Upcoming VIPs

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Recently published VIPs:

- Copper-Catalyzed Asymmetric Conjugate Addition of Aryl Aluminum Reagents to Trisubstituted Enones: Construction of Aryl-Substituted Quaternary Centers
- Nanoscale Corona Discharge in Liquids Enabling Nanosecond Optical Emission Spectroscopy
- Highly Emissive Fluorescent Nucleoside Signals the Activity of Toxic Ribosome-Inactivating Proteins

Enantioselective C–C Bond Activation of Allenylcyclobutanes: Access to Cyclohexenones with Quaternary Stereogenic Centers

Tobias Seiser and Nicolai Cramer*

An efficient activation of allenyl-*tert*-cyclobutanols was achieved through an enantioselective insertion of a chiral rhodium(I) complex into the C–C σ bond of the cyclobutane. The method allows the preparation of cyclohexenones with quaternary stereogenic centers in excellent enantioselectivities of up to 99 % *ee*. The catalyst loading can be reduced to 0.1 mol% rhodium.

Robust Self-Assembly of Highly Ordered Complex Structures by Controlled Evaporation of Confined Microfluids

Suck Won Hong, Myunghwan Byun, and Zhiqun Lin*

A facile, robust, and one-step evaporation method is presented for rationally synthesizing "coffee rings" of different shapes and sizes of high regularity and fidelity, dispensing with the need for lithographic techniques and externally applied fields. Polymer solutions are confined in a simple geometry comprised of a curved surface placed upon a flat substrate. Simply by changing the shape of the upper surface of the imposed geometry, the controlled, evaporative self-assembly of polymer solutions yields a variety of complex, intriguing, and well-ordered structures over large areas.

Unprecedented and Differently Applicable Pentagonal Units in a Dynamic Library: A Keplerate of the Type $\{(W)W_5\}_{12}\{Mo_2\}_{30}$

Christian Schäffer, Alice Merca, Hartmut Bögge, Ana Maria Todea, Melissa L. Kistler, Tianbo Liu, René Thouvenot, Pierre Gouzerh*, and Achim Müller*

Whereas several giant spherical clusters, called Keplerates, and other giant curved species based on pentagonal $(Mo)Mo_5$-type units and available in a dynamical library could be prepared easily, related tungsten compounds were not known. Correspondingly, no $\{(W)W_5\}$ unit had been observed to date now among the thousands of polyoxotungstates. The $\{(W)W_5\}_{12}\{Mo_2\}_{30}$-type Keplerate with the mentioned units is now presented, and this knowledge allows other tungsten oxide based species to be prepared.

Early Main-Group Metal Catalysts for the Hydrogenation of Alkenes with Hydrogen

Jan Spielmann, Frank Buch, and Sjoerd Harder*

Transition-metal-free catalysts for the hydrogenation of conjugated alkenes are introduced. Reactions mediated by well-defined alkaline earth metal catalysts show signicant advantages over alkali-metal-catalyzed conversions and the reactions can be performed under relatively mild conditions, namely room temperature and 20 bar.

Bond- and Energy-Selective Carbon Abstraction from D-Ribose by Hyperthermal Nitrogen Ions

Zongwu Deng, Ilko Bald, Eugen Illenberger, and Michael A. Huels*

When highly charged ions traverse cells, they create hyperthermal secondary fragment ions, which in turn cause reactive scattering damage to DNA. Among these ions, atomic nitrogen cations efficiently abstract carbon from DNA components, forming CN^- anions at collision energies down to 5 eV. This reaction is strongly site- and energy-selective for C5 of D-ribose, owing to the weak local bond strength at C5. Our results imply that in RNA or DNA the sugar backbone will be a vulnerable point of attack by secondary nitrogen ions created during heavy-ion irradiation.

Critical Importance of the Nine-Membered F Ring of Ciguatoxin for Potent Bioactivity: Total Synthesis and Biological Evaluation of F-Ring-Modified Analogues

Masayuki Inoue,* Nayoung Lee, Keisuke Miyazaki, Toyonobu Usuki, Shigeru Matsuoka, and Masahiro Hirama*

Ciguatoxin, a potent neurotoxin, spans a length of over 3 nm and consists of thirteen fused ether rings, from the A ring to the M ring. Two fully synthetic F-ring modified analogues have markedly diminished biological activities, which demonstrate that the central F-ring plays a major role in organizing the ciguatoxin molecule into a shape suitable for bioactivity.

Structure of the Observable Histidine Radical Cation in the Gas Phase: a Captodative α Radical Ion

Jeffrey Steill, Junfang Zhao, Chi-Kit Siu, Yuyong Ke, Udo H. Verkerk, Jos Oomens, Robert C. Dunbar, Alan C. Hopkinson, and K.W. Michael Siu*

The observable histidine radical cation generated by collision-induced dissociations of the $[Cu^{II}(2,2':6',2''\text{-terpyridine})(His)]^{\cdot 2+}$ ion in the gas phase has the positive charge on the protonated imidazole ring and the radical formally on the α carbon. This captodative α radical ion structure is confirmed by infrared multiple photon dissociation spectroscopic experiments and density functional calculations.

Structurally Distinct Homoleptic Anthracene Complexes $[M(C_{14}H_{10})_3]^{2-}$, M=Ti, Zr, Hf: Tris(arene) Complexes for a Triad of Transition Metals

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Robert E. Jilek, Meehae Jang, Eric D. Smolensky, J. Doyle Britton, and John E. Ellis*

Unprecedented tris(arene) complexes for a triad of transition metals have been obtained in the form of the tris(anthracene)metalates(2-) of titanium, zirconium, and hafnium. The hafnium complex, along with the naphthalene analogue, are previously unknown examples of hydrocarbon-stabilized negative-valent hafnium, Hf(2-), and promise to be important precursors for studies on low-valent hafnium chemistry. The homoleptic anthracene and naphthalene titanates(2-) are also unique examples of isolable tris(arene)metal complexes for 3d elements and the only known 16-electron homoleptic arene complexes to contain arenes of different hapticities within the same molecule.

Received June 12, 2008, published online October 02, 2008, DOI: 10.1002/anie.200802780.

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A Belt-Shaped, Blue-Luminescent and Semiconducting Covalent Organic Framework

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Shun Wan, Jia Guo, Jangbae Kim, Hyotcherl Ihee, and Donglin Jiang*

Condensation polymerization of pyrene and triphenylene monomers leads to the construction of a crystalline covalent organic framework (TP-COF), which adopts a belt shape and has permanent porosity, with a discrete pore width of 3.14 nm. TP-COF has strong blue luminescence and allows energy transfer from triphenylene to pyrene units and excitation energy migration over the framework. TP-COF is semiconductive and capable of repetitive on/off current switching at room temperature.

Received August 04, 2008, published online October 01, 2008, DOI: 10.1002/anie.200803826.

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One- and Two-Dimensional NMR Spectroscopy with a Magnetic-Resonance Force Microscope

Kai W. Eberhardt, Christian L. Degen, Andreas Hunkeler, and Beat H. Meier*

Magnetic-resonance force microscopy was used to locate slices of 2.0 μm thickness in a heterogeneous sample and to perform localized spectroscopy for the characterization of chemical interactions at the atomic level. To recover the chemical shift information, the imaging field gradient was temporarily switched off using a mechanical stage, which allowed one- and two-dimensional NMR spectra to be recorded at high spatial resolution.

Copper-Catalyzed Asymmetric Conjugate Addition of Aryl Aluminum Reagents to Trisubstituted Enones: Construction of Aryl-Substituted Quaternary Centers

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Christine Hawner, Kangying Li, Virginie Cirriez, and Alexandre Alexakis*

Novel aryl aluminum reagents are generated by a halogen/lithium exchange and lithium/aluminum transmetalation sequence. These aryl alanes can be used in the copper-catalyzed asymmetric conjugate addition reaction with a variety of cyclic enones, allowing the creation of chiral aryl-substituted quaternary centers. Both electron-donating and electron-withdrawing groups give full conversion and excellent enantioselectivities. The sequence can further be applied to generate naphthyl and vinyl alanes, which are also successful in the conjugate addition.

Received July 16, 2008, published online September 22, 2008, DOI: 10.1002/anie.200803436.

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Nanoscale Corona Discharge in Liquids Enabling Nanosecond Optical Emission Spectroscopy

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David Staack, Alexander Fridman, Alexander Gutsol, Yury Gogotsi*, and Gary Friedman*

A novel non-thermal corona discharge inside a liquid medium has been created around an electrode with ultrasharp tips or elongated nanoparticles. The nanoscale plasmas created at the tip of a nanowire conducting probe or carbon nanotubes dispersed in solution allow simultaneous chemical analysis of multiple dissolved elements within nanoseconds. The proposed optical emission spectroscopy method can be applied for ultrafast time-resolved multi-elemental analysis of femtoliter volumes of liquid with a one micrometer spatial resolution. Using this method, we have detected parts per million concentrations of sodium, calcium, and other elements in solution.

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Unmasking Representative Structures of TMP-Active Hauser and Turbo Hauser Bases

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Pablo García-Álvarez, David V. Graham, Eva Hevia, Alan R. Kennedy, Jan Klett, Robert E. Mulvey,* Charles T. O'Hara, and Susan Weatherstone

There has been an explosion of interest in TMP-Hauser bases and related "turbo Grignard" chemistry recently, which is fueled by a range of new, improved synthetic methods for the regioselective functionalization of aryl, heteroaryl, and metallocenyl compounds. To date, the structures of these important reagents have been a mystery. Now the molecular engines that drive these enhanced magnesiations are unveiled through structural elucidation of key reagents.

Received June 04, 2008, published online August 01, 2008, DOI: 10.1002/anie.200802618. No. 42/2008.

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Direct, High-Yield Conversion of Cellulose into Biofuel

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Mark Mascal* and Edward B. Nikitin

Cellulose is converted into furanic biofuels in unprecedented yields using an inexpensive, simple process involving concurrent hydrolysis, dehydration, and chlorine substitution reactions coupled with continuous extraction into an organic phase.

Received April 05, 2008, published online August 01, 2008, DOI: 10.1002/anie.200801594. No. 41/2008.

Highly Emissive Fluorescent Nucleoside Signals the Activity of Toxic Ribosome-Inactivating Proteins

Seergazhi G. Srivatsan, Nicholas J. Greco, and Yitzhak Tor*

Synthetically modified emissive RNA constructs, which are complementary to the α sarcin/ricin loop, signal the presence of RNA abasic sites generated by ribosome inactivating proteins by enhanced emission intensity. This approach to toxin sensing relies on detecting the specific enzymatic activity associated with these poisonous proteins, regardless of the toxin's specific identity. The method is potentially amenable to high-throughput inhibitor screening and sensor development.

Received May 11, 2008, published online August 06, 2008, DOI: 10.1002/anie.200802199.