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:*

*J. Masuda, W. Schoeller, B. Donnadieu, G. Bertrand**
Carbene Activation of P_4 and Subsequent Derivatization

K. Moehle, Z. Athanassiou, K. Patora, A. Davidson, G. Varani, J. Robinson**
Design of β-Hairpin Peptidomimetics That Inhibit Binding of α-Helical HIV-1 Rev Protein to the Rev Response Element RNA

*P. Chase, G. Welch, T. Jurca, D. Stephan**
Metal-Free Catalytic Hydrogenations

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

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

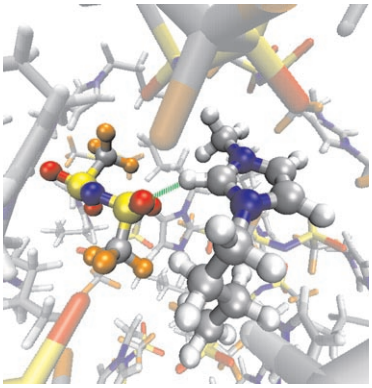
*G. Veitch, E. Beckmann, B. Burke, A. Boyer, S. Maslen, S. Ley**
The Synthesis of Azadiractin: A Long But Successful Journey

Obituary

Books

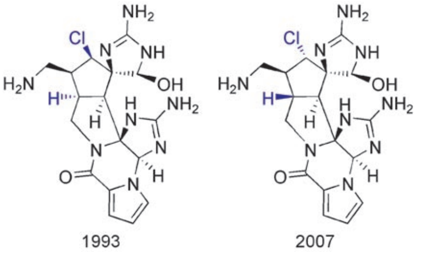
Highlights

The volatile nature of ionic liquids: Ionic liquids are recognized as "green" solvents because of their essentially null volatility. Ironically, it is the low vapor pressure, the large enthalpy of vaporization, and the high boiling point of ionic liquids that make it difficult to study their macroscopic behavior at a molecular level. Recent studies, however, have shed light on their thermochemical properties (picture: snapshot of an ionic liquid from molecular dynamics simulations).



Ionic Liquids

Minireviews



The plot thickens in the story of the pyrrole–imidazole alkaloid family, specifically for the members related to palau'amine. The recent structural reassignment of palau'amine suggests a unified biosynthetic pathway. The background to the reassignment and the ramifications of this discovery to the biosynthesis and total synthesis of the pyrrole–imidazole alkaloids are discussed in this Minireview.

Marine Natural Products

Contents

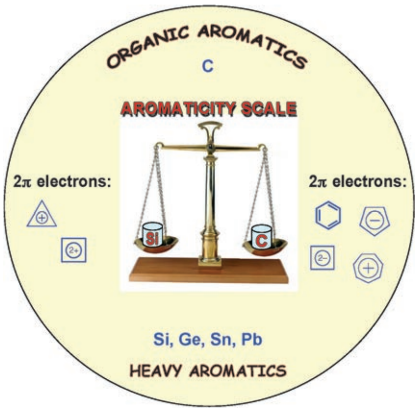
Reviews

Aromaticity

V. Ya. Lee, A. Sekiguchi* ____ **6596 – 6620**

Aromaticity of Group 14 Organometallics: Experimental Aspects

Aromatic heavyweights: In this Review the latest experimental accomplishments and relevant theoretical contributions in the field of aromatic compounds of the heavier Group 14 elements are discussed. Particular attention is focused on charged arenes with two or six π electrons, derivatives of the cyclopropenylium, cyclopentadienide, and cycloheptatrienylium ions and cyclobutadiene dianion, and their application as ligands.



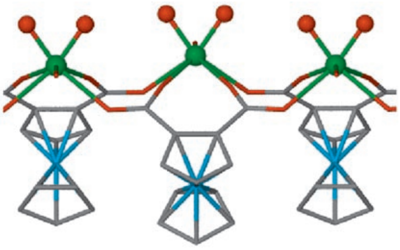
Communications

Actinides

A. E. Vaughn, C. L. Barnes,
P. B. Duval* ____ **6622 – 6625**

A *cis*-Dioxido Uranyl: Fluxional Carboxylate Activation from a Reversible Coordination Polymer

Big bend: An air-stable carboxylate-bridged uranium(VI) coordination polymer that possesses a terminal *cis*-dioxido unit has been prepared. The polymer is reversibly soluble and undergoes fluxional behavior that involves a concerted carboxylate-ligand activation. Steric pressure from this fluxional process probably accounts for this unprecedented dioxido geometry in actinyl chemistry.

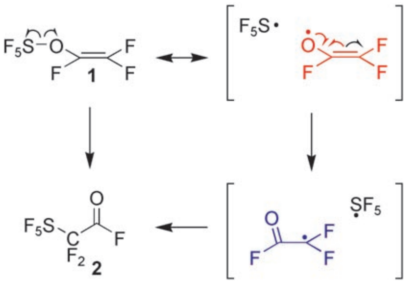


Fluorine Chemistry

L. Du, B. Elliott, L. Echegoyen,
D. D. DesMarteau* ____ **6626 – 6628**

Synthesis of Pentafluorosulfanyl Trifluorovinyl Ether and Its Facile Rearrangement to Difluoro(pentafluorosulfanyl)acetyl Fluoride

A radical departure: A novel fluorinated vinyl ether **1** was synthesized and was found to undergo an unexpected facile rearrangement to give compound **2**, which was confirmed to be a radical process by EPR spectroscopy.



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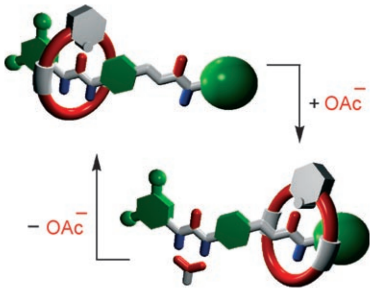
Rotaxanes

Y.-L. Huang, W.-C. Hung, C.-C. Lai, Y.-H. Liu, S.-M. Peng, S.-H. Chiu* ———— **6629 – 6633**

Using Acetate Anions To Induce Translational Isomerization in a Neutral Urea-Based Molecular Switch

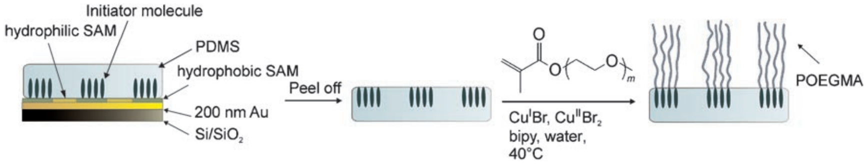


Vying for urea: The translational isomerism of a neutral [2]rotaxane can be controlled in solution through the addition and removal of acetate anions. In the absence of acetate ions, the macrocyclic host recognizes a diphenylurea derivative; recognition of acetate ions by the urea-based station causes relocation of the macrocycle to another binding site (see picture).

Chemical Micropatterning

M. L. van Poll, F. Zhou, M. Ramstedt, L. Hu, W. T. S. Huck* ———— **6634 – 6637**

A Self-Assembly Approach to Chemical Micropatterning of Poly(dimethylsiloxane)

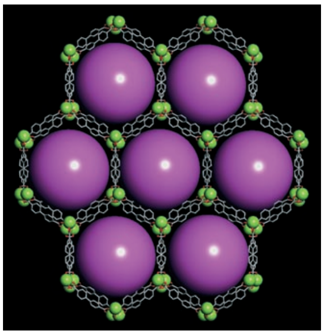


Brushing the surface: The surface of a silicone elastomer (poly(dimethylsiloxane); PDMS) can be selectively modified through minimization of interfacial free energy and self-assembly of functional molecules at the surface by mirroring the distribution of template surface energies (see scheme for formation of POEGMA brushes; SAM = self-assembled monolayer, bipy = 2,2′-bipyridyl, POEGMA = poly[oligo(ethylene glycol) methacrylate]).

Porous Materials

Q. R. Fang, G. S. Zhu,* Z. Jin, Y. Y. Ji, J. W. Ye, M. Xue, H. Yang, Y. Wang, S. L. Qiu* ———— **6638 – 6642**

Mesoporous Metal–Organic Framework with Rare etb Topology for Hydrogen Storage and Dye Assembly

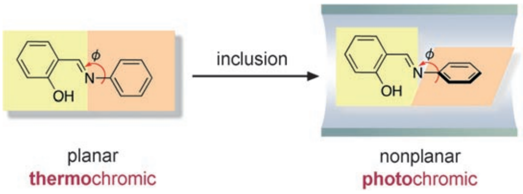


More holes than Swiss cheese: A new MOF with the largest reported 1D hexagonal nanotube-like channels of 24.5 Å × 27.9 Å and rare etb topology has been synthesized (see picture). It exhibits good fluorescence properties and substantial hydrogen uptake. For the first time, the compound was assembled with Rh6G dye molecules, and the product showed favorable temperature-dependent luminescent properties.

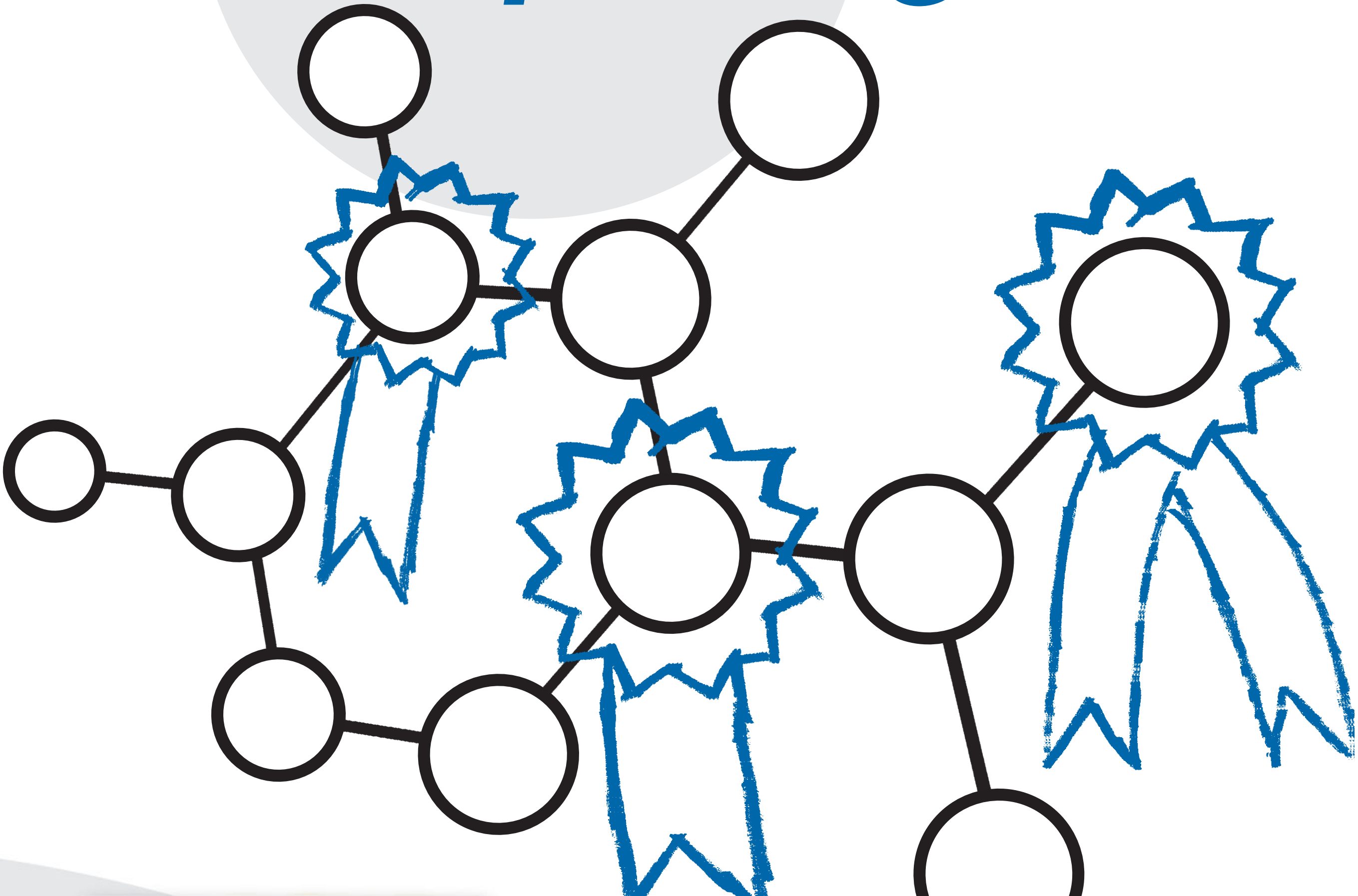
Porous Networks

T. Haneda, M. Kawano,* T. Kojima, M. Fujita* ———— **6643 – 6645**

Thermo-to-Photo-Switching of the Chromic Behavior of Salicylideneanilines by Inclusion in a Porous Coordination Network



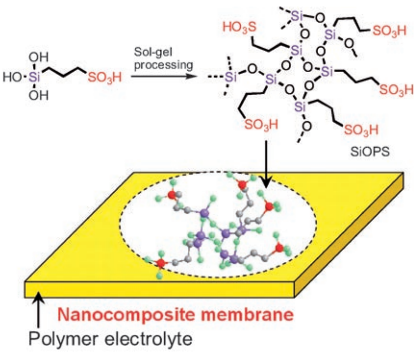
Insert and twist: By inclusion in the channel of a porous coordination network, an otherwise thermochromic salicylideneaniline derivative becomes photochromic because its intrinsic planar conformation is transformed into a nonplanar one. The photochromic properties of the nonplanar guest molecule can be tuned by changing the co-included solvent in the channel.



Conductive Membranes

K. Miyatake, T. Tombe, Y. Chikashige, H. Uchida, M. Watanabe* ——— 6646 – 6649

Enhanced Proton Conduction in Polymer Electrolyte Membranes with Acid-Functionalized Polysilsesquioxane

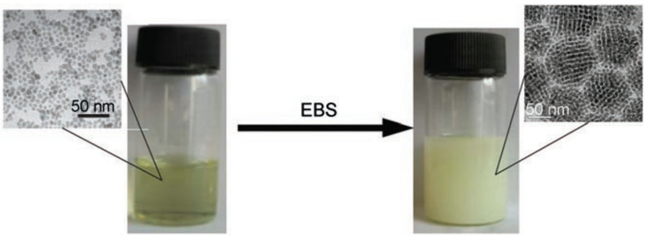


In the membrane: A simple but effective approach to improving the conducting properties of polymer electrolyte membranes has been developed by incorporating acid-functionalized polysilsesquioxane (SiOPS). The nanocomposite membranes showed 30 times higher proton conductivity than that of the original membrane and may find application in sensors, batteries, and most likely fuel cells.

Colloidal Spheres

F. Bai, D. Wang, Z. Huo, W. Chen, L. Liu, X. Liang, C. Chen, X. Wang, Q. Peng, Y. Li* ——— 6650 – 6653

A Versatile Bottom-up Assembly Approach to Colloidal Spheres from Nanocrystals

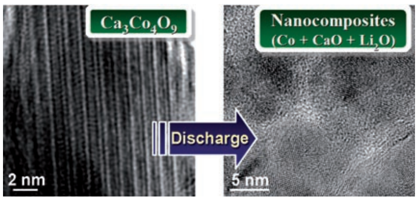


Well-rounded: Water-dispersed colloidal spheres that are self-assembled from nanocrystals with different size, shape, composition, and surface ligand were prepared through a versatile emulsion-based self-assembly (EBS) approach. Through this emulsification process, a dispersion of $BaCrO_4$ nanocrystals in cyclohexane (see picture, left) can be transformed into a dispersion of colloidal spheres of $BaCrO_4$ (see picture, right).

Lithium-Ion Batteries

D.-W. Kim,* Y.-D. Ko, J.-G. Park, B.-K. Kim ——— 6654 – 6657

Formation of Lithium-Driven Active/Inactive Nanocomposite Electrodes Based on $Ca_3Co_4O_9$ Nanoplates

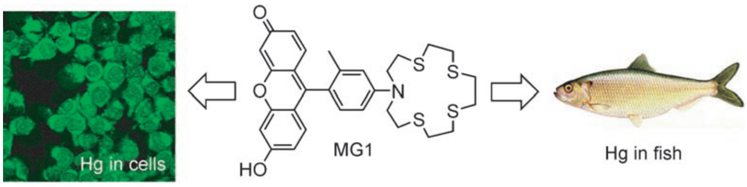


A new electrode material that is expected to have promising applications in energy storage and energy-harvesting systems is presented. In this material, which consists of $Ca_3Co_4O_9$ nanoplates with a high theoretical gravimetric capacity, the lithium-driven conversion process results in the formation of active/inactive nanocomposite electrodes that mitigate the aggregation of the active nanometals (see picture).

Mercury Detection

S. Yoon, E. W. Miller, Q. He, P. H. Do, C. J. Chang* ——— 6658 – 6661

A Bright and Specific Fluorescent Sensor for Mercury in Water, Cells, and Tissue

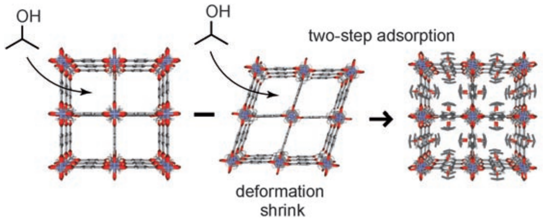


A bright idea: By restricting the rotation between receptor and reporter units of the fluorescent chemosensor Mercury Green 1 (MG1), a remarkably high quantum efficiency is achieved in its Hg^{2+}-ion-bound form in water ($\Phi = 0.72$). MG1 is specific to environmentally and biologically relevant mercury levels (ppm to ppb range), and can assay levels of Hg^{2+} ion in living cells and in edible fish.

Coordination Polymers

K. Uemura,* Y. Yamasaki, Y. Komagawa, K. Tanaka, H. Kita ______ **6662 – 6665**

Two-Step Adsorption/Desorption on a Jungle-Gym-Type Porous Coordination Polymer



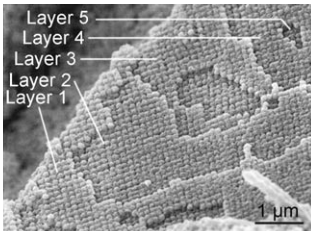
Flexible frameworks: Unique two-step isotherms were observed for the adsorption/desorption of propan-2-ol on [{Zn_2(1,4-benzenedicarboxylate)$_2$(1,4-diazabicyclo[2.2.2]octane)}$_n$] with hydrophobic open spaces. The isotherms were characterized by means of thermal analysis and single-crystal X-ray diffraction (see picture).

Nanostructure Transformation

F. Li, S. A. Delo, A. Stein* __ **6666 – 6669**

Disassembly and Self-Reassembly in Periodic Nanostructures: A Face-Centered-to-Simple-Cubic Transformation

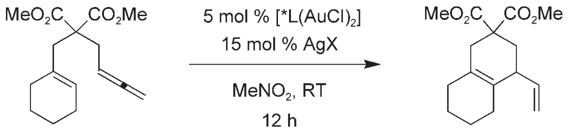
Cube it: Ordered three-dimensional arrays of nanocubes with an unusual simple-cubic packing geometry are formed when a TiO_2–P_2O_5 inverse opal structure disassembles and self-reassembles during a synthesis involving a face-centered-cubic colloidal crystal template. In this way, it may be possible to alter nanoparticle shapes and achieve more-complex geometries in colloidal crystal systems.



Gold Catalysis

M. A. Tarselli, A. R. Chianese, S. J. Lee, M. R. Gagné* ______ **6670 – 6673**

Gold(I)-Catalyzed Asymmetric Cycloisomerization of Eneallenes into Vinylcyclohexenes



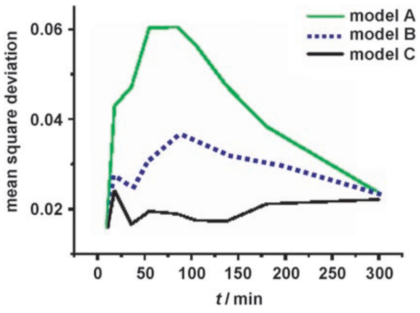
Coming around: Cycloisomerization of eneallenes by cationic gold(I) catalysts produces vinylcyclohexene derivatives in up to 77% *ee*, using [3,5-xylyl-binap-$(AuCl)_2$] and AgOTf additive (see scheme; 3,5-xylyl-binap = 2,2′-bis(di(3,5-xylyl)phosphino)-1,1′-binaphthyl). The procedure is amenable to the synthesis of mono- and bicyclic products and is tolerant of ester, alcohol, and amide groups.

Silicates

S. A. Pelster, B. Weimann, B. B. Schaack, W. Schrader, F. Schüth* ___ **6674 – 6677**

Dynamics of Silicate Species in Solution Studied by Mass Spectrometry with Isotopically Labeled Compounds

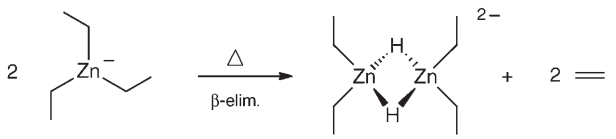
Concerted exchange of four and three Si atoms is respectively responsible for interconversion of cubic octameric (picture: quality of a fit for single- (A), two- (B), and four-atom exchange (C); C fits the experimental pattern best) and prismatic hexameric silicate species in solution according to mass spectrometry with isotopically labeled compounds. These findings have important implications for nucleation and growth processes of zeolites and other silicates.



Zincate Ions

A. Lennartson, M. Håkansson,*
S. Jagner ______ 6678 – 6680

Facile Synthesis of Well-Defined Sodium Hydridoalkylzincates(II)

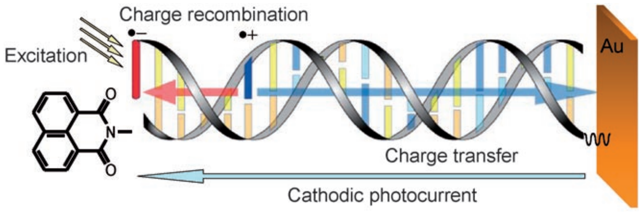


After you, Sir Edward: By following in the footsteps of Frankland and Wanklyn, it has been discovered that simple hydridoalkylzincates(II) (see picture) can be prepared in essentially quantitative yield from mixtures of sodium and an excess of neat dialkylzinc reagent, which also acts as solvent.

Photocurrents in DNA

T. Takada, C. Lin, T. Majima* 6681 – 6683

Relationship between Charge Transfer and Charge Recombination Determines Photocurrent Efficiency through DNA Films

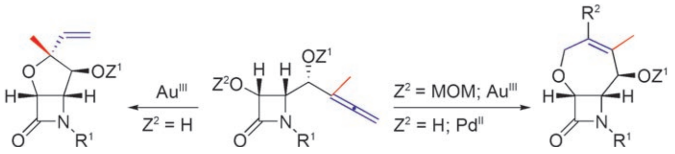


Got a light? The importance of the relationship between the charge recombination and charge transfer during photocurrent generation through DNA films is described. The photocurrent efficiency for DNA films, in which the charge-transfer and recombination rates were modulated by changing the sequence, was investigated by using the photoelectrochemical measurements on an Au electrode.

Synthetic Methods

B. Alcaide,* P. Almendros,*
T. Martínez del Campo ______ 6684 – 6687

Metal-Catalyzed Regiodivergent Cyclization of γ-Allenols: Tetrahydrofurans versus Oxepanes



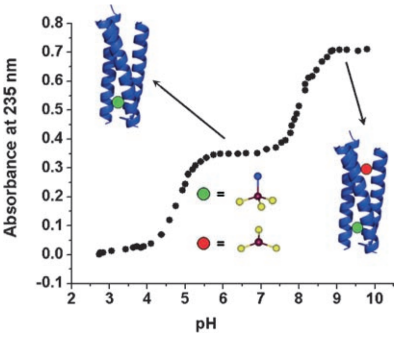
Ringing the changes: The 5-*exo-trig* cyclization pathway of γ-allenols can be completely reversed by either changing the metal (Pd instead of Au) or using a (methoxymethyl)oxy protecting group. As a result, the 7-*endo-trig* alkoxycyclization dominates instead (see scheme; MOM = $MeOCH_2$; Z^1 = tBuMe$_2$Si, ArCO).

Protein Design

O. Iranzo, C. Cabello,
V. L. Pecoraro* ______ 6688 – 6691

Heterochromia in Designed Metallopeptides: Geometry-Selective Binding of Cd^{II} in a De Novo Peptide

Molecular recognition and control of the physical properties of metal ions are major challenges in metalloprotein design. The newly designed peptide Grand L16PenL26AL30C binds two Cd^{II} ions, each with a different coordination geometry—trigonal planar or pseudotetrahedral (see picture; Cd purple, S yellow, O blue). The physical properties of the two centers, such as site selectivity and pH dependence of binding, differ as well.



C–H Bond Formation

W. H. Monillas, G. P. A. Yap,
K. H. Theopold* ———— **6692 – 6694**

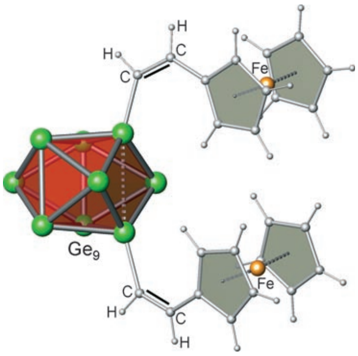
A Tale of Two Isomers: A Stable Phenyl Hydride and a High-Spin ($S=3$) Benzene Complex of Chromium

Staying put: A binuclear phenyl hydride complex of chromium resists benzene formation by reductive elimination, even though the isomeric μ-η^6:η^6 benzene complex can be prepared independently (see scheme, Ar = 2,6-iPr$_2$(C$_6$H$_3$)). Whereas the phenyl hydride shows evidence for metal–metal bonding and antiferromagnetic coupling, the bridging benzene complex features extremely strong ferromagnetic coupling with an $S=3$ ground state.

Cluster Compounds

M. W. Hull, S. C. Sevov* ——— **6695 – 6698**

Addition of Alkenes to Deltahedral Zintl Clusters by Reaction with Alkynes: Synthesis and Structure of [Fc–CH=CH–Ge$_9$–CH=CH–Fc]$^{2-}$, an Organo-Zintl–Organometallic Anion



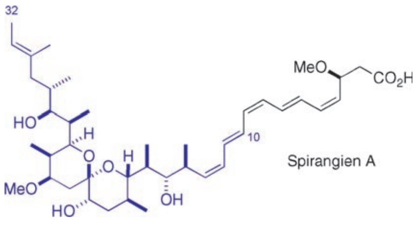
Zintly the best? The reaction of K$_4$Ge$_9$ with Fc–C≡CH in ethylenediamine solution yields the title Ge$_9$ cluster functionalized with two ferrocene groups that are attached to the cluster by double bonds (see picture), thus further expanding the emerging class of organo-Zintl compounds.

Polyketide Synthesis

I. Paterson,* A. D. Findlay,
E. A. Anderson ———— **6699 – 6702**

Synthesis of an Advanced C10–C32 Spiroacetal Fragment and Assignment of the Absolute Configuration of Spirangien A

A bit on the side: A highly convergent and flexible synthetic strategy has been developed for spirangiens A and B that made use of a common stereotetrad building block and led to an advanced C10–C32 spiroacetal fragment, thus enabling the unambiguous assignment of the absolute configuration of these potent cytotoxic polyketide metabolites isolated from the myxobacterium *Sorangium cellulosum*.

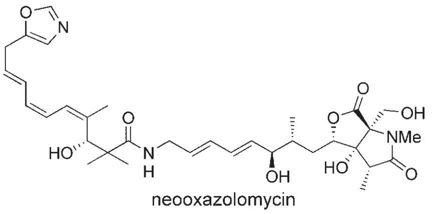


Natural Products

E. O. Onyango, J. Tsurumoto, N. Imai,
K. Takahashi, J. Ishihara,
S. Hatakeyama* ———— **6703 – 6705**

Total Synthesis of Neooxazolomycin

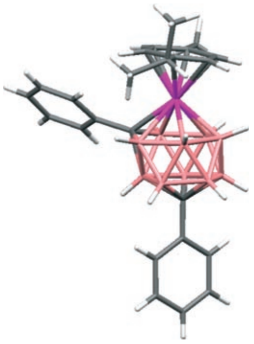
Two sides to the story: Neooxazolomycin, a member of the oxazolomycin family of antibiotics, was synthesized in naturally occurring form by a convergent approach. This highly stereoselective strategy consists of a Tamao hydrosilylation, palladium-catalyzed enolate alkenylation, dihydroxylation accompanied by lactonization, and a Nozaki–Hiyama–Kishi reaction to construct the right-hand segment as well as an improved route to the left-hand segment.



Metallacarboranes

S. Zlatogorsky, M. J. Edie, D. Ellis,
S. Erhardt, M. E. Lopez, S. A. Macgregor,*
G. M. Rosair, A. J. Welch* ____ 6706 – 6709

The Mechanism of Reduction and Metalation of *para* Carboranes: The Missing 13-Vertex MC_2B_{10} Isomer

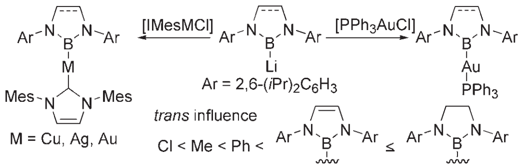


Unanticipated complexity: The first example of a 4,1,11-MC_2B_{10} metallacarborane (see picture; Ru magenta, B pink, C gray, H white) is reported. Reduction and metalation of 1,12-Ph_2-1,12-*closo*-$C_2B_{10}H_{10}$ at both room temperature and low temperature yields no fewer than five isomeric supraicosahedral metallacarborane products. Calculations identify two initial *nido*-$[C_2B_{10}H_{12}]^{2-}$ species, each with one C atom that is not in the open face.

Boryl Complexes

Y. Segawa, M. Yamashita,*
K. Nozaki* ____________ 6710 – 6713

Boryl Anion Attacks Transition-Metal Chlorides To Form Boryl Complexes: Syntheses, Spectroscopic, and Structural Studies on Group 11 Borylmetal Complexes

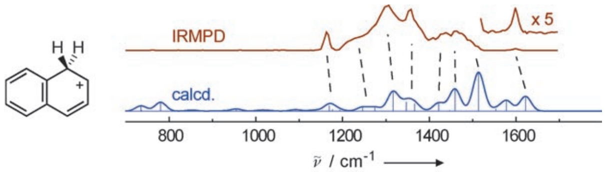


Nucleophilic borylation: Transmetalation from boryllithium compounds to Group 11 transition-metal chlorides gives the corresponding boryl complexes (see scheme). Borylsilver and borylgold complexes that have three-center-two-electron M—B bonds are fully characterized for the first time. The NMR spectra and solid-state structures of the resulting boryl complexes reveal that the boryl ligand is one of the strongest known σ-donor ligands.

Polycyclic Arenes

U. J. Lorenz, N. Solcà, J. Lemaire,
P. Maître, O. Dopfer* ______ 6714 – 6716

Infrared Spectra of Isolated Protonated Polycyclic Aromatic Hydrocarbons: Protonated Naphthalene

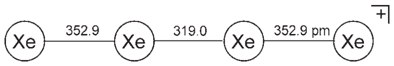


Fingerprinting: The IR spectrum of protonated naphthalene, the smallest member of the class of protonated polycyclic aromatic hydrocarbons (PAHs), has identified the C_α atom as the preferred protonation site of the isolated molecule (see the figure; IRMPD: infrared multiple-photon dissociation). Significant deviations from the corresponding IR spectrum of protonated benzene demonstrate the large impact of additional aromatic rings on the IR fingerprint of protonated PAHs.

Xenon

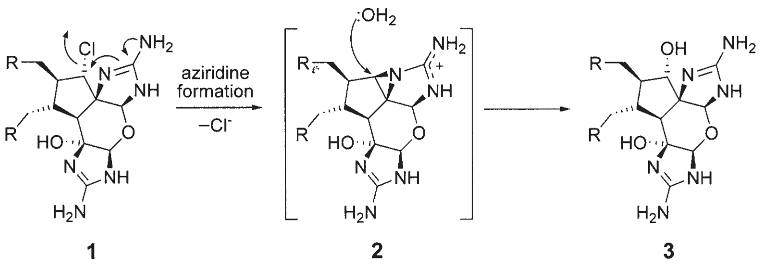
S. Seidel, K. Seppelt,* C. van Wüllen,*
X. Y. Sun ____________ 6717 – 6720

The Blue Xe_4^+ Cation: Experimental Detection and Theoretical Characterization



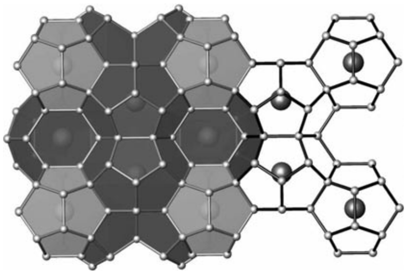
Feeling blue: Green Xe_2^+ reacts with excess xenon under pressure to form a blue compound. According to spectroscopic measurements and theoretical calculations, the blue compound, as shown in the picture, is most likely Xe_4^+ with a linear, symmetric structure ($D_{\infty h}$).

Natural Products



The dimeric pyrrole–imidazole alkaloid massadine chloride (**1**, see scheme) was isolated from the Caribbean sponge *Stylissa caribi*ca. The structure elucidation of massadine chloride and its transformation into massadine (**3**) via an intermediate "massadine aziridine" (**2**) is discussed.

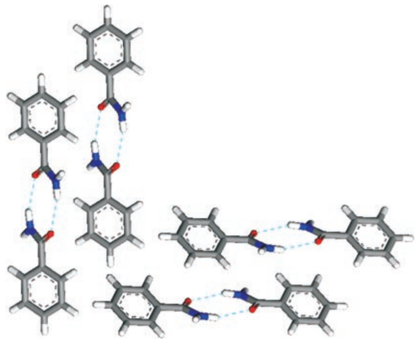
Clathrates



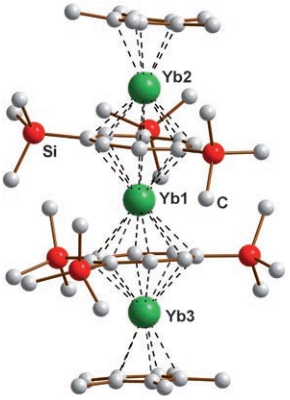
Including boron: $K_7B_7Si_{39}$ (see structure; large spheres: K, small spheres: Si, B) is the first clathrate I compound with boron atoms. With 9.952(1) Å, the borosilicide exhibits the smallest lattice parameter among all intermetallic clathrate I compounds. The composition is in agreement with the Zintl rule.

Polymorphism

A third form of benzamide has been characterized 175 years after the first report of polymorphism in benzamide; the metastable silky needlelike form first described by Wöhler and Liebig was "hidden" for so long owing to the similarities between the metrics of its unit cell and those of the stable form I (the H-bonding motif is depicted). Selective crystallization techniques taking advantage of modern online sensors were crucial in this work.



Lanthanide Sandwich Complexes



All stacked up: The f elements, too, can form well-defined multidecker sandwich complexes—as long as a suitable ligand set is chosen. In the case of the title compound, a combination of pentamethylcyclopentadienyl and 1,3,6-tris(trimethylsilyl)cyclooctatetraenyl ligands (cot‴) was employed to give a nearly linear stacked Yb_3 arrangement (see picture).

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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