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:*

*H. Jiang, P. Elsner, K. L. Jensen, A. Falcicchio, V. Marcos, K. A. Jørgensen**
Achieving Molecular Complexity by Organocatalytic One-Pot Strategies: A Fast Entry for the De Novo Synthesis of Sphingoids, Amino Sugars, and Polyhydroxylated α-Amino Acids

*T. J. Kucharski, Z. Huang, Q.-Z. Yang, Y. Tian, N. C. Rubin, C. D. Concepcion, R. Boulatov**
Kinetics of Thiol/Disulfide Exchange Correlates Weakly with the Restoring Force in the Disulfide Moiety

*W. Xu, X. Xue, T. Li, H. Zeng, X. Liu**
Ultrasensitive and Selective Colorimetric DNA Detection by Nicking Endonuclease-Assisted Nanoparticle Amplification

G. A. Zelada, J. Riu, A. Düzgün, F. X. Rius**
Immediate Detection of Living Bacteria at Ultra-Low Concentrations Using a Carbon-Nanotube-Based Potentiometric Aptasensor

H. Ueda, H. Satoh, K. Matsumoto, K. Sugimoto, T. Fukuyama, H. Tokuyama**
Total Synthesis of (+)-Haplophytine

*K. Fuchibe, T. Kaneko, K. Mori, T. Akiyama**
Expedient Synthesis of N-Fused Indoles: A C–F Activation and C–H Insertion Approach

A. Giannis, P. Heretsch, V. Sarli, A. Stößel*
Synthesis of Cyclopamine Using a Biomimetic and Diastereoselective Approach

*W. A. Chalifoux, R. McDonald, M. J. Ferguson, R. R. Tykwinski**
***t*-Butyl Endcapped Polyynes: Crystallographic Evidence of Reduced Bond-Length Alternation**

*F. Carniato, C. Bisio, G. Gatti, E. Boccaleri, L. Bertinetti, S. Coluccia, O. Monticelli, L. Marchese**
Titanosilsesquioxanes Embedded in Synthetic Clay as a Hybrid Material for Polymer Science

Author Profile

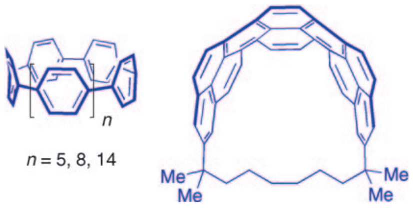
*"My most exciting discovery to date has been asymmetric epoxidation of allylic alcohols in the Sharpless lab.
If I wasn't a scientist, I would be a high-school teacher. …"*
This and more about Tsutomu Katsuki can be found on page 5398.

Books

Highlights

Cyclophanes

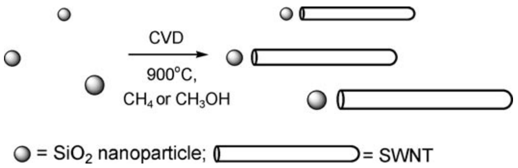
Harbingers of single-chirality nanotubes: Lessons learned from recent syntheses of cyclophanes with record numbers of benzene rings embedded in the macrocycle (see picture) have brought chemists closer to the goal of obtaining structurally uniform single-walled carbon nanotubes made-to-order. The syntheses of the cyclophanes rely on the aromatization of less-strained dihydroaromatic ring systems in the last step to build in the strain.



Nanotube Synthesis

A. Hirsch* ____________ **5403 – 5404**

Growth of Single-Walled Carbon Nanotubes without a Metal Catalyst—A Surprising Discovery



SiO_2 nanoparticles alone can catalyze the formation of single-walled carbon nanotubes (SWNTs). Since transition-metal catalysts are not required, clean SWNT materials can be prepared whose intrinsic property profile is not obscured by metal catalyst particles.

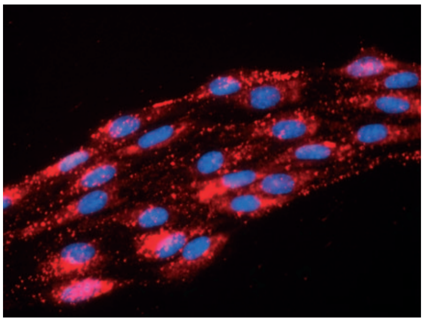
Minireviews

Cell Function

C. J. Bettinger, R. Langer,*
J. T. Borenstein* ________ **5406 – 5415**

Engineering Substrate Topography at the Micro- and Nanoscale to Control Cell Function

Grounded: Substrate nanotopography is known to profoundly influence the behavior of cells both in vitro and in vivo. Recent developments have demonstrated the use of engineered synthetic substrates to control complex cell function, including differentiation and tissue formation. The fluorescent micrograph in the picture depicts a multicellular structure of endothelial cells that was assembled using substrates with synthetic nanotopography.



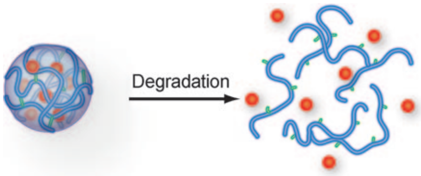
Reviews

Drug Delivery

A. V. Kabanov,*
S. V. Vinogradov ________ **5418 – 5429**

Nanogels as Pharmaceutical Carriers: Finite Networks of Infinite Capabilities

Drug protection: Nanogels—swollen nanosized networks of hydrophilic neutral or ionic polymer chains—can spontaneously incorporate low-molecular-mass drugs or biomacromolecules such as oligonucleotides, siRNA, DNA, and proteins. Numerous chemical functionalities can be employed for the introduction of imaging molecules and the targeted release of drugs (see picture).



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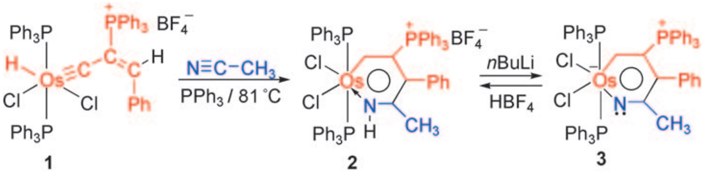
Metallacycles

B. Liu, H. Wang, H. Xie, B. Zeng, J. Chen, J. Tao, T. B. Wen, Z. Cao, H. Xia* ——— 5430 – 5434

Osmapyridine and Osmapyridinium from a Formal [4+2] Cycloaddition Reaction



Metalla-cycloaddition: An unprecedented formal [4+2] cycloaddition reaction takes place when osmium hydrido alkenylcarbyne **1** reacts with acetonitrile to afford the first metallapyridinium complex **2** in high yield (see scheme). Deprotonation of **2** gives the first osmapyridine compound **3**. Treatment of **3** with HBF_4 can regenerate **2** in almost quantitative yield.

Carbon Nanotubes

Y. Kato, Y. Niidome,* N. Nakashima* ——— 5435 – 5438

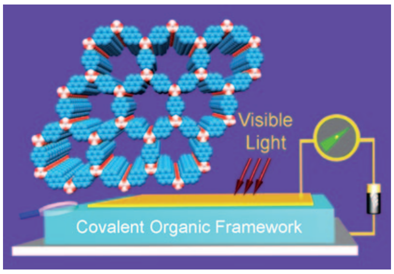
Efficient Separation of (6,5) Single-Walled Carbon Nanotubes Using a “Nanometal Sinker”

Sort it out! Density-gradient ultracentrifugation is used to separate single-walled carbon nanotubes (SWNTs) of a single chirality. A “nanometal sinker” ($AuCl_4^-$ ions) adsorbs onto specific SWNTs and allows the separation of adsorbed SWNTs and nonfunctionlized SWNTs (see picture). (6,5) SWNTs have been successfully separated from as-prepared SWNTs in a process termed “SWNT chirality fishing”.

Photoconductive Structures

S. Wan, J. Guo, J. Kim, H. Ihee, D. Jiang* ——— 5439 – 5442

A Photoconductive Covalent Organic Framework: Self-Condensed Arene Cubes Composed of Eclipsed 2D Polypyrene Sheets for Photocurrent Generation

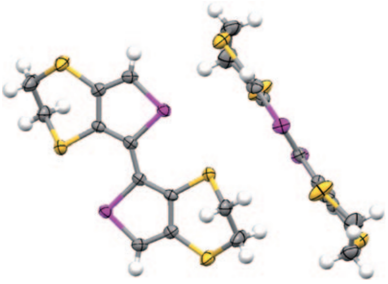


On again, off again: A pyrene-based covalent organic framework (see structure: blue pyrene, white B, red O) facilitates exciton migration and carrier transportation, harvests visible-light photons, and responds quickly to irradiation with light to enable the generation of a significant photocurrent. The framework is capable of repetitive photocurrent switching with a large on–off ratio.

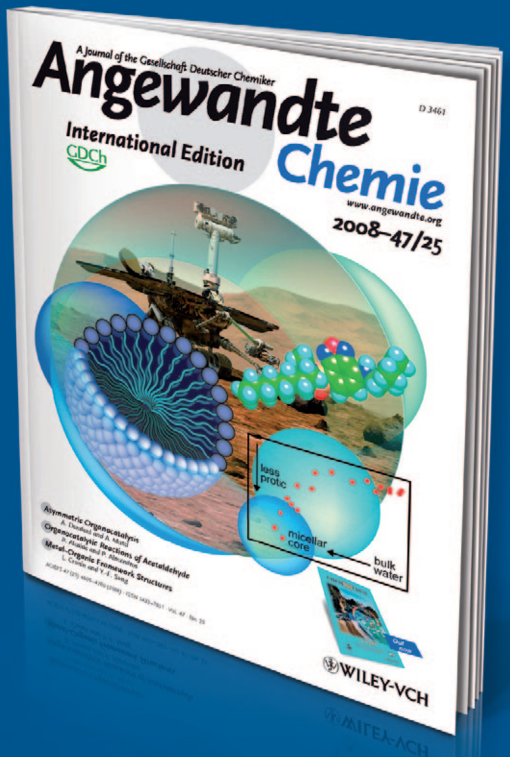
Conjugated Polymers

Y. H. Wijsboom, A. Patra, S. S. Zade, Y. Sheynin, M. Li, L. J. W. Shimon, M. Bendikov* ——— 5443 – 5447

Controlling Rigidity and Planarity in Conjugated Polymers: Poly(3,4-ethylenedithioselenophene)



Staying on a plane: Even small substituents on the backbone of conjugated polymers can cause them to twist significantly, lowering conjugation and leading to wider band gaps. Oligo- and polyselenophenes are more rigid than their thiophene analogues, and can maintain their planarity and low band gap with substituents that otherwise cause considerable twisting. The picture shows two selenophene dimers; Se magenta, S yellow.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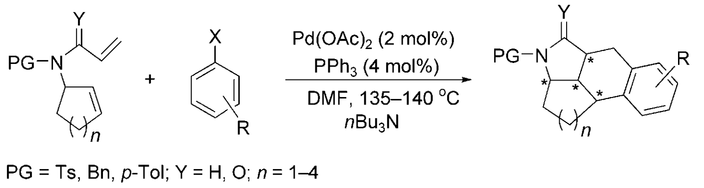
Fused Polycycles

Y. Hu,* C. Yu, D. Ren, Q. Hu, L. Zhang,
D. Cheng ——— 5448 – 5451

One-Step Synthesis of the Benzocyclo[penta- to octa-]isoindole Core

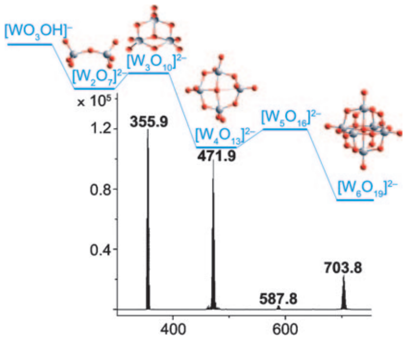


Three in one go: Unactivated dienes containing a cycloalkenyl moiety reacted with a range of substituted aryl halides in the presence of $Pd(OAc)_2/PPh_3$ to afford fused polycyclic heterocycles (see scheme). Three carbon–carbon bonds are formed in this domino reaction, which involves highly regioselective C–C coupling and C–H functionalization steps. DMF = *N*,*N*-dimethylformamide; Bn = benzyl, Ts = *p*-toluenesulfonyl.

Polyoxometalate Formation

L. Vilà-Nadal, A. Rodríguez-Fortea,*
L.-K. Yan, E. F. Wilson, L. Cronin,*
J. M. Poblet* ——— 5452 – 5456

Nucleation Mechanisms of Molecular Oxides: A Study of the Assembly–Dissassembly of $[W_6O_{19}]^{2-}$ by Theory and Mass Spectrometry

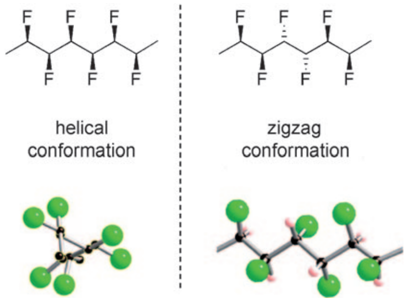


Step by step: The combined use of ESI mass spectrometry and complementary DFT approaches allows the proposal of a formation mechanism for the Lindqvist anion. The mechanism is based on successive aggregation steps of hydrogentungstate anion as the "building block" with subsequent protonation and water condensation. The Lindqvist anion is formed after five steps.

Molecular Conformation

L. Hunter, P. Kirsch, A. M. Z. Slawin,
D. O'Hagan* ——— 5457 – 5460

Synthesis and Structure of Stereoisomeric Multivicinal Hexafluoroalkanes

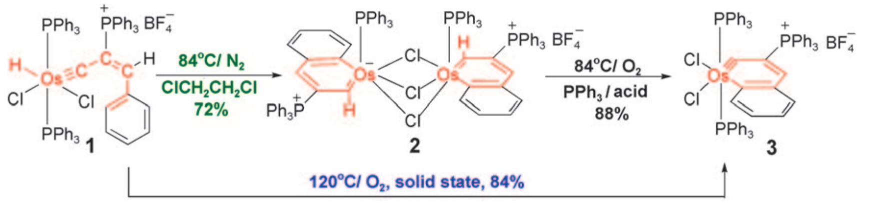


Rational expectations: Molecules containing six contiguous fluorine atoms along a carbon backbone have been synthesized in a stereocontrolled manner. X-ray crystallography shows that the fluoroalkane can adopt a helical or a zigzag shape depending on the stereochemical pattern (see structures). These findings are rationalized by simple stereochemical effects associated with C–F bonds.

C–H Activation

B. Liu, H. Xie, H. Wang, L. Wu, Q. Zhao,
J. Chen, T. B. Wen, Z. Cao,*
H. Xia* ——— 5461 – 5464

Selective Synthesis of Osmanaphthalene and Osmanaphthalyne by Intramolecular C–H Activation

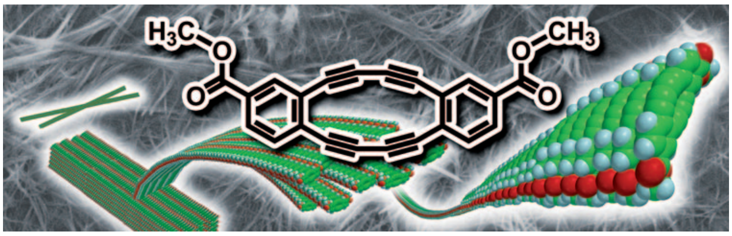


Bisosmanaphthalene 2 and osmanaphthalyne **3** can conveniently be synthesized selectively and in high yield from osmium hydride–alkenylcarbyne **1** by intramolecular C–H activation under an inert or oxidizing atmosphere (N_2 or O_2, respectively). The transformation of bisosmanaphthalene **2** into osmanaphthalyne **3** represents the first conversion from metallabenzene into metallabenzyne.

Supramolecular Chemistry

I. Hisaki,* H. Shigemitsu, Y. Sakamoto, Y. Hasegawa, Y. Okajima, K. Nakano, N. Tohnai, M. Miyata* ____ **5465 – 5469**

Octadehydrodibenzo[12]annulene-Based Organogels: Two Methyl Ester Groups Prevent Crystallization and Promote Gelation

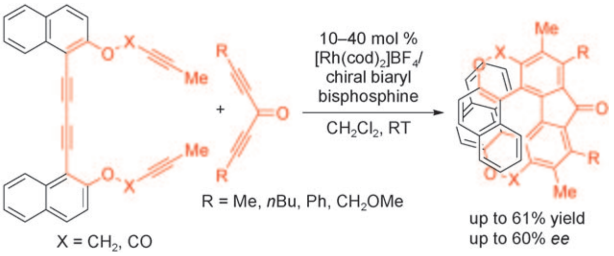


A boomerang-shaped organic gelator, a dehydrobenzo[12]annulene derivative with two methyl ester groups (see picture), successfully forms an organogel in various organic solvents.

Helical Structures

K. Tanaka,* N. Fukawa, T. Suda, K. Noguchi ____ **5470 – 5473**

One-Step Construction of Five Successive Rings by Rhodium-Catalyzed Intermolecular Double [2+2+2] Cycloaddition: Enantioenriched [9]Helicene-Like Molecules

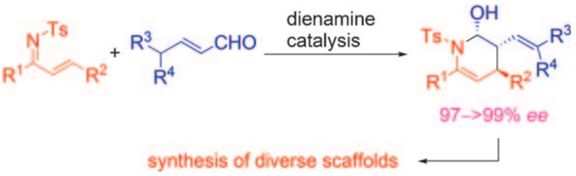


Spiraling upwards: Enantioenriched fluorenone-containing [9]helicene-like molecules have been successfully synthesized through the formation of five successive rings by rhodium-catalyzed intermolecular double [2+2+2] cycloadditions of 2-naphthol-linked tetraynes with dialkynylketones (see scheme; cod = cycloocta-1,5-diene). Their unique crystal structures and photophysical properties have also been determined.

Asymmetric Aminocatalysis

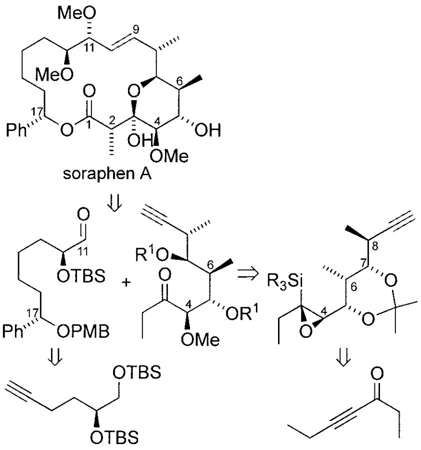
B. Han, Z.-Q. He, J.-L. Li, R. Li, K. Jiang, T.-Y. Liu, Y.-C. Chen* ____ **5474 – 5477**

Organocatalytic Regio- and Stereoselective Inverse-Electron-Demand Aza-Diels–Alder Reaction of α,β-Unsaturated Aldehydes and N-Tosyl-1-aza-1,3-butadienes



Dienamines formed in situ from a chiral secondary amine and an α,β-unsaturated aldehyde undergo the highly α-regioselective title reaction to give densely functionalized piperidine derivatives with excellent enantioselectivity (see scheme). The products were converted into a variety of versatile cyclic frameworks. Ts = 4-toluenesulfonyl.

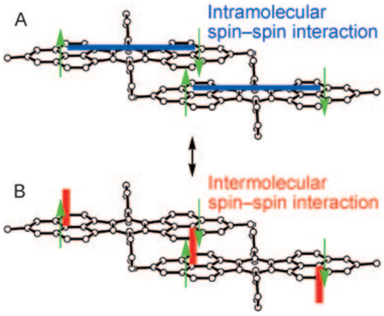
A triple-bond bonanza: The alkyne functional group can be a valuable handle for organic synthesis because the alkyne unit can function both as a nucleophile or as an electrophile when activated with an appropriate metal catalyst. This dual nature of the alkyne moiety has been exploited for the concise total synthesis of the natural product soraphen A (see retrosynthesis; PMB = *para*-methoxybenzyl, TBS = *tert*-butyldimethylsilyl).



Natural Product Synthesis

B. M. Trost,* J. D. Sieber, W. Qian, R. Dhawan, Z. T. Ball ——— **5478 – 5481**

Asymmetric Total Synthesis of Soraphen A: A Flexible Alkyne Strategy



Two flavors: Intra- and intermolecular spin–spin interactions of unpaired electrons coexist and correlate in stacks of phenalenyl-based singlet biradicals. The electronic structure of the one-dimensional π–π chain is best represented by the superposition of formulas **A** and **B** in terms of the resonating valence-bond (RVB) model. Lower temperatures and higher pressures induce a resonance balance shift to the formula **B**.

Singlet Biradicals

A. Shimizu, M. Uruichi, K. Yakushi, H. Matsuzaki, H. Okamoto, M. Nakano, Y. Hirao, K. Matsumoto, H. Kurata, T. Kubo* ——— **5482 – 5486**

Resonance Balance Shift in Stacks of Delocalized Singlet Biradicals

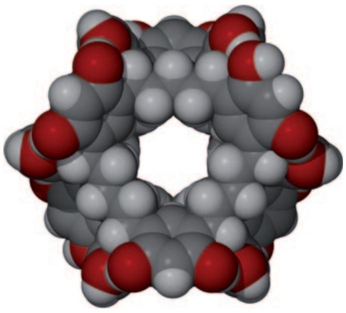
A mind-bending compound: 1,1,8,8-Tetramethyl[8](2,11)teropyrenophane (see picture) has been synthesized in just eight steps and 10% overall yield from dimethyl suberate. The teropyrene system and its two benzylic carbon atoms are close in structure to half of an 80-carbon atom aromatic belt (Vögtle belt) and a segment of an (8,8) single-walled carbon nanotube.

Cyclophanes

B. L. Merner, L. N. Dawe, G. J. Bodwell* ——— **5487 – 5491**

1,1,8,8-Tetramethyl[8](2,11)teropyrenophane: Half of an Aromatic Belt and a Segment of an (8,8) Single-Walled Carbon Nanotube

Fixing the hole: Molecular organic compounds with large accessible internal cavities display gas-storage ability in the amorphous solid state. This finding suggests for the first time that long-range molecular order is not a prerequisite for organic molecules to be engineered as porous materials.



Gas Adsorption

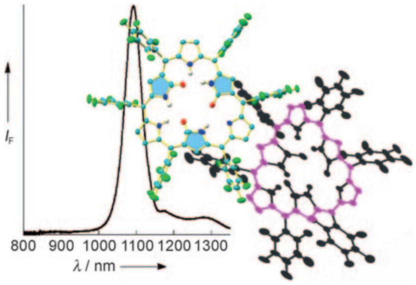
J. Tian, P. K. Thallapally, S. J. Dalgarno, P. B. McGrail, J. L. Atwood* **5492 – 5495**

Amorphous Molecular Organic Solids for Gas Adsorption

Porphyrinoids

Y.-S. Xie, K. Yamaguchi, M. Toganoh, H. Uno, M. Suzuki, S. Mori, S. Saito, A. Osuka,* H. Furuta* ______ **5496 – 5499**

Triply N-Confused Hexaphyrins: Near-Infrared Luminescent Dyes with a Triangular Shape

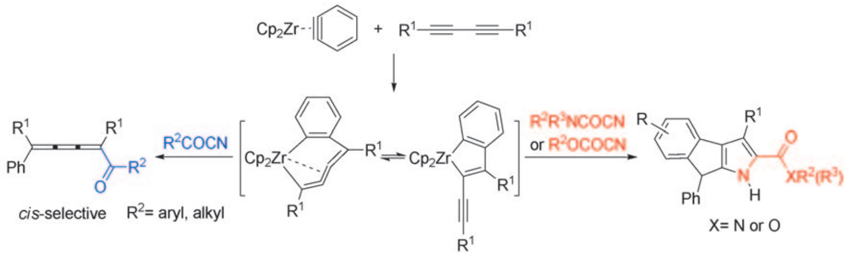


Getting in shape: Meso-pentafluorophenyl triply N-confused hexaphyrins have been synthesized in the free-base and oxidized forms and shown to have a triangular shape and efficient emission in the NIR region (see picture). The triangular shape is achieved by the presence of alternating confused and normal pyrrole rings. DFT calculations show that the triangular shape is more stable than a rectangular form.

Synthetic Methods

X.-P. Fu, J.-J. Chen, G.-Y. Li, Y.-H. Liu* ______ **5500 – 5504**

Diverse Reactivity of Zirconacyclocumulenes Derived from Coupling of Benzynezirconocenes with 1,3-Butadiynes towards Acyl Cyanides: Synthesis of Indeno[2,1-*b*]pyrroles or [3]Cumulenones

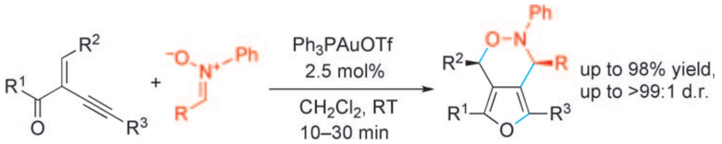


Versatility: Cycloaddition of carbamoyl cyanides to 1,3-butadiynes via seven-membered zirconacyclocumulenes yields dihydroindeno[2,1-*b*]pyrroles (see scheme, right); a C(sp^2)—H bond on the aromatic substituent of the 1,3-butadiyne reactant is activated in the process. In contrast, reactions with aryl or alkyl acyl cyanides provide a stereoselective route to *cis*-[3]cumulenones (left).

Synthetic Methods

F. Liu, Y. Yu, J. Zhang* ______ **5505 – 5508**

Highly Substituted Furo[3,4-*d*][1,2]oxazines: Gold-Catalyzed Regiospecific and Diastereoselective 1,3-Dipolar Cycloaddition of 2-(1-Alkynyl)-2-alken-1-ones with Nitrones

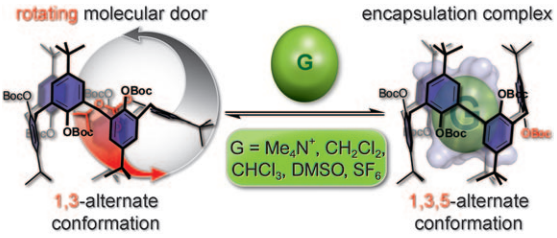


Rapid access: A gold(I)-catalyzed 1,3-dipolar cycloaddition of 2-(1-alkynyl)-2-alken-1-ones with nitrones provides a practical, regiospecific, and stereoselective access to highly substituted fused bicyclic furo[3,4-*d*][1,2]oxazines under mild conditions (see scheme). These fused heterobicyclic compounds can be readily converted into furans or 3,6-dihydro-2*H*-1,2-oxazines in a chemoselective fashion.

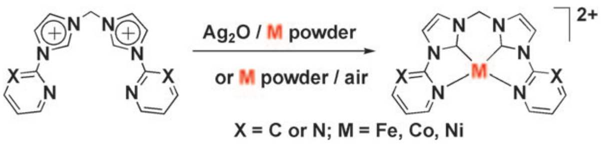
Host–Guest Systems

M. Ménand, A. Leroy, J. Marrot, M. Luhmer, I. Jabin* ______ **5509 – 5512**

Induced-Fit Encapsulation by a 1,3,5-Alternate Calix[6]arene



A little bit of flexibility: Charged or neutral species can be accommodated in solution and in the solid state by the closed hydrophobic cavity of the first calix[6]arene to adopt a 1,3,5-alternate conformation (see picture, Boc = *tert*-butoxycarbonyl). The encapsulation involves an induced-fit process that is reminiscent of the rotation of a door and is characterized by large activation barriers for guest exchange.

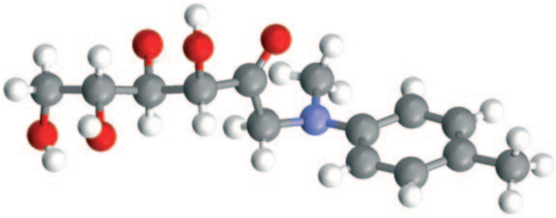


Move to the first row: Simple and practical synthetic methods have been developed for metal complexes of N-heterocyclic carbenes. A number of Fe^{II}, Co^{II}, Ni^{II}, as well as divalent and mixed-valent Cu carbene complexes were obtained in good yields by treating metal powders with imidazolium salts in the presence of Ag_2O or air.

N-Heterocyclic Carbenes

B. Liu, Q. Xia, W. Chen* ___ **5513 – 5516**

Direct Synthesis of Iron, Cobalt, Nickel, and Copper Complexes of N-Heterocyclic Carbenes by Using Commercially Available Metal Powders

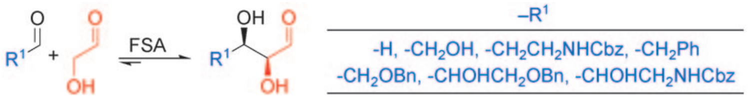


Sweet structure: Acyclic reducing carbohydrate intermediates are typically impossible to crystallize. 1-Amino-1-deoxy-D-fructose derivatives afford an exceptional example of the keto form in the crystalline state (see structure), possibly as a consequence of an interplay between the hydrophobic microenvironment around the carbonyl group and hydrogen-bonding patterns.

Carbohydrate Isomerization

V. V. Mossine,* C. L. Barnes, D. L. Chance, T. P. Mawhinney ___ **5517 – 5520**

Stabilization of the Acyclic Tautomer in Reducing Carbohydrates



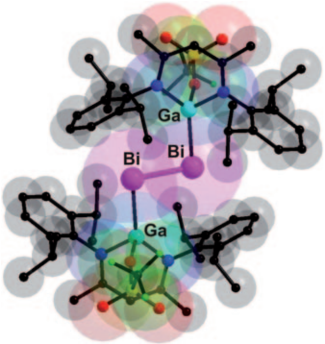
New facets of enzyme activity: D-Fructose-6-phosphate aldolase (FSA) catalyzes the self-aldol reaction of glycolaldehyde (GA) and its cross-aldol addition to other aldehydes. As the affinity of GA for FSA as a donor is higher than that as an acceptor, cross-aldol reactions are possible with good to poor aldehyde acceptors if the concentration of GA in the reaction is kept low.

Biocatalysis

VIP

X. Garrabou, J. A. Castillo, C. Guérard-Hélaine, T. Parella, J. Joglar, M. Lemaire, P. Clapés* ___ **5521 – 5525**

Asymmetric Self- and Cross-Aldol Reactions of Glycolaldehyde Catalyzed by D-Fructose-6-phosphate Aldolase



Bismuth goes GaGa: Dibismuthenes are derived from commercially available bismuth(III) triflate or aryloxide salts by employing [Ga(ddp)] (ddp = CH-[MeC(2,6-iPr$_2$C$_6$H$_3$)N]$_2$) as an efficient reducing agent and trapping ligand. Apart from the shortest bismuth–bismuth bonds known to date, the compounds demonstrate the unique synthetic potential in main-group chemistry of low-coordinate Group 13 compounds analogous to N-heterocyclic carbenes.

Main-Group Chemistry

G. Prabusankar, C. Gemel, P. Parameswaran, C. Flener, G. Frenking,* R. A. Fischer* ___ **5526 – 5529**

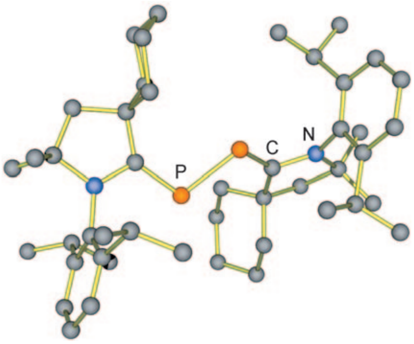
A Short Bi=Bi Bond Supported by a Metalloid Group 13 Ligand

Contents

P–P Activation

O. Back, G. Kuchenbeiser, B. Donnadieu, G. Bertrand* ________ **5530–5533**

Nonmetal-Mediated Fragmentation of P_4: Isolation of P_1 and P_2 Bis(carbene) Adducts



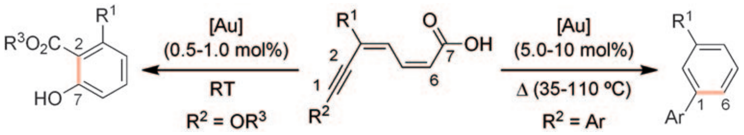
Cutting P_4 in pieces! Stable singlet carbenes react with white phosphorus at room temperature to afford P_4, P_3, P_2, and even P_1 fragments that are stabilized by the carbene moiety (see picture). This process of activation and fragmentation, which was previously carried out using transition metals, can lead to the environmentally friendly production of phosphorus derivatives.

Gold Catalysis

VIP

P. García-García, M. A. Fernández-Rodríguez, E. Aguilar* ________ **5534–5537**

Gold-Catalyzed Cycloaromatization of 2,4-Dien-6-yne Carboxylic Acids: Synthesis of 2,3-Disubstituted Phenols and Unsymmetrical Bi- and Terphenyls

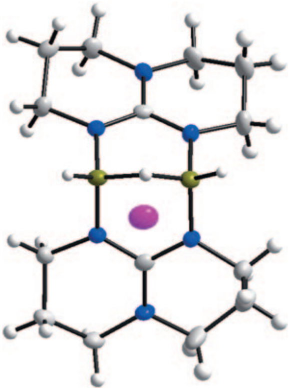


Round numbers: A gold-catalyzed 2,7-cycloaromatization of captodative dienyne carboxylic acids has been developed that occurs at room temperature with low catalyst loading and total regioselective control (see scheme). The reaction is totally dependent on the electronic properties of the dienyne acid: if a strong electron-donating group is not directly linked to the triple bond, a 1,6-cyclization/decarboxylation sequence takes place.

B–B Bond Protonation

O. Ciobanu, E. Kaifer, M. Enders, H.-J. Himmel* ________ **5538–5541**

Synthesis of a Stable $B_2H_5^+$ Analogue by Protonation of a Double Base-Stabilized Diborane(4)

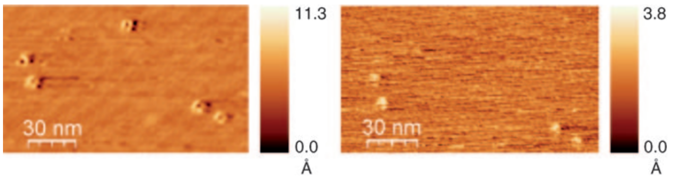


Polarity of H^+ reversed: The synthesis of $[B_2H_3(hpp)_2]^+I^-$,a dinuclear borohydride with terminal and bridging H atoms (see picture; B yellow, N blue, C gray, H white, I purple), is made possible with the ligand hexahydropyrimidopyrimidate (hpp). In the course of the reaction the proton is converted into a hydride.

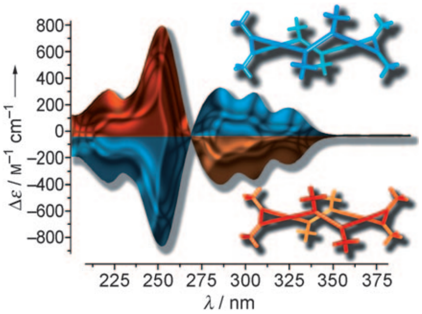
Bio-Electrochemistry

C. Baier, U. Stimming* ____ **5542–5544**

Imaging Single Enzyme Molecules under In Situ Conditions



A change of image: Single molecules of horseradish peroxidase are investigated by scanning electrochemical potential microscopy (SECPM) and electrochemical STM (EC-STM). SECPM delivers images (left) of single enzymes that are of greater detail than those obtained by EC-STM (right) and even shows an enzyme molecule not visible in the STM image.



The unique combination of geometric and electronic properties explains the remarkable magnitude of the Cotton effects in the circular dichroism spectra of new enantiomerically pure alleno-acetylenic macrocycles (see picture). The macrocycles (P,P,P,P)-(−)-**1** (red) and (M,M,M,M)-(+)-**1** (blue) were prepared in three steps starting from optically pure 1,3-di-*tert*-butyl-1,3-diethynylallenes.

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