-Iron-Dependent Activation Mechanism for Semisynthetic and Synthetic Endoperoxide Antimalarial Drugs

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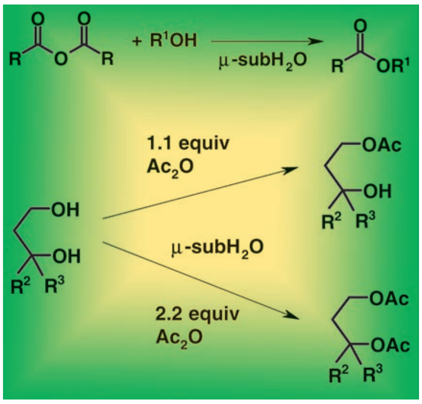


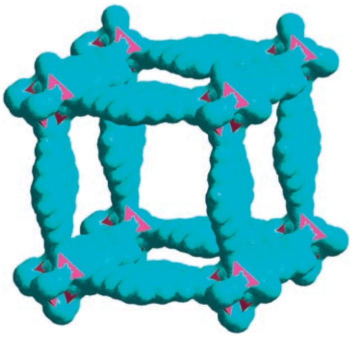
Fast and furious: A wide range of alcohols are acylated by acetic anhydride, in the absence of catalyst, in subcritical water in a flow-type microreaction system. The esters are selectively produced in high yields at temperatures of 200 to 250 °C. Varying the amount of acetic anhydride added with respect to the alcohols allows the regioselective acylation of one or both hydroxy groups of various dihydroxy compounds (see picture).

Mono- and Diacylation

M. Sato,* K. Matsushima, H. Kawanami,* Y. Ikuhsima **6284 – 6288**

A Highly Selective, High-Speed, and Hydrolysis-Free O-Acylation in Subcritical Water in the Absence of a Catalyst

Quick on the uptake: The metal–organic framework Mg-MOF-C30 (see picture) contains $Mg_4O(CO_2)_6$ building units (pink) and aromatic organic linkers containing 30 carbon atoms (teal). This material leads to 8.08 wt% H_2 uptake at 77 K and 20 bar, the highest among investigated MOF structures.

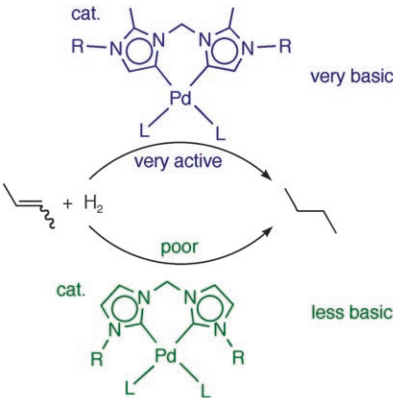


Hydrogen Storage

S. S. Han, W.-Q. Deng,
W. A. Goddard, III* ——— **6289 – 6292**

Improved Designs of Metal–Organic Frameworks for Hydrogen Storage

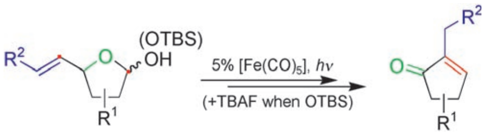
With four site: Catalytic olefin hydrogenation is observed with palladium complexes when the N-heterocyclic carbene ligand is changed from the normal C2- to the unusual C4-bonding mode (see scheme). In a *cis* coordinating framework, the electron density at the metal center is substantially increased as a result of the exceptionally strong donor ability of C4-bound carbenes.



N-Heterocyclic Carbenes

M. Heckenroth, E. Kluser, A. Neels,
M. Albrecht* ——— **6293 – 6296**

Neutral Ligands with Exceptional Donor Ability for Palladium-Catalyzed Alkene Hydrogenation

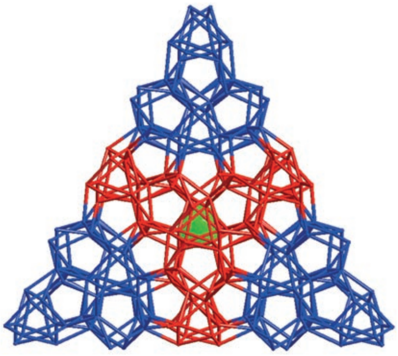


From sugars to carbocycles: Pentacarbonyl iron is a cheap and efficient catalyst for mediating an isomerization–aldolization–dehydration sequence that converts vinyl sugars into cyclopentenones, which are very useful intermediates in the total synthesis of various types of bioactive molecules.

Synthetic Methods

J. Petrignet, I. Prathap, S. Chandrasekhar,
J. S. Yadav, R. Grée* ——— **6297 – 6300**

A Catalytic Method for Converting Vinylic Furanoses into Cyclopentenones



A holey host: An octupolar porous metal–organic framework with a T_d-symmetric supercage structure (see picture; green: center of the octapolar structure) exhibits a powder second harmonic generation (SHG) intensity about 15 times higher than that of KH_2PO_4. This anionic open framework is highly thermally stable, displays high ion-exchange capacities with the cations NH_4^+, Na^+, and K^+, and, more importantly, exhibits an unprecedented cation-dependent NLO activity.

Tunable NLO Behavior

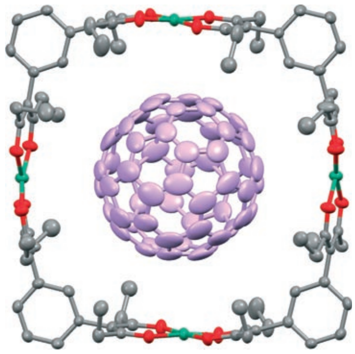
Y. Liu, G. Li, X. Li, Y. Cui* — **6301 – 6304**

Cation-Dependent Nonlinear Optical Behavior in an Octupolar 3D Anionic Metal–Organic Open Framework

Supramolecular Chemistry

C. Pariya, C. R. Sparrow, C.-K. Back,
G. Sandí, F. R. Fronczek,
A. W. Maverick* ________ **6305 – 6308**

Copper β-Diketonate Molecular Squares and Their Host–Guest Reactions

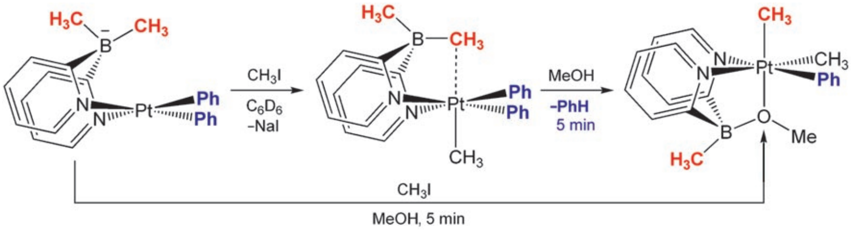


All square: Treatment of *m*-phenylenebis(β-diketones) with $[Cu(NH_3)_4]^{2+}$ yields molecular squares rather than the expected hexagons. The squares react readily with guests such as C_{60} (see structure) and 4,4′-bipyridine. They are also effective for the storage of H_2 gas, both at 77 K and at room temperature.

Methyl-Group Transfer

E. Khaskin, P. Y. Zavalij,
A. N. Vedernikov* ________ **6309 – 6312**

Oxidatively Induced Methyl Transfer from Boron to Platinum in Dimethyldi(2-pyridyl)boratoplatinum Complexes

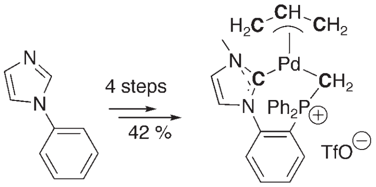


A hydroxlic solvent promoted reaction: Boron-to-platinum methyl-group transfer occurs in the title complexes in the presence of an oxidant (O_2 or MeI) and a protic solvent (water, alcohols; see scheme). With MeI as oxidant the reaction intermediate is shown to be a five-coordinate Pt^{IV} species containing a Pt···CH agostic interaction.

Carbon Ligands

Y. Canac,* C. Duhayon,
R. Chauvin* ________ **6313 – 6315**

A Diaminocarbene–Phosphonium Ylide: Direct Access to C,C Chelating Ligands



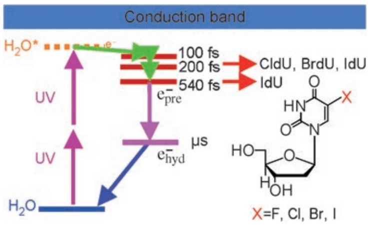
Captured and surrounded by C: A strongly σ-donating C,C ligand and an allyl ligand surround the palladium center in the complex shown in the scheme. The chelate, with three different types of carbon atoms, is soluble and stable in water and readily accessible on a multigram scale. It serves as the precursor to an efficient catalyst for Tsuji–Trost allylic substitution. Tf = trifluoromethanesulfonyl.

Ultrafast Electron Transfer

C.-R. Wang, Q.-B. Lu* ________ **6316 – 6320**

Real-Time Observation of a Molecular Reaction Mechanism of Aqueous 5-Halo-2′-deoxyuridines under UV/Ionizing Radiation

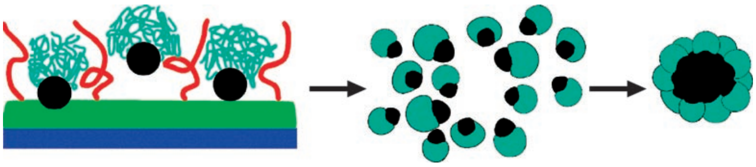
Life's not too short: 5-Halo-2′-deoxyuridines (XdUs) have been tested as hypoxic radiosensitizers in cancer therapy, but their molecular reaction mechanism is poorly understood. Time-resolved femtosecond laser spectroscopic measurements show that dissociative attachment of prehydrated electrons (e_{pre}^-) to XdUs is responsible for the formation of a reactive radical dU$^\bullet$ that causes the radiosensitivity enhancement. e_{hyd}^- = hydrated electron.



Supermicelles

L. Nie, S. Liu, W. Shen, D. Chen,* M. Jiang ______ 6321 – 6324

One-Pot Synthesis of Amphiphilic Polymeric Janus Particles and Their Self-Assembly into Supermicelles with a Narrow Size Distribution

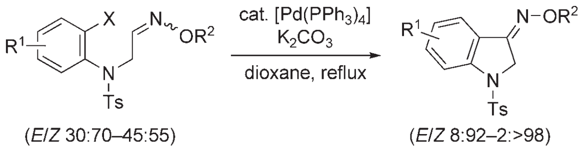


Not just a pretty structure: Water-dispersible hybrid nanotubes were used as a desymmetrization tool to prepare Janus nanoparticles consisting of a hydrophobic sphere with water-soluble polymer chains grafted on one side (see picture). The Janus micelles undergo self-assembly to form supermicelles with a flowerlike morphology in which the constituent Janus particles are the "petals".

Transition-Metal Catalysis

H. Ohno,* A. Aso, Y. Kadoh, N. Fujii, T. Tanaka* ______ 6325 – 6328

Heck-Type Cyclization of Oxime Ethers: Stereoselective Carbon–Carbon Bond Formation with Aryl Halides To Produce Heterocyclic Oximes

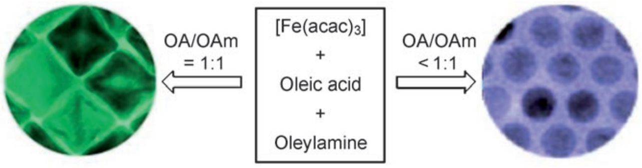


Irrespective of the isomeric ratio of the starting material, the palladium-catalyzed cyclization of oxime ethers with an aryl halide moiety proceeds in a highly *Z*-selective manner to give indolin-3-one *O*-alkyl oximes in good yields (see scheme). The reaction is also applicable to the construction of benzofuran-3-one and fused-indole frameworks. $R^1 = H$, Me, OMe, CO_2Me; $R^2 = Me$, benzyl; Ts = *p*-toluenesulfonyl.

Reactions of FeO Nanoparticles

Y. Hou, Z. Xu, S. Sun* ______ 6329 – 6332

Controlled Synthesis and Chemical Conversions of FeO Nanoparticles



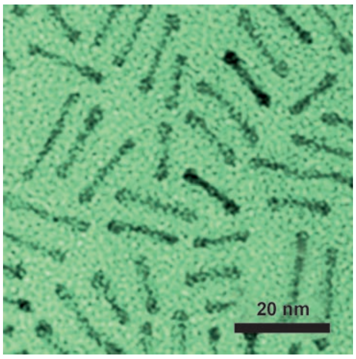
Shaping up for conversion: Monodisperse FeO nanoparticles were synthesized by reductive decomposition of iron(III) acetylacetonate with oleic acid (OA) and oleylamine (OAm). The nanoparticle sizes were tunable from 14 to 100 nm and their shapes were controlled to be either spherical or truncated octahedral (see images). The FeO nanoparticles were converted into diverse Fe_xO_y nanoparticles, which have potential in magnetic and catalytic applications.

Nanostructure Growth

C. Wang, Y. Hou,* J. Kim, S. Sun* ______ 6333 – 6335

A General Strategy for Synthesizing FePt Nanowires and Nanorods

Length made to order: Controlled reduction of $[Pt(acac)_2]$ and decomposition of $[Fe(CO)_5]$ in a mixture of oleylamine and octadecene leads to the facile synthesis of FePt nanowires and nanorods with diameters of 2–3 nm (see TEM image). The length of the nanowires/nanorods is tunable from greater than 200 nm down to 20 nm by simply controlling the volume ratio of oleylamine and octadecene.

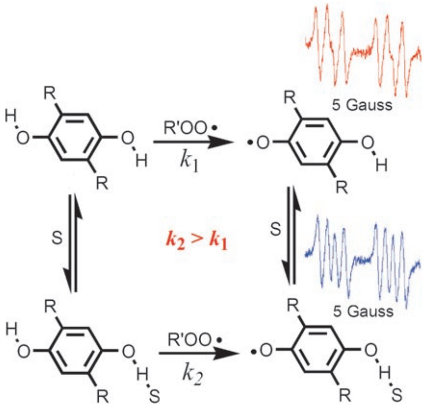


Radical Reactions

R. Amorati,* P. Franchi,
G. F. Pedulli ________ 6336 – 6338

Intermolecular Hydrogen Bonding Modulates the Hydrogen-Atom-Donating Ability of Hydroquinones

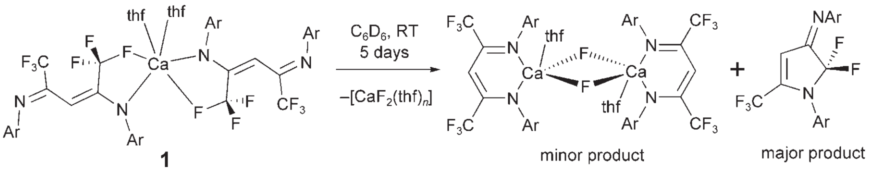
Radical measures: Kinetic measurements on peroxyl radicals showed that the reactivity of a 1,4-dihydroxybenzene is enhanced by the selective interaction of one OH group with a cosolvent molecule (see scheme; S = DMSO, 2.3 mM). The preferential solvation of the radical over the parent phenol causes a decrease in the bond dissociation enthalpy of the free OH group and an increase in the rate constant for abstraction of a hydrogen atom.



C–F Activation

A. G. M. Barrett,* M. R. Crimmin,
M. S. Hill,* P. B. Hitchcock,
P. A. Procopiou ________ 6339 – 6342

Trifluoromethyl Coordination and C–F Bond Activation at Calcium

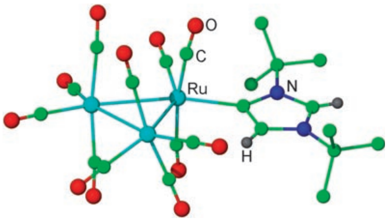


Fluoral arrangement: The calcium β-diketiminate complex **1** (see scheme) not only exhibits an unexpected and unprecedented binding mode of a CF_3 group, from which one fluorine atom coordinates to the Ca center, but also undergoes C–F bond cleavage through the formation of a heteroleptic calcium fluoride complex.

Carbene Ligands

C. E. Ellul, M. F. Mahon, O. Saker,
M. K. Whittlesey* ________ 6343 – 6345

Abnormally Bound N-Heterocyclic Carbene Complexes of Ruthenium: C–H Activation of Both C4 and C5 Positions in the Same Ligand

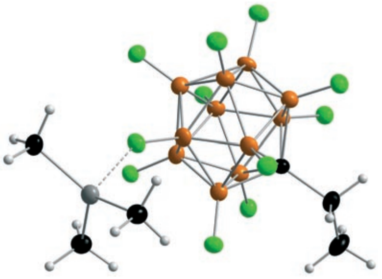


A bit unusual: "Abnormal" carbene formation from a free monodentate N-heterocyclic carbene occurs upon the room temperature reaction of $[Ru_3(CO)_{12}]$ with 1,3-di-*tert*-butylimidazol-2-ylidene. Subsequent heating leads to C–H activation at the remaining C5 position to afford a μ_3-bridging heterocycle, which is eliminated as imidazolium upon reaction with H_2.

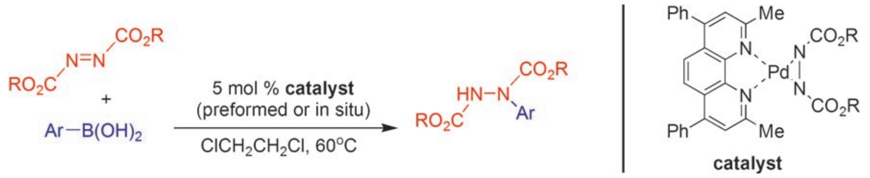
Silyl Cations

T. Küppers, E. Bernhardt, R. Eujen,
H. Willner,*
C. W. Lehmann* ________ 6346 – 6349

$[Me_3Si][R\text{-}CB_{11}F_{11}]$—Synthesis and Properties



Trimethylsilyl cations in a molten salt: The weakly coordinating anions $[RCB_{11}F_{11}]^-$ (R = H, C_2H_5; see structure; F green, B orange, Si gray, C black) stabilize the $[Me_3Si]^+$ cation so well that the ^1H, ^{13}C, and ^{29}Si NMR spectroscopic parameters could be measured in the melt without using a solvent. The crystal structures and the synthesis of the solid super acids $H[RCB_{11}F_{11}]$ (R = H, C_2H_5) are also reported.



An easy couple: A new protocol for the synthesis of N-arylated amides, based on a coupling between azodicarboxylates and aryl boronic acids, has been developed (see scheme). Palladadiaziridines serve as catalysts for this process and the key step consists of a reductive elimination from a hydrazinato palladium aryl intermediate that shows an unprecedented reactivity for this class of compounds in aryl–amide bond formation.

Aryl–Nitrogen Coupling Reactions

K. Muñiz,* A. Iglesias ______ **6350–6353**

Phenanthroline Ligands in Aryl Palladium Hydrazinato Complexes: Catalysts for Efficient Coupling of Azo Componds with Aryl Boronic Acids

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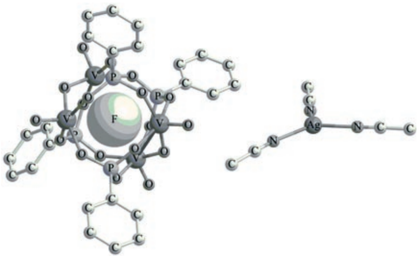


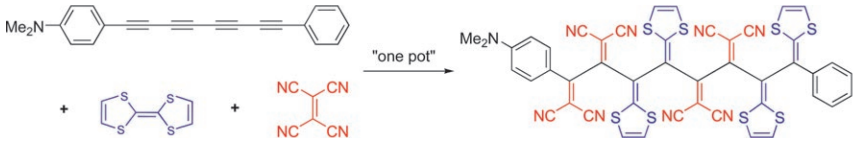
Highly adaptable: Vanadium cage compounds templated on F^- (see picture) offer unique possibilities for tuning properties and exhibit unexpected redox behavior with respect to NO and H_2. When adsorbed on the surface of γ-Al_2O_3 coated with Ag^+, they react in the singlet state with both NO and H_2. In both cases, the vanadium mixed-valence state of the cage could be identified by EPR spectroscopy.

Metal Organophosphonates

VIP

J. K. Jabor, R. Stößer, N. H. Thong,
B. Ziemer, M. Meisel* ______ **6354–6356**

Unexpected Reactions of $[Ag(NCCH_3)_3][(V_2O_3)_2(RPO_3)_4\subset F]$ Cage Compounds with H_2 and NO



It all clicks into place: The cycloaddition of tetracyanoethylene (TCNE) to electron-rich alkynes (“click” reaction) followed by retro-electrocyclization affords multivalent charge-transfer chromophores that accept up to 24 electrons. The cascade additions of TCNE and tetrathiafulvalene (TTF) to polyynes provides access to conjugated donor–acceptor-substituted [AB] oligomers with promising optoelectronic properties (see scheme).

Charge-Transfer Chromophores

M. Kivala, C. Boudon, J.-P. Gisselbrecht,
P. Seiler, M. Gross,
F. Diederich* ______ **6357–6360**

Charge-Transfer Chromophores by Cycloaddition–Retro-electrocyclization: Multivalent Systems and Cascade Reactions

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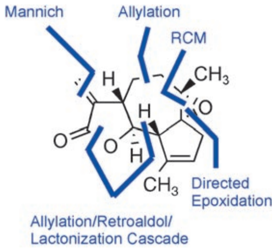


Closing the ring: The first enantioselective synthesis of the guanianolide natural product arglabin and its dimethylamino adduct, which shows promising results in the treatment of various tumors, has been achieved. Key steps include a Cu^I-catalyzed asymmetric cyclopropanation, a stereoselective Sakurai allylation with a retroaldol/lactonization cascade, and a second Sakurai allylation with ring-closing metathesis (RCM).

Natural Products

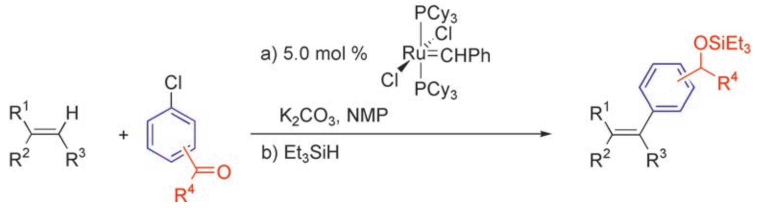
S. Kalidindi, W. B. Jeong, A. Schall,
R. Bandichhor, B. Nosse,
O. Reiser* ______ **6361–6363**

Enantioselective Synthesis of Arglabin

Sequential Catalysis

L. Ackermann,* R. Born,
P. Álvarez-Bercedo ________ **6364 – 6367**

Ruthenium(IV) Alkylidenes as Precatalysts for Direct Arylations of Alkenes with Aryl Chlorides and an Application to Sequential Catalysis

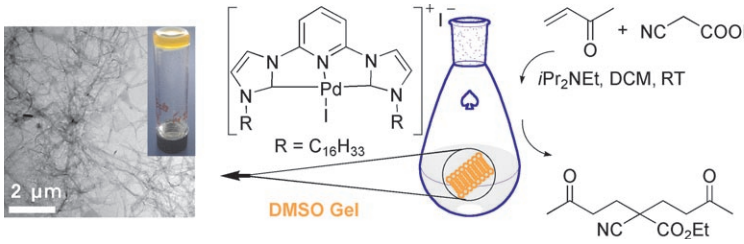


Jack of all trades? A ruthenium(IV) carbene complex catalyzes the diastereoselective direct arylation of alkenes using aryl chlorides with high efficiency, which sets the stage for the development of a direct arylation–hydrosilylation sequence (see scheme).

Gel Catalysis

T. Tu,* W. Assenmacher, H. Peterlik,
R. Weisbarth, M. Nieger,
K. H. Dötz* ____________ **6368 – 6371**

An Air-Stable Organometallic Low-Molecular-Mass Gelator: Synthesis, Aggregation, and Catalytic Application of a Palladium Pincer Complex

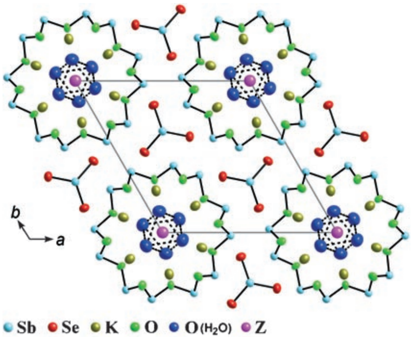


An efficient organometallic gelator can gel a variety of organic solvents even in concentrations as low as 0.2 wt%. π Stacking of the heteroarene moieties, van der Waals interactions between the alkyl chains, and metal–metal interactions may be responsible for the aggregation. This palladium pincer bis(carbene) complex (see scheme) is the first air-stable organometallic low-molecular-mass gelator that reveals promising catalytic activity in the gel state.

Gas Detectors

D. Sendor, B. P. T. Fokwa, R. Dronskowski,
U. Simon* ____________ **6372 – 6375**

Noble Gases Influence the Conductance of Cetineite-Type Nanoporous Semiconductors



Recognizing nobility: The photoconduction of cetineites, crystalline nanoporous oxoselenoantimonates, is suppressed by the adsorption of noble gases. The gas uptake decreases with increasing atomic radius of the noble gas, leading to a smaller change in resistance upon adsorption. Thus, cetineites can be applied in noble-gas detection.

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).

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