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:

*P. Agarwal, N. A. Piro, K. Meyer, P. Müller, C. C. Cummins**
An Isolable and Monomeric Phosphorus Radical That Is Resonance-Stabilized by the Vanadium(IV/V) Redox Couple

*C. Chatterjee, R. K. McGinty, J.-P. Pellois, T. W. Muir**
Auxiliary-Mediated Site-Specific Peptide Ubiquitylation

G. A. Pierce, S. Aldridge, C. Jones, T. Gans-Eichler, A. Stasch, N. D. Coombs, D. J. Willock*
Cationic Terminal Aminoborylene Complexes: Controlled Stepwise Insertion into M–B and B–N Double Bonds

*K. Ono, M. Yoshizawa, T. Kato, K. Watanabe, M. Fujita**
Porphine Dimeric Assemblies in Organic-Pillared Coordination Cages

*S. T. Selvan, P. K. Patra, C. Y. Ang, J. Y. Ying**
Synthesis of and Live Cell Imaging with Silica-Coated Semiconductor and Magnetic Quantum Dots

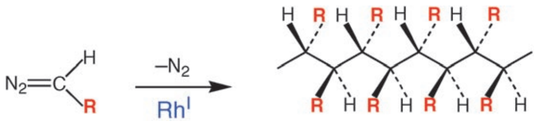
S. I. Chan, V. C.-C. Wang, J. C.-H. Lai, S. S.-F. Yu, P. P.-Y. Chen, K. H.-C. Chen, C.-L. Chen, M. K. Chan*
Redox Potentiometric Studies of the Particulate Methane Monooxygenase: Support for a Trinuclear Copper Cluster Active Site

News

Books

Highlights

Carbene Polymerization

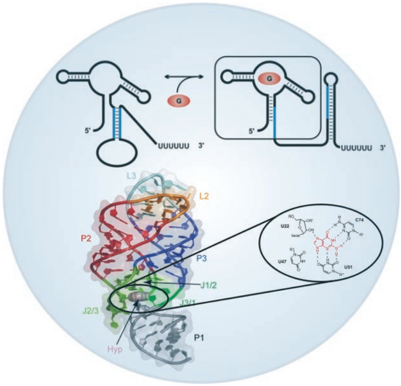


From carbenes to polymers: The synthesis of polymers that bear a polar group (R) on every main-chain carbon atom, while controlling their stereochemistry, was an elusive goal until quite recently, when it was reported that rhodium(I)-catalyzed polymerization of functionalized carbenes (from diazo compounds) provides access to such stereoregular polymers (see scheme).

Minireviews

RNA Switches

An important mode of action in gene expression is based on the highly specific and high-affinity binding of ligands to, and the resultant conformational switching of, RNA switches (riboswitches). Structures of RNA–ligand complexes give insight into the molecular recognition of small metabolites by riboswitches and into the stabilizing interactions of tertiary structures, aiding the targeted design of new high-affinity RNA-binding molecules.

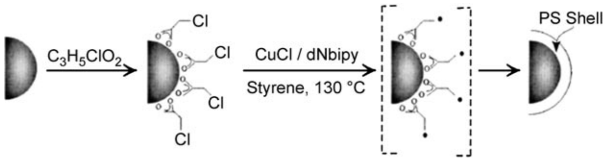


Reviews

Magnetic Nanoparticles

A.-H. Lu, E. L. Salabas,
F. Schüth* ________________ 1222 – 1244

Magnetic Nanoparticles: Synthesis, Protection, Functionalization, and Application



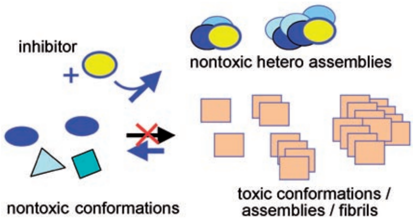
Particularly attractive: Magnetic nanoparticles can be prepared and protected against corrosion in a variety of ways (Scheme: polystyrene (PS) coating of $MnFe_2O_4$ particles by atom-transfer radical polymerization). The protected magnetic nanoparticles can be further functionalized for many applications including catalysis and biotechnology.

Communications

Protein Aggregation

L.-M. Yan, A. Velkova, M. Tatarek-Nossol, E. Andreetto,
A. Kapurniotu* ___________ 1246 – 1252

IAPP Mimic Blocks Aβ Cytotoxic Self-Assembly: Cross-Suppression of Amyloid Toxicity of Aβ and IAPP Suggests a Molecular Link between Alzheimer's Disease and Type II Diabetes

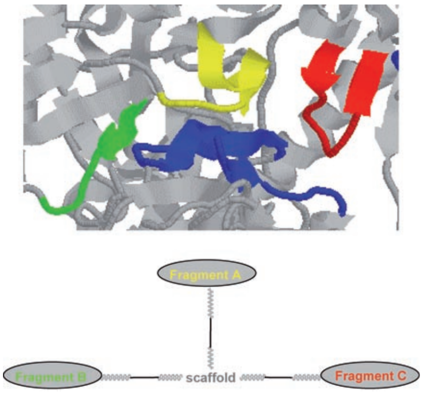


Le fabuleux destin d'amyloid disease: A peptide-derived inhibitor for amyloid diseases binds the Alzheimer's disease β-amyloid peptide (Aβ40) and the type II diabetes islet amyloid polypeptide (IAPP) and blocks cytotoxic self-assembly of both peptides. Evidence is also presented for a high-affinity interaction between Aβ40 and IAPP that results in cross-suppression of cytotoxic self-association of both peptides.

Peptidomimetics

R. Franke, T. Hirsch, H. Overwin,
J. Eichler* ________________ 1253 – 1255

Synthetic Mimetics of the CD4 Binding Site of HIV-1 gp120 for the Design of Immunogens



Do you copy? The epitope of the broadly neutralizing anti-HIV-1 antibody mAb b12 overlaps the CD4 binding site (CD4bs) of the viral envelope glycoprotein gp120 (see picture). Synthetic mimetics of the CD4bs are therefore promising immunogen candidates to elicit a broadly neutralizing immune response. Polyclonal antisera against such a mimetic molecule specifically recognize gp120 and compete with mAb b12 for binding to gp120.

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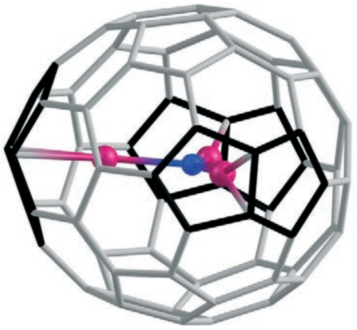
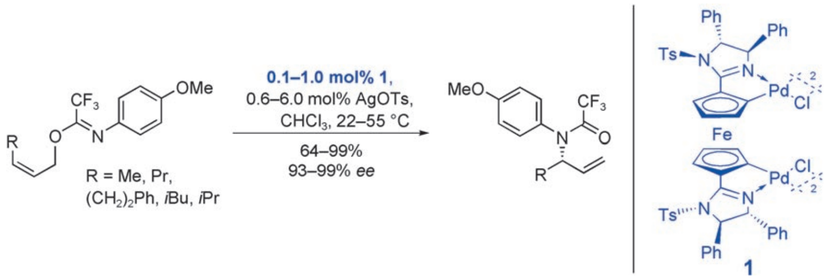
Breaking the rule: The first isolated endohedral cluster fullerene of C_{70} ($Sc_3N@C_{70}$) exhibits a cage structure that does not obey the isolated pentagon rule. It contains three pairs of adjacent pentagons, which are coordinated to the three Sc atoms of the asymmetrical Sc_3N cluster (see the DFT-optimized structure; red Sc, blue N).



Endohedral Fullerenes

S. Yang,* A. Popov,
L. Dunsch* ———— **1256–1259**

Violating the Isolated Pentagon Rule (IPR): The Endohedral Non-IPR C_{70} Cage of $Sc_3N@C_{70}$



In just four steps from ferrocene, macrocyclic ferrocenyl bispalladacyles have been synthesized by using a diastereoselective biscyclopalladation reaction as the key step. The complexes not only possess a fascinating structure but are also the first highly active catalysts for the title reaction (see scheme), requiring as little as 0.1 mol% of catalyst for most of the substrates. Ts = toluene-4-sulfonyl.

Asymmetric Rearrangements

S. Jautze, P. Seiler,
R. Peters* ———— **1260–1264**

Macrocyclic Ferrocenyl–Bisimidazoline Palladacycle Dimers as Highly Active and Enantioselective Catalysts for the Aza-Claisen Rearrangement of *Z*-Configured *N*-*para*-Methoxyphenyl Trifluoroacetimidates

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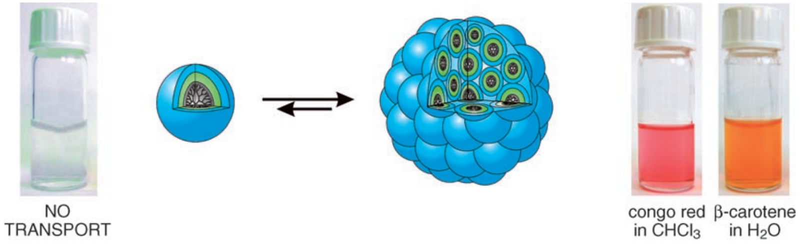

Chemical chameleons: Highly stable supramolecular aggregates built from dendritic multishell architectures show a universal transport ability for both polar and nonpolar guest molecules and can adapt to various solvent environments, ranging from toluene to water.

Nanotransport Systems

VIP

M. R. Radowski, A. Shukla,
H. von Berlepsch, C. Böttcher, G. Pickaert,
H. Rehage, R. Haag* ———— **1265–1269**

Supramolecular Aggregates of Dendritic Multishell Architectures as Universal Nanocarriers

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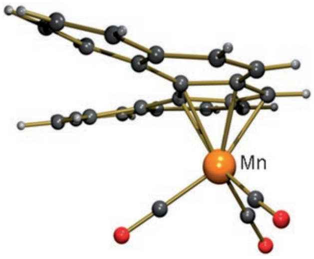


Fluorene's big brother: The first transition-metal complexes of the dibenzo[*c*,*g*]fluorenyl anion (Dbf), an intrinsically chiral derivative of the cyclopentadienyl anion, are reported (see structure of $[(Dbf)Mn(CO)_3]$). According to density functional calculations, the electronic properties of this ligand differ significantly from those of the fluorenyl anion.

Organometallic Chemistry

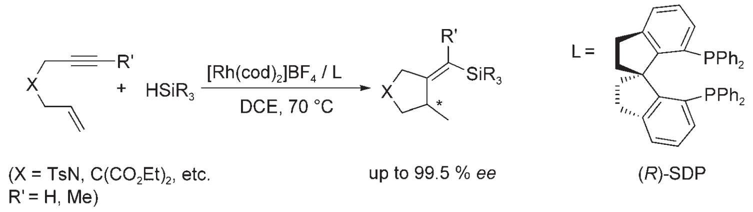
F. Pammer, Y. Sun, C. May,
G. Wolmershäuser, H. Kelm, H.-J. Krüger,
W. R. Thiel* ———— **1270–1273**

Dibenzo[*c*,*g*]fluorene: The Combination of Cyclopentadiene and 1,1′-Binaphthyl in One Ligand

Asymmetric Catalysis

B.-M. Fan, J.-H. Xie, S. Li, L.-X. Wang, Q.-L. Zhou* ———— **1275 – 1277**

Highly Enantioselective Hydrosilylation/Cyclization of 1,6-Enynes Catalyzed by Rhodium(I) Complexes of Spiro Diphosphines



Highly enantioselective synthesis: The rhodium(I) complex of the chiral ligand SDP is successfully used as a catalyst for the hydrosilylation/cyclization of 1,6-enynes with silanes. Under the optimized reaction conditions, optically active silylalkenes containing cyclopentane or pyrrolidine rings are obtained in good yields with excellent enantioselectivities (see scheme). DCE = 1,2-dichloroethane

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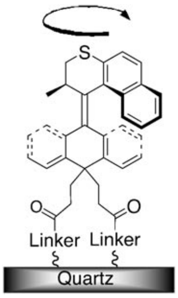
Nanoscale Rotary Motors

M. M. Pollard, M. Lubomska, P. Rudolf,* B. L. Feringa* ———— **1278 – 1280**

Controlled Rotary Motion in a Monolayer of Molecular Motors



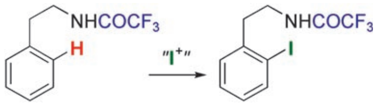
All for one: The relative unidirectional rotary motion of light-driven molecular motors in solution was transformed into controlled rotary motion in a monolayer on quartz. The correlation of the CD spectroscopic behavior of the monolayer with its solution counterpart suggests that the motors retain their function when grafted to the surface.

Electrophilic Substitution

J. Barluenga,* J. M. Álvarez-Gutiérrez, A. Ballesteros, J. M. González ———— **1281 – 1283**

Direct *ortho* Iodination of β- and γ-Aryl Alkylamine Derivatives

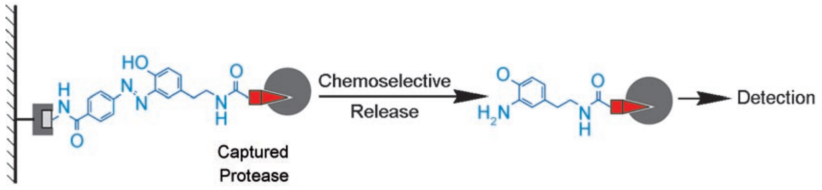
Two in one! A trifluoroacetamide protecting group not only masks an amine functionality, but also mimics peptidyl directing effects as a controlling unit in an efficient *ortho* iodination of a variety of biologically relevant small molecules (see example).



Protein Cleavage

S. H. L. Verhelst, M. Fonović, M. Bogyo* ———— **1284 – 1286**

A Mild Chemically Cleavable Linker System for Functional Proteomic Applications

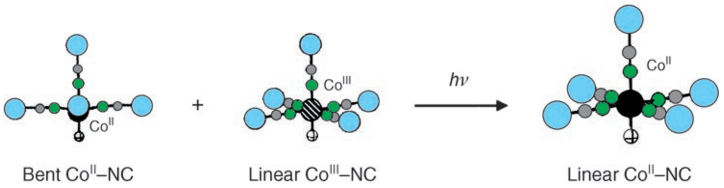


An amicable split: Small-molecule probes can be applied for the enrichment of specific protein targets from a complex proteome. A cleavable linker system, which prevents the release of unwanted, nonspecifically bound proteins, can be used for a very mild and highly selective cleavage of probe-labeled proteins.

Prussian Blue Derivatives

C. Cartier dit Moulin, G. Champion, J.-D. Cafun, M.-A. Arrio, A. Bleuzen* ———— **1287 – 1289**

Structural Rearrangements Induced by Photoexcitation in a RbCoFe Prussian Blue Derivative

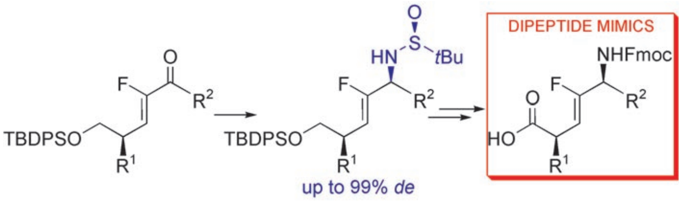


Light influence: The Co crystal-field parameter was used as a probe of the photoinduced metastable state of a RbCoFe Prussian blue analogue. From the light-induced change in this parameter, a scheme of the photoinduced structural rearrangement is proposed in which cooperative interactions within the three-dimensional structure impose linear geometry on all Co-NC-Fe entities in the metastable state (see picture).

Peptide Mimics

G. Dutheuil, S. Couve-Bonnaire, X. Pannecoucke* ———— **1290 – 1292**

Diastereomeric Fluoroolefins as Peptide Bond Mimics Prepared by Asymmetric Reductive Amination of α-Fluoroenones

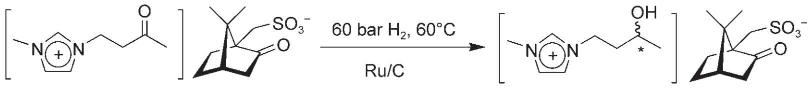


Fluoropeptidomimetics: An efficient asymmetric reductive amination of fluoroenones has been developed that affords potential precursors of fluoropeptide isosteres. Stereoselective routes with different reductive agents provided both diastereomers from the same nonracemic sulfinyl imine. The method was applied to the synthesis of different dipeptide analogues.

Asymmetric Catalysis

P. S. Schulz,* N. Müller, A. Bösmann, P. Wasserscheid* ———— **1293 – 1295**

Effective Chirality Transfer in Ionic Liquids through Ion-Pairing Effects



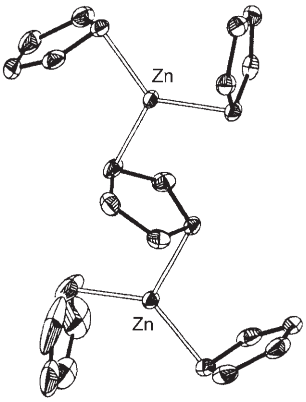
Passing it on: Since every reaction at a prochiral ion must take place in close proximity to its counterion, it should be possible to transfer chiral information between the ions of an ionic liquid. Indeed, the hydrogenation of a prochiral, keto-functionalized cation was found to proceed in the presence of (*R*)-camphorsulfonate in up to 80% *ee* (see scheme).

Metallocenes

E. Alvarez, A. Grirrane, I. Resa, D. del Río, A. Rodríguez, E. Carmona* **1296 – 1299**

Cyclopentadienyl Zincates: Synthesis and X-ray Studies of Sodium and Potassium Salts of the $[Zn(C_5H_5)_3]^-$ and $[Zn_2(C_5H_5)_5]^-$ Ions

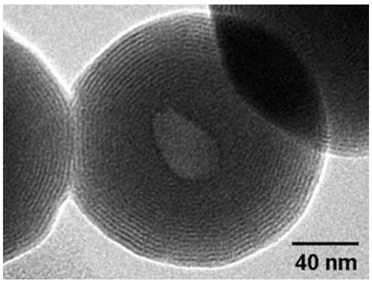
Zigzag zinc: The Na^+ and K^+ salts of the $[Zn(C_5H_5)_3]^-$ ion exhibit polymeric 1D and 2D structures, respectively. In contrast, the dizincate $[Na(thf)_6][Zn_2(C_5H_5)_5]$ contains discrete $[Zn_2(C_5H_5)_5]^-$ ions that consist of two $\{Zn(C_5H_5)_2\}$ groups with $\eta^1(\pi)/\eta^1(\pi)$ binding, bridged by a C_5H_5 ring $\eta^1(\pi)$-coordinated to each zinc atom (see structure).



Layered Assemblies

H. Li, H. Sun, W. Qi, M. Xu,
L. Wu* ———————— 1300 – 1303

Onionlike Hybrid Assemblies Based on Surfactant-Encapsulated Polyoxometalates

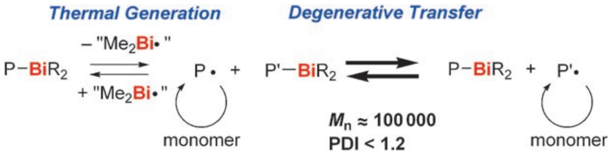


Know your onions: Layered onionlike assemblies of surfactant-encapsulated polyoxometalates have been constructed in organic solution (see TEM image of $(DODA)_4SiW_{12}O_{40}$; DODA = dimethyldioctadecylammonium). The hybrid structure arises from the rearrangement of surfactants on the polyoxometalate, which is driven by hydrophobic forces.

Polymerization

S. Yamago,* E. Kayahara, M. Kotani,
B. Ray, Y. Kwak, A. Goto,
T. Fukuda ———————— 1304 – 1306

Highly Controlled Living Radical Polymerization through Dual Activation of Organobismuthines

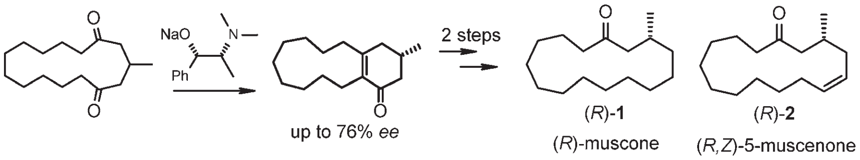


The living end: Organobismuthines promote highly controlled living radical polymerization through two activation mechanisms, namely, thermal generation and degenerative transfer (see scheme). Both conjugated and nonconjugated vinyl monomers are polymerized to give well-defined polymers with predetermined molecular weight (M_n) and low polydispersity index (PDI).

Musk Odorants

O. Knopff,* J. Kuhne, C. Fehr 1307 – 1310

Enantioselective Intramolecular Aldol Addition/Dehydration Reaction of a Macrocyclic Diketone: Synthesis of the Musk Odorants (*R*)-Muscone and (*R*,*Z*)-5-Muscenone



One hundred years after the first isolation of natural (*R*)-muscone [(*R*)-**1**], a short and efficient access to the outstanding odorants (*R*)-**1** and (*R*,*Z*)-5-muscenone [(*R*)-**2**] has become possible thanks to an unprecedented, reversible intramolecular aldol addition/enantioselective dehydration (up to 76% *ee*; see scheme).

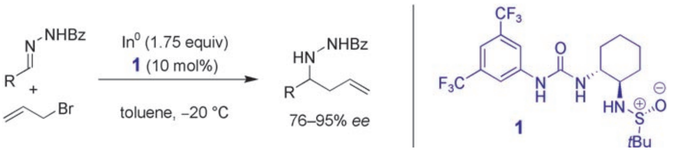
Arene Methylation

D. Lesthaeghe,* B. De Sterck,
V. Van Speybroeck, G. B. Marin,
M. Waroquier* ———————— 1311 – 1314

Zeolite Shape-Selectivity in the *gem*-Methylation of Aromatic Hydrocarbons

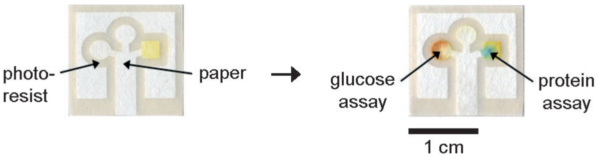
A glove for the purpose: The kind of olefins obtained from methanol in zeolites is strongly dependent on specific combinations of the intermediate organic hydrocarbon-pool species and zeolite topology (see picture). If the cage is too large, neutral species are favored over reactive cations. If the cage is too small, transition-state-shape selectivity poses severe limitations on the reactivity of bulkier species.

Asymmetric Allylations



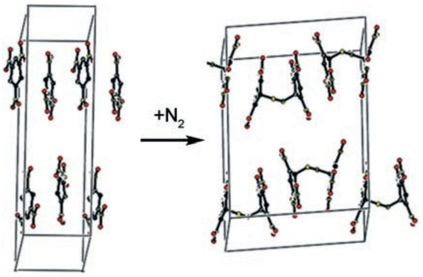
Urea-ka! A new role for urea-based chiral catalysts has been uncovered in the asymmetric allylation of acylhydrazones with allylindium reagents (see scheme; Bz: benzoyl). The best results were obtained using the bifunctional catalyst **1**, which bears a Lewis basic sulfinamide. This example represents the first highly enantioselective addition of an organometallic reagent catalyzed by a chiral urea catalyst.

Bioassays



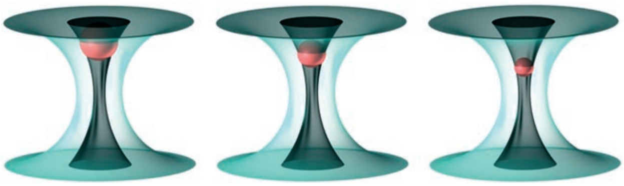
By the book: A method for patterning paper with photoresist to create well-defined, millimeter-sized channels comprising hydrophilic paper bounded by hydrophobic polymer is described. This type of patterned paper is a prototype of a class of low-cost, portable, and technically simple platforms for running multiplexed bioassays with microliter volumes of a single biological sample.

Electrochemistry



Electrochemical reduction of 1,3,5-trinitrobenzene (**1**) forms π dimer **2**, which evolves to a more stable σ complex. The crystal structure of the NEt_4^+ salt of **2** shows π-stacked chains of radical anions. Solid **2** or dimeric **2** in solution reacts with N_2 to give a dianion in which an azo group links two 1,3,5-trinitrobenzene units (see picture). The azo derivative is reversibly electrochemically oxidized to **1**.

Dynamic Droplet Modulation



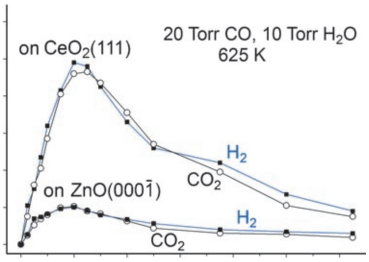
The shrinkage factor: Chemical and biological processes are governed by the frequency of molecular collisions, which are dictated by the concentration of the dissolved species. Dynamic control over the concentrations of dissolved species in a nanoscale reaction vessel (droplet; colored pink in the picture) provides a new degree of control that will aid in the study of fundamental chemical processes.

Heterogeneous Catalysis

J. A. Rodriguez,* P. Liu, J. Hrbek, J. Evans, M. Pérez ———— **1329 – 1332**

Water Gas Shift Reaction on Cu and Au Nanoparticles Supported on $CeO_2(111)$ and $ZnO(000\bar{1})$: Intrinsic Activity and Importance of Support Interactions

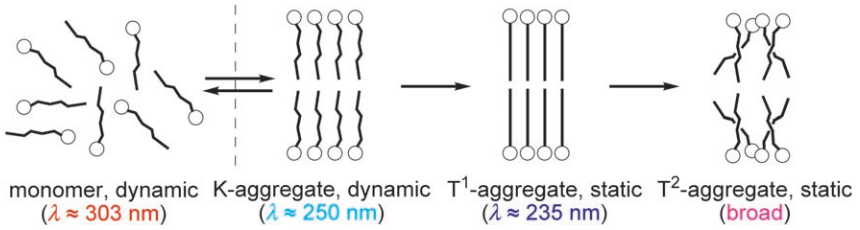
A cerious contender: The catalytic activity in the water gas shift reaction of Au and Cu nanoparticles supported on $CeO_2(111)$ is superior to that of these nanoparticles on a $ZnO(000\bar{1})$ support or of the bulk metals (the diagram shows the results depending on the Au nanoparticle coverage). These results illustrate the essential role that an oxide can have in the activity of supported Au nanocatalysts.



Fatty Acid Aggregation

Y. Wang, J. Ma, H.-S. Cheon, Y. Kishi* ———— **1333 – 1336**

Aggregation Behavior of Tetraenoic Fatty Acids in Aqueous Solution

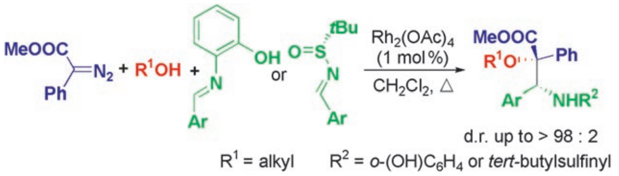


Why so blue? Unique blue-shifted UV absorptions were used to follow the aggregation of C_{24} tetraene fatty acids in aqueous solution. Aggregation takes place through three distinct states (i.e. $K \rightarrow T^1 \rightarrow T^2$; see picture). It is suggested that all of these aggregates are lamellar-type in a local sense but differ in the packing mode of the fatty acid backbone.

Multicomponent Reactions

H. Huang, X. Guo, W. Hu* **1337 – 1339**

Efficient Trapping of Oxonium Ylides with Imines: A Highly Diastereoselective Three-Component Reaction for the Synthesis of β-Amino-α-hydroxyesters with Quaternary Stereocenters

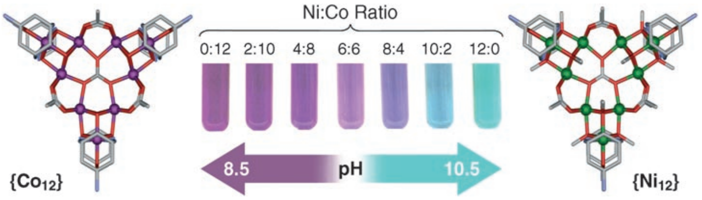


In one huge stride: The single-step construction of polyfunctionalized compounds with a quaternary stereocenter is possible through a highly diastereoselective multicomponent reaction of phenyldiazoacetates, alcohols, and imines (see scheme). The use of *N*-(*tert*-butylsulfinyl)imines as the imine component provides ready access to β-amino-α-hydroxyesters of high optical purity.

Coordination Chemistry

G. J. T. Cooper, G. N. Newton, P. Kögerler,* D.-L. Long, L. Engelhardt, M. Luban, L. Cronin* ———— **1340 – 1344**

Structural and Compositional Control in $\{M_{12}\}$ Cobalt and Nickel Coordination Clusters Detected Magnetochemically and with Cryospray Mass Spectrometry



Control, but not a freak: A series of dodecanuclear coordination clusters of Ni^{II} and Co^{II} with isostructural frameworks is prepared with unparalleled structural and compositional control. At different pH values, the respective clusters can be detected in solution by cryospray mass spectrometry. The positions of the metal centers in the mixed-metal clusters are determined from the magnetic properties.

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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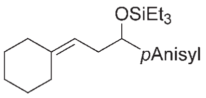
Corrigendum

In this Communication, structure **III** in Table 1 was incorrect. The correct structure is shown below.



III

Highly Selective Coupling of Alkenes and Aldehydes Catalyzed by [Ni(NHC){P(OPh)$_3$}]: Synergy Between a Strong σ Donor and a Strong π Acceptor

C.-Y. Ho, T. F. Jamison* ______ **782–785**

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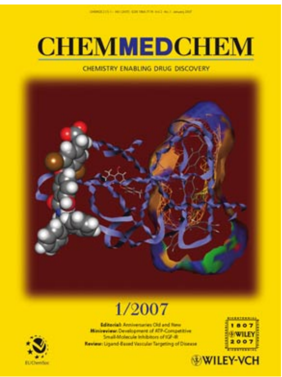

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