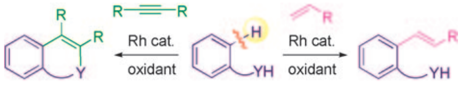
REVIEWS

Homogeneous Catalysis

T. Satoh, M. Miura** .... 11212 – 11222

Oxidative Coupling of Aromatic Substrates with Alkynes and Alkenes under Rhodium Catalysis



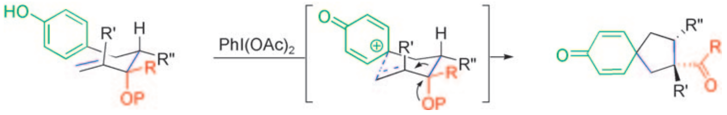
Controlled fusion: Aromatic substrates with oxygen- and nitrogen-containing substituents undergo oxidative coupling with alkynes and alkenes under rhodium catalysis through regioselective C–H bond cleavage. Coordination of the substituents to the rhodium center is the key to activate the C–H bonds effectively. Various fused-ring systems can be constructed through these reactions.

COMMUNICATIONS

Aromatic Ring Umpolung

*M.-A. Beaulieu, C. Sabot, N. Achache, K. C. Guérard, S. Canesi** .... 11224 – 11228

An Oxidative Prins–Pinacol Tandem Process and its Application to the synthesis of (−)-Platensimycin

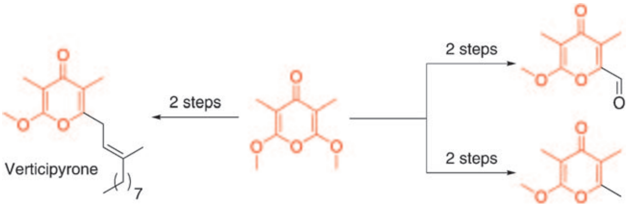


Center stage: An oxidative Prins–pinacol tandem process mediated by a hypervalent iodine reagent has been accomplished. The strategy allows rapid access to highly functionalized spirocyclic cores (see scheme) present in many natural products. A first application to the formal synthesis of (−)-platensimycin has been achieved.

Synthetic Methodology

M. De Paolis, H. Rosso, M. Henrot, C. Prandi, F. d'Herouville, J. Maddaluno** .... 11229 – 11232

A Concise Route to α′-Methoxy-γ-pyrones and Verticipyrone Based Upon the Desymmetrization of α,α′-Dimethoxy-γ-pyrone

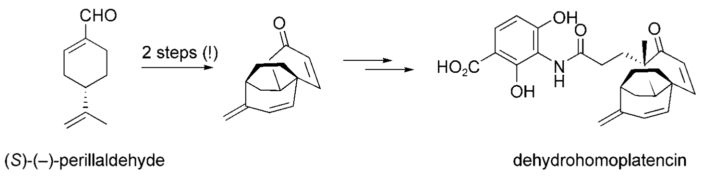


Two steps is the rule: A concise synthesis of versatile α′-methoxy-γ-pyrones (see scheme) is described that uses an innovative desymmetrization of α,α′-dimethoxy-γ-pyrone, relying upon conjugate addition of nucleophiles. This new strategy is applied to the preparation of α-methyl- and α-carboxaldehyde-α′-methoxy-γ-pyrones and to a short synthesis of verticipyrone.

Synthesis Design

*D. C. J. Waalboer, S. H. A. M. Leenders, T. Schülin-Casonato, F. L. van Delft, F. P. J. T. Rutjes** .... 11233 – 11236

Total Synthesis and Antibiotic Activity of Dehydrohomoplatencin

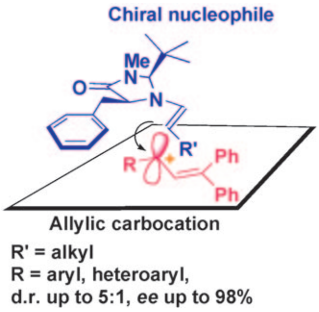


Expanding antibiotics: A concise synthesis of dehydrohomoplatencin, a novel derivative of the naturally occurring antibiotic platencin, has been realized (see scheme). Notably, the synthesis of the ketolide portion of the molecule was achieved in only two exceedingly simple steps. Compared to platencin, dehydrohomoplatencin showed virtually equipotent antibacterial activity against Gram-positive bacteria and may serve as a novel lead structure for the development of new antibiotics.

Organocatalysis

*M. G. Capdevila, F. Benfatti, L. Zoli, M. Stenta, P. G. Cozzi** . . 11237 – 11241

Merging Organocatalysis with an Indium(III)-Mediated Process: A Stereoselective α-Alkylation of Aldehydes with Allylic Alcohols

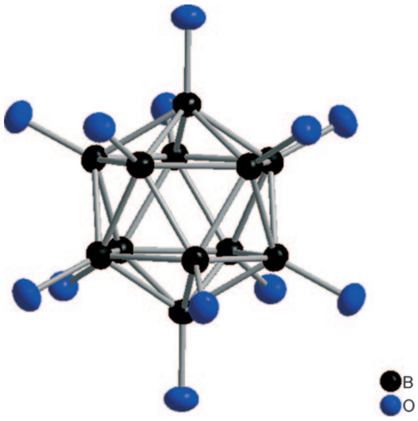


Curiosity killed the CAT…ions! The use of stabilized cationic intermediates can be considered as a new frontier in the development of stereoselective reactions. An organocatalytic procedure mediated by the MacMillan imidazolidinone catalyst was coupled with an $InBr_3$-mediated process for the development of a novel stereoselective allylation reaction of aldehydes. Up to 98% *ee* and up to 5:1 d.r. were obtained in the process.

Radical Clusters

*Ng.-Duc Van, I. Tiritiris, R. F. Winter, B. Sarkar, P. Singh, C. Duboc, A. Muñoz-Castro, R. Arratia-Pérez, W. Kaim, T. Schleid** ..... 11242 – 11245

Oxidative Perhydroxylation of [*closo*-$B_{12}H_{12}$]$^{2-}$ to the Stable Inorganic Cluster Redox System [$B_{12}(OH)_{12}$]$^{2-/\bullet-}$: Experiment and Theory

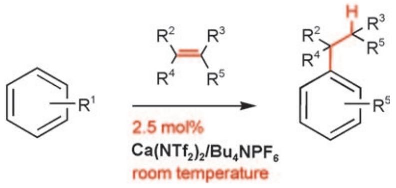


It's radical: A surprisingly simple reaction converts the normally inert prototypical hydridoborate cluster [*closo*-$B_{12}H_{12}$]$^{2-}$ not only to [*closo*-$B_{12}(OH)_{12}$]$^{2-}$ but also, at less-elevated temperatures, to the new [*hypocloso*-$B_{12}(OH)_{12}$]$^{\bullet-}$ radical anion (see figure). Both approximately icosahedral *closo* and *hypocloso* cluster ions were structurally characterized as the cesium salts and their properties were assessed experimentally and theoretically.

Hydroarylation

M. Niggemann, N. Bisek* .... 11246 – 11249

Calcium-Catalyzed Hydroarylation of Alkenes at Room Temperature

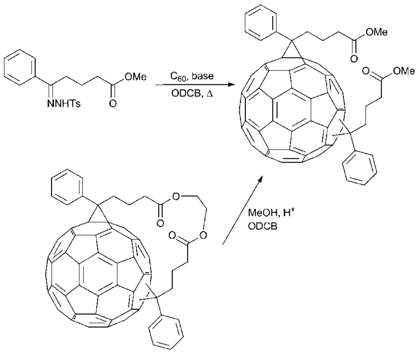


Calcium-catalyst gaining ground: A variety of electron-poor, electron-rich, and trisubstituted styrene derivatives were reacted to give the desired diarylalkanes within less than an hour at room temperature in the presence of 2.5 mol% of $Ca(NTf_2)_2/Bu_4NPF_6$ (see scheme). Additionally, the highly reactive calcium catalyst was successfully applied for the hydroarylation of dienes and even trisubstituted olefins.

Synthesis Design

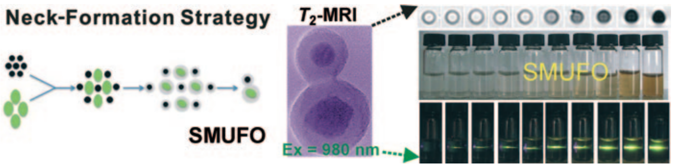
*R. K. M. Bouwer, J. C. Hummelen** .... 11250 – 11253

The Use of Tethered Addends to Decrease the Number of Isomers of Bisadduct Analogues of PCBM



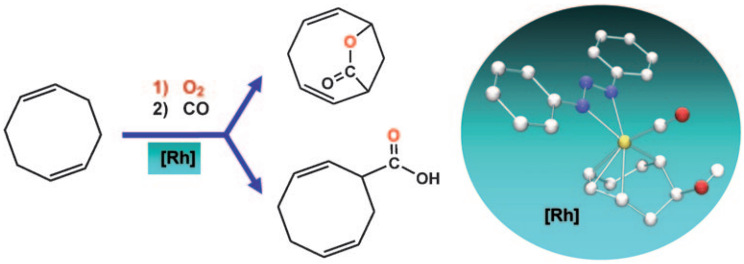
Roped in: The number of isomers present in the bisadduct analogue PCBM (bis-PCBM; PCBM = phenyl-C_{61}-butyric acid methyl ester), a recently introduced acceptor for bulk heterojunction organic photovoltaic devices, has been reduced to seven by linking two tosylhydrazone addends with an ethylene glycol tether and reacting them with C_{60}.

Antitumor Agents



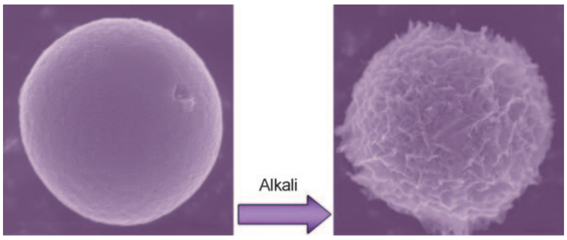
Up to the neck! Bio-safe upconversion fluorescent nanocrystals ($NaYF_4$:Er,Yb) and biocompatible superparamagnetic iron oxide nanocrystals (SPION) were effectively combined by means of a general "neck-formation" strategy, forming a size-controlled, Cd^{2+}- and Gd^{3+}-free, silica-shielded, magnetic upconversion fluorescent oligomer (SMUFO), bimodal cancer probe that offers high resistance to photoquenching as well as a synergistic T_2-weighted magnetic resonance enhanced effect (see graphic).

Metallaoxetanes



Selective functionalisation of 1,5-cyclooctadiene, either to a carboxylic acid or to a γ-lactone, is achieved by a novel sequence of reactions involving quantitative oxygenation with oxygen and C–C coupling with carbon monoxide (see graphic). The rhodium hydroxy–alkyl–allyl complex shown is the active intermediate that promotes the elimination of the organic compounds.

Nanostructures

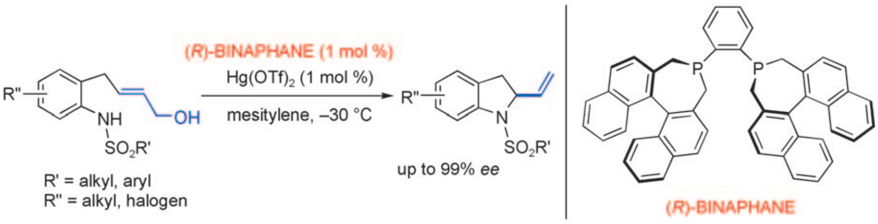


Superior hierarchy: A facile method was developed to synthesize hierarchical TiO_2 microspheres with nanotubular and dendritic structures. Owing to the high surface area and open porous networks, the synthesized TiO_2 microspheres exhibit a superior photocatalytic activity. This method provides a new strategy for the synthesis of hierarchical materials with particular morphologies.

Enantioselectivity

H. Yamamoto, E. Ho, K. Namba, H. Imagawa, M. Nishizawa* .... 11271 – 11274

$Hg(OTf)_2$–BINAPHANE-Catalyzed Enantioselective Anilino Sulfonamide Allyl Alcohol Cyclization



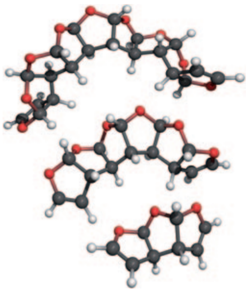
Chiral ligands: $Hg(OTf)_2$-catalyzed cyclization of anilino sulfonamide allyl alcohol is described; this reaction gives 2-vinyl indoline derivatives in good yields and excellent enantioselectivity by using a chiral BINAPHANE ligand (see scheme).

FULL PAPERS

Cyclopropanes

*T. F. Schneider, J. Kaschel, S. I. Awan, B. Dittrich, D. B. Werz** .... 11276 – 11288

From Furan to Molecular Stairs: Syntheses, Structural Properties, and Theoretical Investigations of Oligocyclic Oligoacetals

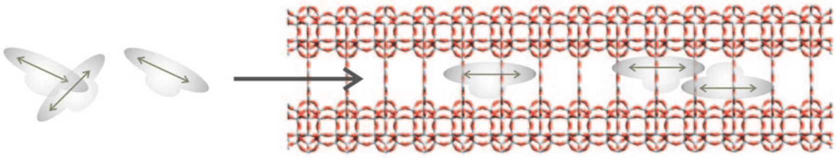


Not a ladder, but stairs: A repetition of a three-step sequence consisting of twofold cyclopropanation, reduction, and oxidation starting from furan leads to *anti*-oligoannelated tetrahydrofuran moieties. The structures were investigated by X-ray diffraction and computational methods (see figure).

Supramolecular Chemistry

G. Calzaferri, D. Brühwiler,* T. Meng, L.-Q. Dieu, V. L. Malinovskii, R. Häner** .... 11289 – 11299

Surprising Properties of a Furo-Furanone

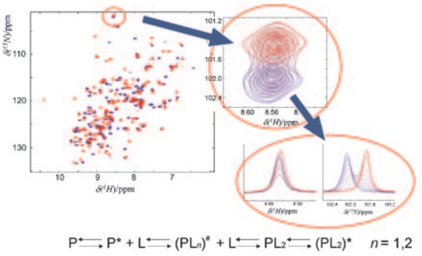


Nanochannel: Insertion of molecules into a nanochannel helps us to understand weak intermolecular interactions. Molecules that form different kinds of aggregates in solution arrange into well-oriented molecular aggregates when embedded in the nanochannels of zeolite L (see graphic).

Lipid-Binding Proteins

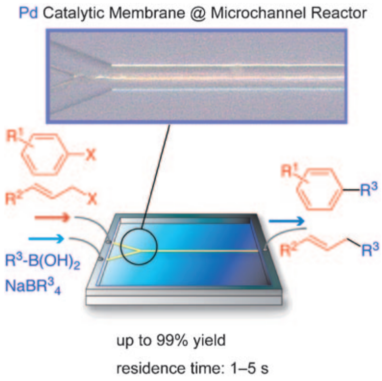
C. Cogliati, L. Ragona, M. D'Onofrio, U. Günther, S. Whittaker, C. Ludwig, S. Tomaselli, M. Assfalg, H. Molinari** .... 11300 – 11310

Site-Specific Investigation of the Steady-State Kinetics and Dynamics of the Multistep Binding of Bile Acid Molecules to a Lipid Carrier Protein



Stuck together: Line-shape analysis provides a direct view of the mechanism and the kinetic rate constants for the binding events in a complex macromolecular system (see figure). Two probes (^1H, ^{15}N) provide information on the effect of binding along the entire titration pathway. The two neighbouring nuclei experience the same kinetic mechanism, overcoming a possible lack of resolution in one dimension.

Obtained in the membrane: Instantaneous catalytic carbon–carbon bond-forming reactions were achieved in catalytic membrane-installed microchannel devices that have a polymeric Pd membrane. The Suzuki–Miyaura reaction was performed with these devices to give quantitative yields of the corresponding products within 5 s of residence time (see image).

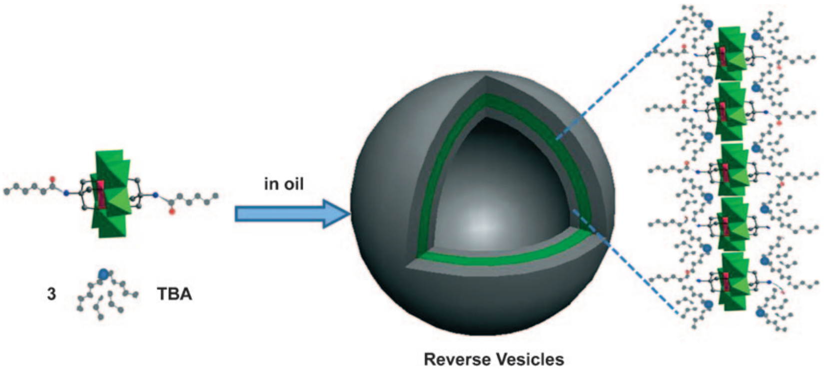


Microreactors

*Y. M. A. Yamada, T. Watanabe, T. Beppu, N. Fukuyama, K. Torii, Y. Uozumi** .... 11311 – 11319

Palladium Membrane-Installed Microchannel Devices for Instantaneous Suzuki–Miyaura Cross-Coupling

---



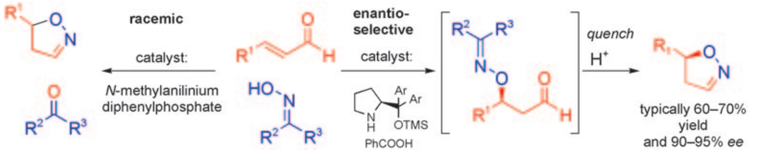
Getting in shape: The formation of reverse vesicles of polyoxometalate-containing hybrid surfactants in nonpolar medium was achieved by titration with toluene (see scheme; TBA = $n\mathrm{Bu_4N}$). The impact of the toluene content and the alkyl chain length of the hybrid surfactant were investigated by light scattering and transmission electron microscopy.

Vesicle Formation

J. Zhang, Y.-F. Song, L. Cronin, T. Liu** .... 11320 – 11324

Reverse-Vesicle Formation of Organic–Inorganic Polyoxometalate-Containing Hybrid Surfactants with Tunable Sizes

---



A salty solution: Acidic anilinium salts catalyze the direct formation of racemic 2-isoxazolines from enals and oximes by means of consecutive oxime conjugate-addition and oxime-transfer reactions (see scheme). This process can also be rendered enantioselective.

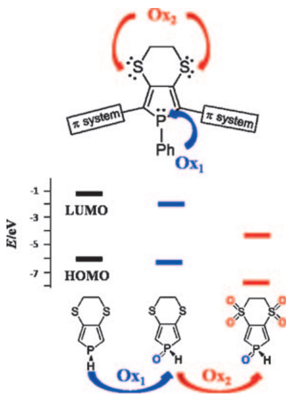
Amine Catalysis

A. Pohjakallio, P. M. Pihko, U. M. Laitinen* .... 11325 – 11339

Synthesis of 2-Isoxazolines: Enantioselective and Racemic Methods Based on Conjugate Additions of Oximes

---

The S effect: Introducing S atoms at the 3,4-positions of phospholes (see figure) results in many appealing properties: a decrease of the HOMO–LUMO separation, electron affinity enhancement, and the possibility to perform multiaddressing by means of chemoselective transformations of the heteroatoms.

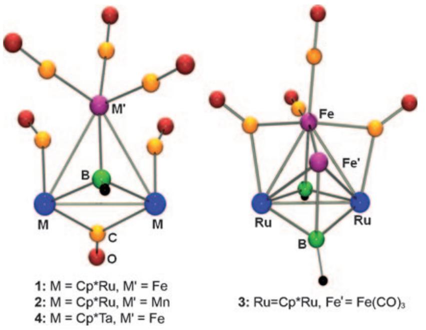


π-Conjugated Systems

O. Fadhel, Z. Benkö, M. Gras, V. Deborde, D. Joly, C. Lescop, L. Nyulászi, M. Hissler,* R. Réau** .... 11340 – 11356

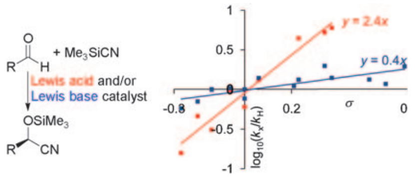
3,4-Dithiaphosphole and 3,3′,4,4′-Tetrathia-1,1′-Biphosphole π-Conjugated Systems: S Makes the Impact

Metallaboranes



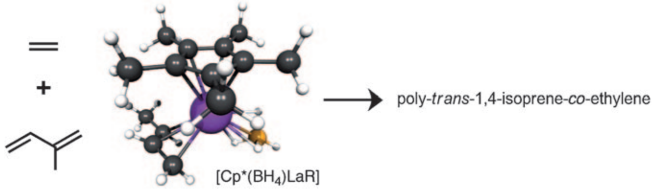
Arachnophilia: Mild reaction of *arachno*-$[(Cp^*RuCO)_2B_2H_6]$ with $[Fe_2(CO)_9]$ and $[Mn_2(CO)_{10}]$ yielded triply bridged borylene species **1** and **2** and bis-borylene complexes **3** and $[\{(\mu_3\text{-}BH)(Cp^*Ru)Fe(CO)_3\}_2(\mu\text{-}CO)]$. The first bridged tantalum borylene complex, **4**, was synthesized by the reaction of $[(Cp^*Ta)_2B_4H_8(\mu\text{-}BH_4)]$ with $[Fe_2(CO)_9]$ at ambient temperature (see picture).

Asymmetric Catalysis



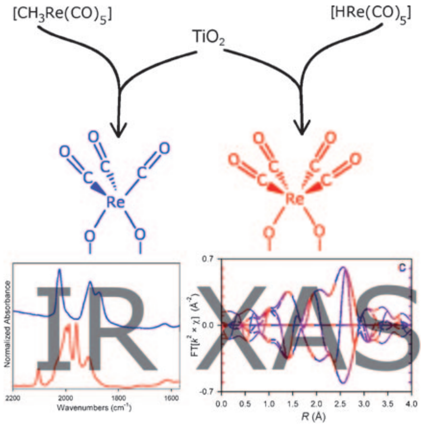
To be (Lewis acid catalysed) or not to be, that is the question: A Hammett analysis based on the structure of aldehyde substrates allows the determination of the relative importance of Lewis acid and Lewis base catalysis. The methodology is applied to asymmetric cyanohydrin synthesis catalysed by four complexes and shows that they differ in the degree of Lewis acid catalysis (see figure). Based on the results, it was predicted, and experimentally verified, that an aluminium-based catalyst would accept ketones as substrates.

Copolymerization



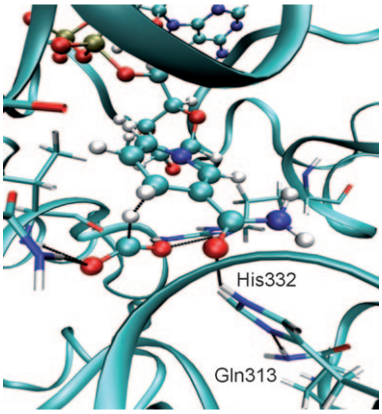
Copolymerization catalyzed: Statistical copolymerization of a mono- and a diene was achieved by using a borohydride hemilanthanidocene (see figure). Analysis of the microstructure of the copolymers revealed successive short sequences of ethylene/ethylene, 1,4-isoprene/ethylene, and 1,4-isoprene/1,4-isoprene. DFT calculations of the initial steps in the copolymerization provides some insight into the catalyst's activity and selectivity.

Surface Chemistry

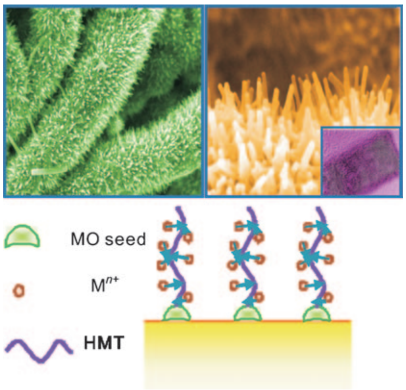


Adsorb and release: $[HRe(CO)_5]$ and $[CH_3Re(CO)_5]$ were used as probes to elucidate the reactivity of the surface of the anatase phase of titania (see scheme). The adsorbed species were characterized by EXAFS and IR spectroscopy. During the adsorption, OH groups were found to react with the probes and form carbonates and water. This information was used to provide a ranking of the various OH groups based on their reactivity and ease of removal by thermal treatment.

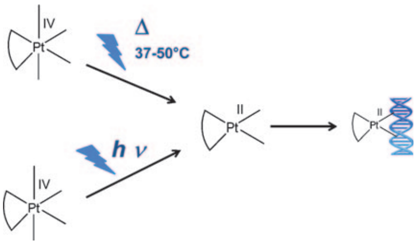
Molecular dynamic trajectories: A theoretical study of the protein dynamics effects on hydride transfer between formate anions and nicotinamide adenine dinucleotide (NAD$^+$) catalyzed by formate dehydrogenase (FDH) has allowed the estimation of a contribution to catalysis of 0.5 kcal mol^{-1} (see figure). This result, although small, is not negligible considering the low efficiency of FDH. The results also reveal how the relative movements of some amino acids precede and promote the chemical reaction.

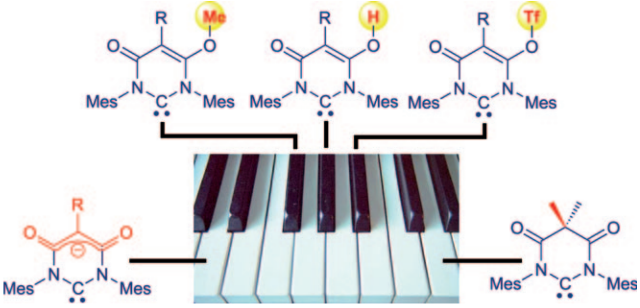


The power of magic fabric: A family of branched hierarchical heterostructure fabrics can be synthesized on a large scale by a general approach that combines the electrospinning technique with a controllable hydrothermal method (see picture; MO = metal oxide, HMT = hexamethylenetetramine). The fabric exhibits high mobility of charge carriers and enhanced photocatalytic activity.



Spontaneous reduction of two Pt^{IV} complexes containing a 2,2′-bipyridine (bpy) ligand to the corresponding Pt^{II} complexes occurs not only under light irradiation but also upon moderate heating (37 or 50 °C) in the dark. In the presence of DNA the Pt^{II} complexes readily form (bpy)Pt–DNA adducts (see scheme).



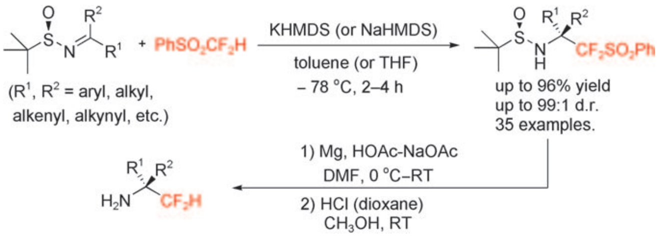


The right tone: The donor properties of a metal-bound NHC ligand possessing a malonate backbone can be finely tuned by simple addition of a selected electrophile interacting with the remote nucleophilic part of the ligand in the outer coordination sphere of the complex. Relevant consequences on the catalytic behavior of these species were observed and rationalized on the basis of two test catalytic reactions.

Fluorinated Amines

*J. Liu, J. Hu** .... 11443 – 11454

Highly Diastereoselective Synthesis of α-Difluoromethyl Amines from *N-tert*-Butylsulfinyl Ketimines and Difluoromethyl Phenyl Sulfone

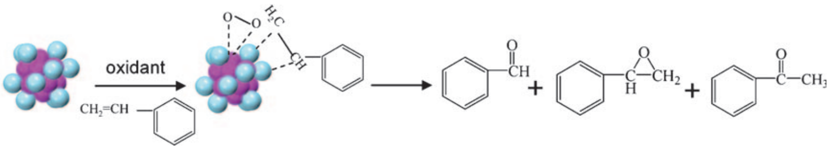


Difluoromethylation of ketimines: A highly efficient and stereoselective difluoromethylation of *N-tert*-butylsulfinyl ketimines has been achieved with an in situ generated $PhSO_2CF_2^-$ anion, which provides a powerful synthetic method for the preparation of structurally diverse homochiral α-difluoromethyl tertiary carbinamines (see scheme). The use of an appropriate base, such as potassium hexamethyldisilazide (KHMDS), was crucial in these nucleophilic difluoromethylation reactions.

Gold Nanocatalysis

*Y. Zhu, H. Qian, R. Jin** 11455 – 11462

An Atomic-Level Strategy for Unraveling Gold Nanocatalysis from the Perspective of $Au_n(SR)_m$ Nanoclusters

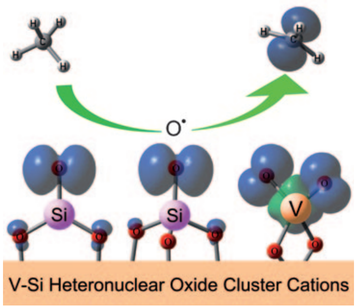


All that glitters: An atomic-level strategy is adopted to reveal the fundamentals of nanogold catalysis for styrene oxidation by using the atomically monodisperse $Au_n(SR)_m$/support nanoclusters as catalysts (see scheme).

Methane Activation

*X.-L. Ding, Y.-X. Zhao, X.-N. Wu, Z.-C. Wang, J.-B. Ma, S.-G. He** .... 11463 – 11470

VIP Hydrogen-Atom Abstraction from Methane by Stoichiometric Vanadium–Silicon Heteronuclear Oxide Cluster Cations

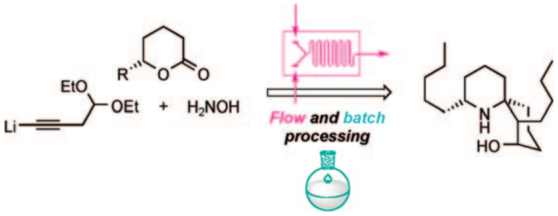


Art of abstraction: Hydrogen abstraction reactions over the stoichiometric V–Si heteronuclear oxide cluster cations $[(V_2O_5)_n(SiO_2)_m]^+$ ($n=1$, $m=1$–4; $n=2$, $m=1$) are identified. Terminal-oxygen-centered radicals ($O_t^•$) in these clusters are the active sites for CH_4 activation. The $O_t^•$ radicals are bonded to Si rather than V in $[V_2O_5(SiO_2)_{1-4}]^+$ clusters (see figure). The multivalence states of V (+5 and +4) are also found in some of the cluster isomers.

Total Synthesis

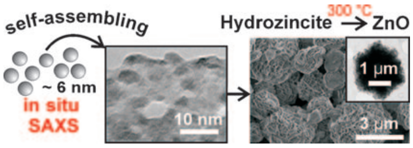
M. Brasholz, J. M. Macdonald, S. Saubern, J. H. Ryan, A. B. Holmes* .... 11471 – 11480

A Gram-Scale Batch and Flow Total Synthesis of Perhydrohistrionicotoxin



The best of both worlds: A combined flow and batch approach leads to the spirocyclic poison frog alkaloid (−)-perhydrohistrionicotoxin on a gram scale. Microreactor processing of key synthetic intermediates, including organometallic species, gave similar yields and stereoselectivites to conventional round-bottomed flask procedures, but at milder temperatures, in shorter reaction times and in a telescoped fashion (see scheme).

Two-minute mechanism: The formation of a layered hydrozincite precursor was studied with the combination of in situ and ex situ techniques. The growth mechanism follows the "non-classical crystallization" concept of a rapid (≈2 min) self-assembling mechanism (see graphic).



Hydrozincite

*M. Bitenc, P. Podbrščček, P. Dubček, S. Bernstorff, G. Dražić, B. Orel, S. Pejovnik, Z. Crnjak Orel** .... 11481 – 11488

In and Ex Situ Studies of the Formation of Layered Microspherical Hydrozincite as Precursor for ZnO

---

* Author to whom correspondence should be addressed

Supporting information on the WWW (see article for access details).

VIP Full Papers labeled with this symbol have been judged by two referees as being "very important papers".

A video clip is available as Supporting Information on the WWW (see article for access details).

SERVICE