Density Functional Theory: Not Quite the Right Answer for the Right Reason Yet

Prof. Dr. Martin Korth


Abstract

More insight or only more parameters? A recent claim that the development of new density functional theory (DFT) functionals is straying from the right path has sparked a lively discussion among theoretical chemists about the future of DFT.

Power-to-Syngas: An Enabling Technology for the Transition of the Energy System?

Dipl.-Chem. Severin R. Foit, Dr. Izaak C. Vinke, Dr. Lambertus G. J. de Haart and Prof. Dr. Rüdiger-A. Eichel


Abstract

Power-to-X concepts promise a reduction of greenhouse gas emissions simultaneously guaranteeing a safe energy supply even at high share of renewable power generation, thus becoming a cornerstone of a sustainable energy system. Power-to-syngas, that is, the electrochemical conversion of steam and carbon dioxide with the use of renewably generated electricity to syngas for the production of synfuels and high-value chemicals, offers an efficient technology to couple different energy-intense sectors, such as “traffic and transportation” and “chemical industry”. Syngas produced by co-electrolysis can thus be regarded as a key-enabling step for a transition of the energy system, which offers additionally features of CO₂ valorization and closed carbon cycles. Here, we discuss advantages and current limitations of low- and high-temperature co-electrolysis. Advances in both fundamental understanding of the basic reaction schemes and stable high-performance materials are essential to further promote co-electrolysis.
Advanced Biofuels and Beyond: Chemistry Solutions for Propulsion and Production

Prof. Walter Leitner, Prof. Jürgen Klankermayer, Prof. Stefan Pischinger, Prof. Heinz Piltsch and Prof. Katharina Kohse-Höinghaus

Angew. Chem. Int. Ed. 2017, 56(20), 5412

Abstract

Sustainably produced biofuels, especially when they are derived from lignocellulosic biomass, are being discussed intensively for future ground transportation. Traditionally, research activities focus on the synthesis process, while leaving their combustion properties to be evaluated by a different community. This Review adopts an integrative view of engine combustion and fuel synthesis, focusing on chemical aspects as the common denominator. It will be demonstrated that a fundamental understanding of the combustion process can be instrumental to derive design criteria for the molecular structure of fuel candidates, which can then be targets for the analysis of synthetic pathways and the development of catalytic production routes. With such an integrative approach to fuel design, it will be possible to improve systematically the entire system, spanning biomass feedstock, conversion process, fuel, engine, and pollutants with a view to improve the carbon footprint, increase efficiency, and reduce emissions.

Cu/Pd Synergistic Dual Catalysis: Asymmetric α-Allylation of an α-CF₃ Amide

Dr. Akira Saito, Dr. Naoya Kumagai and Prof. Dr. Masakatsu Shibasaki

Angew. Chem. Int. Ed. 2017, 56(20), 5551

Abstract

Despite the burgeoning demand for fluorine-containing chemical entities, the construction of CF₃-containing stereogenic centers has remained elusive. Herein, we report the strategic merger of Cu'/base-catalyzed enolization of an α-CF₃ amide and Pd⁰-catalyzed allylic alkylation in an enantioselective manner to deliver chiral building blocks bearing a stereogenic carbon center connected to a CF₃, an amide carbonyl, and a manipulable allylic group. The phosphine complexes of Cu¹ and Pd⁰ engage in distinct catalytic roles without ligand scrambling to render the dual catalysis operative to achieve asymmetric α-allylation of the amide. The stereoselective cyclization of the obtained α-CF₃-γ,δ-unsaturated amides to give tetrahydropyran and γ-lactone-fused cyclopropane skeletons highlights the synthetic utility of the present catalytic method as a new entry to non-racemic CF₃-containing compounds.
Iridium-Catalyzed Regio- and Enantioselective Hydroarylation of Alkenyl Ethers by Olefin Isomerization

Yusuke Ebe, Mitsuki Onoda, Dr. Takahiro Nishimura and Prof. Dr. Hideki Yorimitsu


Abstract

Iridium-catalyzed hydroarylation of alkenyl ethers, such as allylic and homoallylic ethers, by C–H bond activation gave high yields of the corresponding addition products, where the aryl groups were selectively installed at the α-carbon atom to the alkoxy group. The reaction involves an isomerization of the alkenyl ethers into the corresponding 1-alkenyl ethers, which then undergo the regio- and enantioselective hydroarylation.

B(C6F5)3-Catalyzed Cascade Reduction of Pyridines

Zhi-Yun Liu, Zhi-Hui Wen and Prof. Dr. Xiao-Chen Wang


Abstract

B(C6F5)3 has been found to be an effective catalyst for reduction of pyridines and other electron-deficient N-heteroarenes with hydrosilanes (or hydroboranes) and amines as the reducing reagents. The success of this development hinges upon the realization of a cascade process of dearomative hydrosilylation (or hydroboration) and transfer hydrogenation. The broad functional-group tolerance (e.g. ketone, ester, unactivated olefins, nitro, nitrile, heterocycles, etc.) implies high practical utility.
A Tale of Two Elements: The Lewis Acidity/Basicity Umpolung of Boron and Phosphorus

Prof. Dr. Douglas W. Stephan

*Angew. Chem. Int. Ed.* 2017, 56(21), 5984

**Abstract**

**Basically acidic:** In the Lewis acidity/basicity “umpolung”, elements that traditionally exhibit acidity or basicity are modified to behave as Lewis bases or acids, respectively. This inversion of reactivity provides significant synthetic challenges, but also provides uniquely reactive species as demonstrated by recent attention on boron-based nucleophiles and phosphorus-based electrophiles.

A Method for the Late-Stage Formation of Ketones, Acyloins, and Aldols from Alkenylstannanes: Application to the Total Synthesis of Paecilonic Acid A

Dr. Heiko Sommer, Dr. James Y. Hamilton and Prof. Dr. Alois Fürstner

*Angew. Chem. Int. Ed.* 2017, 56(21), 6161

**Abstract**

Treatment of alkenylstannanes with Cu(OAc)$_2$/Et$_3$N affords the corresponding enol esters or ketones under conditions that proved compatible with many common functionalities; these include groups that would neither survive under the standard Tamao–Fleming conditions for the oxidation of C–SiR$_3$ bonds nor under the conditions commonly used to oxidize C–B bonds. Chiral centers adjacent to the unveiled carbonyls are not racemized and competing protodestannation is marginal, even if the substrate carries unprotected –OH groups as internal proton sources. Therefore, the procedure is well suited for the preparation of acyloin and aldol derivatives. These enabling virtues are illustrated by a concise approach to the bicyclic lipid paecilonic acid A.
Palladium-Catalyzed Carbonylation of sec- and tert-Alcohols (pages 6203–6207)

Dr. Kaiwu Dong, Rui Sang, Jie Liu, Dr. Rauf Razzaq, Prof. Dr. Robert Franke, Dr. Ralf Jackstell and Prof. Dr. Matthias Beller

Angew. Chem. Int. Ed. 2017, 56(21), 6203

Abstract

A general palladium-catalyzed synthesis of linear esters directly from sec- and tert-alcohols is described. Compared to the classic Koch–Haaf reaction, which leads to branched products, this new transformation gives the corresponding linear esters in high yields and selectivity. Key for this protocol is the use of an advanced palladium catalyst system with L2 (pybpx) as the ligand. A variety of aliphatic and benzylic alcohols can be directly used and the catalyst efficiency for the benchmark reaction is outstanding (turnover number up to 89 000).

Rethinking the Claisen–Tishchenko Reaction

Stacey A. Morris and Prof. Dr. Dmitry G. Gusev

Angew. Chem. Int. Ed. 2017, 56(21), 6228

Abstract

Pincer-type complexes [OsH2(CO)(PyCH2NHCH2CH2NHP(tBu)2)] and [OsH2(CO)(HN(CH2CH3P(iPr)2)] catalyze the disproportionation reaction of aldehydes via an outer-sphere bifunctional mechanism achieving turnover frequencies up to 14 000 h⁻¹. The N–H group of the catalysts is a key player in this process, elucidated with the help of DFT calculations.
NHC-Organocatalyzed C<sub>Ar</sub>−O Bond Cleavage: Mild Access to 2-Hydroxybenzophenones (pages 6276–6279)

Daniel Janssen-Müller, Santanu Singha, Fabian Lied, Karin Gottschalk and Prof. Dr. Frank Glorius

Angew. Chem. Int. Ed. 2017, 56(21), 6276

Abstract

A Truce–Smiles rearrangement of acyl-anion equivalents generated by N-heterocyclic carbene (NHC) catalysis has been achieved. The developed method includes C<sub>Ar</sub>−O, C<sub>Ar</sub>−S, or C<sub>Ar</sub>−N bond cleavage for the formation of a C<sub>Ar</sub>−C bond and enables access to 2-hydroxybenzophenones, an important structural motif that is present in several bioactive natural products. By utilizing this procedure, the alkaloid taxilamine was synthesized in three steps. DFT calculations and control experiments support a classical S<sub>N</sub>Ar mechanism with a catalyst-bound Meisenheimer-type intermediate. The method features mild reaction conditions, excellent functional-group tolerance, and a broad substrate scope, including various classes of (hetero)arenes.

Air-Stable Manganese(I)-Catalyzed C−H Activation for Decarboxylative C−H/C−O Cleavages in Water (pages 6339–6342)

Hui Wang, Dr. Mélanie M. Lorion and Prof. Dr. Lutz Ackermann

Angew. Chem. Int. Ed. 2017, 56(21), 6339

Abstract

The decarboxylative C−H/C−O functionalization was accomplished by air- and water-tolerant manganese(I) catalysis. The versatile C−H allylation occurred by facile organometallic C−H metalation on indoles, arenes, amino acids and synthetically meaningful aryl ketimines with ample substrate scope and high levels of chemo-, site- and regio-selectivity.
**Carbonyls as Latent Alkyl Carbanions for Conjugate Additions**

Xi-Jie Dai, Dr. Haining Wang and Prof. Dr. Chao-Jun Li


**Abstract**

Conjugate addition of carbon nucleophiles to electron-deficient olefins is one of the most powerful methods for forming carbon–carbon bonds. Despite great achievements in controlling the selectivity, variation of the carbon nucleophiles remains largely underexplored, with this approach relying mostly on organometallic reagents. Herein, we report that naturally abundant carbonyls can act as latent carbon nucleophiles for conjugate additions through a ruthenium-catalyzed process, with water and nitrogen as innocuous byproducts. The key to our success is homogeneous ruthenium(II) catalysis, combined with phosphines as spectator ligands and hydrazine as the reducing agent. This chemistry allows the incorporation of highly functionalized alkyl fragments into a vast array of electron-deficient olefins under mild reaction conditions in a reaction complementary to the classical organometallic-reagent-based conjugate additions mediated or catalyzed by “soft” transition metals.

**Batch and Continuous-Flow One-Pot Processes using Amine Diazotization to Produce Silylated Diazomethane Reagents**

Clément Audubert, Oscar Javier Gamboa Marin and Prof. Dr. Hélène Lebel


**Abstract**

A novel synthesis of trimethylsilyldiazomethane (TMSCHN$_2$) by diazotization of trimethylsilylmethylamine (TMSCH$_2$NH$_2$) is reported using batch and continuous flow synthesis. The latter affords a daily production of 275 g (2.4 mol) of TMSCHN$_2$. Other silylated methyamines were also successfully reacted under the developed reaction conditions to furnish various silicon-bearing diazomethane reagents. The applicability of the process is highlighted by disclosure of batch and continuous flow one-pot esterification and 1,3-dipolar cycloaddition processes. Furthermore, the high-yielding esterification of carboxylic acids with silylated and substituted methyamines in continuous flow is disclosed. Finally, work-up and purification procedures are reported for the preparation of a 2-MeTHF solution of TMSCHN$_2$, which can be used in rhodium-catalyzed methylenation and homologation reactions.
Coke-Tolerant Gadolinium-Promoted HZSM-5 Catalyst for Methanol Conversion into Hydrocarbons

Dr. Sungtak Kim, Dr. Yong Tae Kim, Ahron Hwang, Dr. Ki-Won Jun and Dr. Geunjae Kwak

*ChemCatChem* 2017, 9(9), 1569

Abstract

The role of Gd as a coke inhibitor was studied for the methanol-to-hydrocarbons reaction. It was revealed that thin films of gadolinium oxide covered the ZSM-5 crystals and that the Gd atoms that were uniformly dispersed on the surface enhanced the basicity of the parent ZSM-5. These synergetic effects improved the durability of the acidic function and diminished the growth of coke precursors, which resulted in an increased lifetime of the catalyst.

Production of High Quality Syncrude from Lignocellulosic Biomass

Dr. Yannick Mathieu, Dr. Laurent Sauvanaud, Dr. Len Humphreys, Dr. William Rowlands, Prof. Thomas Maschmeyer and Prof. Avelino Corma

*ChemCatChem* 2017, 9(9), 1574

Abstract

Wood chips were hydrothermally treated in near critical point water in the presence of a catalyst to yield a raw biocrude, containing a wide range of organic components. This product was subsequently distilled to remove its heaviest fraction, which tends to yield chary products if heated above 350 °C. The biocrude obtained has an oxygen content of 12 wt % and was subsequently hydrotreated to obtain a hydrocarbon stream. Varying the hydrotreatment operating conditions and catalyst yielded a deoxygenated syncrude which quality improved with operation severity. The hydroprocessed stream produced under very mild conditions can be further upgraded in conventional refinery operations while the stream produced after more severe hydrotreatment can be mixed with conventional diesel. This proof of concept was demonstrated with commercial hydrotreating catalysts, operating between 350 and 380 °C, 40 to 120 bar pressure and 0.5 to 1 h⁻¹ contact time.
**Boron Nitride-supported Sub-nanometer Pd6 Clusters for Formic Acid Decomposition: A DFT Study**
Roberto Schimmenti, Dr. Remedios Cortese, Prof. Dario Duca and Prof. Manos Mavrikakis

*ChemCatChem, 2017, 9(9), 1610*

**Abstract**

A periodic, self-consistent planewave DFT study was carried out to explore the potential use of Pd6 clusters supported on a boron nitride sheet as a catalyst for the selective decomposition of formic acid (HCOOH) to CO2 and H2. The competition between formate (HCOO) and carboxyl (COOH) paths on catalytic sites, with different proximities to the support, was studied. Based on energetics alone, the reaction may mainly follow the HCOO route. Slightly lower activation energies were found at the lateral sites of the cluster as compared to top face sites. This is particularly true for the bidentate to monodentate HCOO conversion. Through comparison of results with similar studies on HCOOH decomposition on extended Pd surfaces, it was demonstrated that the existence of undercoordinated sites in the sub-nanometer cluster could play a key role in preferentially stabilizing HCOO over COOH, which is a common CO precursor in this reaction. A hydrogen spillover mechanism was also investigated; migration toward the boron nitride support is not favorable, at least in the early stages of the reaction. However, hydrogen diffusion on the cluster has low barriers compared to those involved in formic acid decomposition.

**Acid Ketonization over Fe3O4/SiO2 for Pyrolysis Bio-Oil Upgrading**
Dr. James A. Bennett, Dr. Christopher M. A. Parlett, Dr. Mark A. Isaacs, Dr. Lee J. Durndell, Dr. Luca Olivi, Prof. Adam F. Lee and Prof. Karen Wilson

*ChemCatChem, 2017, 9(9), 1648*

**Abstract**

A family of silica-supported, magnetite nanoparticle catalysts was synthesised and investigated for continuous-flow acetic acid ketonisation as a model pyrolysis bio-oil upgrading reaction. The physico-chemical properties of Fe3O4/SiO2 catalysts were characterised by using high-resolution transmission electron microscopy, X-ray absorption spectroscopy, X-ray photo-electron spectroscopy, diffuse reflectance infrared Fourier transform spectroscopy, thermogravimetric analysis and porosimetry. The acid site densities were inversely proportional to the Fe3O4 particle size, although the acid strength and Lewis character were size-invariant, and correlated with the specific activity for the vapour-phase acetic ketonisation to acetone. A constant activation energy (∼110 kJ mol⁻¹), turnover frequency (∼13 h⁻¹) and selectivity to acetone of 60 % were observed for ketonisation across the catalyst series, which implies that Fe3O4 is the principal active component of Red Mud waste.
Enantioselective Transfer Hydrogenation of Ketones Catalyzed by a Manganese Complex Containing an Unsymmetrical Chiral PNP’ Tridentate Ligand

Dr. Afrooz Zirakzadeh, Sara R. M. M. de Aguiar, Dr. Berthold Stöger, Prof. Dr. Michael Widhalm and Prof. Dr. Karl Kirchner

ChemCatChem 2017, 9(10), 1744

Abstract

Manganese complexes of the types [Mn(PNP’)(Br)(CO)₂] and [Mn(PNP’)(H)(CO)₂] containing a tridentate ligand with a planar chiral ferrocene and a centro chiral aliphatic unit were synthesized, characterized, and tested in the enantioselective transfer hydrogenations of 13 ketones. The catalytic reactions proceeded with conversions up to 96 % and ee values up to 86 %. The absolute configuration of all products was determined to be (S). Notably, the presence of dihydrogen (up to 20 bar) did not affect the reduction. On the basis of DFT calculations, preliminary mechanistic details including the origin of the (S) selectivity are presented. The molecular structure of [Mn(PNP’)(Br)(CO)₂] was studied by X-ray diffraction.

The Synergistic Effect to Promote the Direct Conversion of Bioethanol into Isobutene over Ternary Multifunctional CrxZnyZrzOn Catalysts

Feng Liu, Prof. Dr. Yong Men, Dr. Jinguo Wang, Xiaoxiong Huang, Dr. Yuanqiang Wang and Prof. Dr. Wei An

ChemCatChem 2017, 9(10), 1758

Abstract

A significant beneficial effect of introducing chromium over mesoporous CrₓZn₁Zr₈On oxide composite catalysts was observed in the upgrading and direct conversion of bioethanol into isobutene (ETIB), and a 38 % enhancement in the selectivity (yield) to isobutene was observed relative to that observed with its binary Zn₁Zr₈On counterpart. Two critical factors were related to the surface properties of this catalyst: a proper surface acid/base balance and favorable redox properties dictated the selectivity to isobutene. Through combined experimental and theoretical efforts, synergistic effects of redox-active Crδ⁺ in promoting the dehydrogenation of ethanol were elucidated and therefore the production of isobutene. This work provides a guide for the rational design of efficient catalysts for a highly active and selective cascade ETIB reaction, for which the relative strengths of the redox/acid and base/acid sites of the catalyst serve as catalytic descriptors.
Cyclopentanone as an Alternative Linking Reactant for Heterogeneously Catalyzed Furfural Aldol Condensation

Jennifer Cueto, Dr. Laura Faba, Dr. Eva Díaz and Prof. Salvador Ordóñez

ChemCatChem 2017, 9(10), 1765

Abstract

The use of cyclopentanone, instead of acetone, in the synthesis of diesel precursors by furfural aldol condensation is proposed. This reaction is catalyzed by a magnesium–zirconium mixed oxide. To optimize the C₁₅ selectivity, different temperatures (293, 303, 313, and 323 K) and initial furfural/cyclopentanone ratios (1:1, 3:1, 5:1, and 10:1) were tested. Under the optimum conditions, yields for the desired C₁₅ adduct are higher than 60 % in less than 4 h under mild conditions (303 K).

Vapor Phase Hydrogenolysis of Furanics Utilizing Reduced Cobalt Mixed Metal Oxide Catalysts

Taylor P. Sulmonetti, Dr. Bo Hu, Zachary Ifkovits, Dr. Sungsik Lee, Prof. Pradeep K. Agrawal and Prof. Christopher W. Jones

ChemCatChem 2017, 9(10), 1815

Abstract

Vapor phase hydrogenolysis of both furfuryl alcohol and furfural are investigated over reduced Co based mixed metal oxides derived from the calcination of a layered double hydroxide precursor. Although a reduced cobalt-aluminum oxide sample displays promising selectivity towards 2-methylfuran (2-MF) production, the addition of an Fe dopant into the oxide matrix significantly enhances the activity and selectivity per gram of catalyst. Approximately 82 % 2-MF yield is achieved at high conversion if furfuryl alcohol is fed into the reactor at 180 °C over the reduced 3Co-0.25Fe-0.75Al catalyst. Based on structural characterization studies including temperature-programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS), and in situ X-ray absorption spectroscopy (XAS) it is suggested that Fe facilitates the reduction of Co, allowing for formation of more metallic species. Overall, this study demonstrates that non-precious metal catalysts offer promise for the selective conversion of a key biomass oxygenate to a proposed fuel additive.
Selective Oxidation of Activated Alcohols by Supported Gold Nanoparticles under an Atmospheric Pressure of O₂: Batch and Continuous-Flow Studies

Pascal D. Giorgi, Dr. Nelli Elizarov and Dr. Sylvain Antoniotti

ChemCatChem 2017, 9(10), 1830

Abstract

In the hunt for a simple, mild, and scalable protocol for gold nanoparticle-catalyzed oxidation of benzylic and allylic alcohols under O₂, we have used commercially available gold nanoparticles supported on alumina to selectively oxidize a large range of activated alcohols to the corresponding carbonyl compounds in good yields (68–99 %) and with excellent selectivity (ca. 100 %). The true heterogeneous nature of the catalysis by gold was demonstrated, allowing us to further adapt this protocol to continuous-flow reactors by using the tube-in-tube technology, in which higher yields were obtained thanks to an improved oxygenation of the reaction medium.
Regio- and stereospecific rhodium-catalyzed allylic alkylation with an acyl anion equivalent: an approach to acyclic α-ternary β,γ-unsaturated aryl ketones


Chemical Science 2017, 8, 4001.

Abstract

The regio- and stereospecific rhodium-catalyzed allylic alkylation of secondary allylic carbonates with cyanohydrin pronucleophiles facilitates the direct construction of acyclic α-ternary β,γ-unsaturated aryl ketones. Interestingly, this study illustrates the impact of deaggregating agents on regiocontrol and the electronic nature of the aryl component to suppress olefin isomerization. In addition, we demonstrate that the dimethylamino substituent, which modulates the pKₐ of the α-ternary β,γ-unsaturated aryl ketone, provides a useful synthetic handle for further functionalization via Kumada cross-coupling of the aryl trimethylammonium salt. Finally, the stereospecific alkylation of a chiral nonracemic secondary allylic carbonate affords the enantioenriched α-ternary aryl ketone, which was employed in a formal synthesis of trichostatic acid to illustrate that the allylic alkylation proceeds with net retention of configuration.
Intra- versus intermolecular electron transfer in radical nucleophilic aromatic substitution of dihalo(hetero)arenes – a tool for estimating π-conjugation in aromatic systems

B. Janhsen, C. G. Daniliuc, A. Studer

Chemical Science 2017, 8, 3547.

Abstract

In this paper, the application of the double radical nucleophilic aromatic substitution (S_{RN1}) in various dihalogenated, mostly diiodinated, π-conjugated systems as a tool for qualitatively estimating their π-conjugation is described. This approach uses electron delocalisation as a measure of π-conjugation. Electron injection into the π-system is achieved via reaction of an intermediate aryl radical, itself generated from a dihalogenated π-system via SET-reduction of the C–I bond and subsequent reaction with a thiolate anion. The generated arene radical anion can then further react with the second aryl-halogen moiety within the π-system via an intramolecular electron transfer process. The efficiency of this intramolecular electron transfer is related to the π-conjugation of the radical anion. If the π-conjugation within the aromatic unit is weak, the arene radical anion reacts via an intermolecular ET with the starting dihalide. The intramolecular ET process delivers a product of a double S_{RN1} substitution whereas the intermolecular ET pathway provides a product of a mono- S_{RN1} substitution. By simple product analysis of mono- versus double substitution, π-conjugation can be qualitatively evaluated. This mechanistic tool is applied to various dihalogenated π-conjugated systems and the results are discussed within the context of π-conjugation. The conjugation mode within the π-system and the length of the aromatic system are varied, and the effect of relative positioning of the two halides within small π-systems is also addressed.
Two-dimensional crystal engineering using halogen and hydrogen bonds: towards structural landscapes

A. Mukherjee, J. Teyssandier, G. Hennrich, S. De Feyter, K. S. Mali

Chemical Science 2017, 8, 3759.

Abstract

Two-dimensional (2D) crystallization on solid surfaces is governed by a subtle balance of supramolecular and interfacial interactions. However, these subtle interactions often make the prediction of supramolecular structure from the molecular structure impossible. As a consequence, surface-based 2D crystallization has often been studied on a case-by-case basis, which hinders the identification of structure-determining relationships between different self-assembling systems. Here we begin the discussion on such structure-determining relationships by comparing the 2D crystallization of two identical building blocks based on a 1,3,5-tris(pyridine-4-ylythynyl)benzene unit at the solution–solid interface. The concepts of supramolecular synthons and structural landscapes are introduced in the context of 2D crystallization on surfaces to identify common structural elements. The systems are characterized using scanning tunneling microscopy (STM). This strategy involves carrying out minor structural modifications on the parent compound to access supramolecular patterns that are otherwise not obtained. We demonstrate that this chemical perturbation strategy translates equally well for 2D co-crystallization experiments with halogen bond donors yielding porous bi-component networks. The holistic approach described here represents a stepping stone towards gaining predictive power over the 2D crystallization of molecules on solid surfaces.
Manganese-catalyzed allylation via sequential C–H and C–C/C–Het bond activation

Q. Lu, F. J. R. Klauck, F. Glorius

*Chemical Science* 2017, 8, 3379.

**Abstract**

Manganese-catalyzed sequential C–H and C–C/C–Het bond activation to synthesize allylic alcohols, allylated arenes, functionalized cyclopentenes and skipped dienes is reported. This protocol can be readily scaled up and various coupling partners are applied in manganese catalysis for the first time. Moreover, manganese-catalyzed alkenyl C(sp2)–H activation is also shown. Complimentary to the standard solution-based protocols, these reactions also proceed efficiently under neat conditions, which is unprecedented for abundant metal catalyzed C–H activation reactions.

Copper-catalyzed oxidative C(sp3)–H/C(sp2)–H cross-coupling *en route* to carbocyclic rings

R. Wang, Y. Li, R.-X. Jin, X.-S. Wang

*Chemical Science* 2017, 8, 3838.

**Abstract**

Copper-catalyzed selective coupling of C(sp3)–H bonds with C(sp2)–H bonds has been developed. An aniline module was used as a directing group to generate an aminyl radical, which selectively cleaves the secondary and tertiary C(sp3)–H bonds via a 1,5-HAT process to forge six-membered carbocyclic rings.
Ligand-assisted palladium-catalyzed C–H alkenylation of aliphatic amines for the synthesis of functionalized pyrrolidines

C. He, M. J. Gaunt

Chemical Science 2017, 8, 3586.

Abstract

The development of a ligand-assisted Pd-catalyzed C–H alkenylation of aliphatic amines is reported. Our studies indicated that an amino-acid-derived ligand renders the C–H bond activation step reversible and promotes the traditionally difficult alkenylation process. The C(sp³)–H alkenylation proceeds through a 5-membered-ring cyclopalladation pathway that allows access to complex aliphatic heterocycles that could be useful to practitioners of synthetic and medicinal chemistry.

Divergent reactivities in fluoronation of allylic alcohols: synthesis of Z-fluoroalkenes via carbon–carbon bond cleavage

T.-L. Liu, J'E. Wu, Yu, Zhao

Chemical Science 2017, 8, 3885

Abstract

An unconventional cleavage of an unstrained carbon–carbon bond in allylic alcohols can be induced by the use of N-fluorobenzenesulfonimide (NFSI) under catalyst-free conditions. By using this simple procedure, a wide range of functionalized Z-fluoroalkenes can be accessed in high yield and selectivity from cyclic and acyclic allylic alcohols.
Anion–π catalysis: bicyclic products with four contiguous stereogenic centers from otherwise elusive diastereospecific domino reactions on π-acidic surfaces

L. Liu, Y. Cotelle, J. Klehr, N. Sakai, T. R. Ward, S. Matile

Chemical Science 2017, 8, 3770.

Abstract

Anion–π interactions have been introduced recently to catalysis. The idea of stabilizing anionic intermediates and transition states on π-acidic surfaces is a new fundamental concept. By now, examples exist for asymmetric enolate, enamine, iminium and transamination chemistry, and the first anion–π enzyme has been created. Delocalized over large aromatic planes, anion–π interactions appear particularly attractive to stabilize extensive long-distance charge displacements during domino processes. Moving on from the formation of cyclohexane rings with five stereogenic centers in one step on a π-acidic surface, we here focus on asymmetric anion–π catalysis of domino reactions that afford bicyclic products with quaternary stereogenic centers. Catalyst screening includes a newly synthesized, better performing anion–π version of classical organocatalysts from cinchona alkaloids, and anion–π enzymes. We find stereoselectivities that are clearly better than the best ones reported with conventional catalysts, culminating in unprecedented diastereospecificity. Moreover, we describe achiral salts as supramolecular chirality enhancers and report the first artificial enzyme that operates in neutral water with anion–π interactions, i.e., interactions that are essentially new to enzymes. Evidence in support of contributions of anion–π interactions to asymmetric catalysis include increasing diastereoselectivity with increasing rates, i.e., asymmetric transition-state stabilization in the presence of π-acidic surfaces and inhibition with the anion selectivity sequence NO₃⁻ > Br⁻ > BF₄⁻ > PF₆⁻.
An automated method to find reaction mechanisms and solve the kinetics in organometallic catalysis

J. A. Varela, S. A. Vázquez, E. Martínez-Núñez

*Chemical Science* 2017, 8, 3843.

Abstract

A novel computational method is proposed in this work for use in discovering reaction mechanisms and solving the kinetics of transition metal-catalyzed reactions. The method does not rely on either chemical intuition or assumed *a priori* mechanisms, and it works in a fully automated fashion. Its core is a procedure, recently developed by one of the authors, that combines accelerated direct dynamics with an efficient geometry-based post-processing algorithm to find transition states (Martinez-Nunez, E., *J. Comput. Chem.* 2015, 36, 222–234). In the present work, several auxiliary tools have been added to deal with the specific features of transition metal catalytic reactions. As a test case, we chose the cobalt-catalyzed hydroformylation of ethylene because of its well-established mechanism, and the fact that it has already been used in previous automated computational studies. Besides the generally accepted mechanism of Heck and Breslow, several side reactions, such as hydrogenation of the alkene, emerged from our calculations. Additionally, the calculated rate law for the hydroformylation reaction agrees reasonably well with those obtained in previous experimental and theoretical studies.
Iron-Catalyzed Amide Formation from the Dehydrogenative Coupling of Alcohols and Secondary Amines

E. M. Lane, K. B. Uttley, N. Hazari, W. Bernskoetter

Abstract

The five-coordinate iron(II) hydride complex ($\text{^6\Pi PNP}$)Fe(H)(CO) ($\text{^6\Pi PNP} = \text{N(CH}_2\text{CH}_2\text{(PPr}_2\text{)})_2$) selectively catalyzes the dehydrogenative intermolecular coupling of alcohols and secondary amines to form tertiary amides. This is the most productive base-metal catalyst for dehydrogenative amidation reported to date, in some cases achieving up to 600 turnovers. The catalyst works well for sterically undemanding amines and alcohols or cyclic substrates and is particularly effective in the synthesis of formamides from methanol. However, the catalyst performance declines rapidly with the incorporation of large substituents on the amine or alcohol substrate. Variable-temperature NMR spectroscopic studies suggest that the catalyst resting state is an off-cycle iron(II) methoxide species, ($\text{^6\Pi PN(H)}$)Fe(H)(OCH$_3$)(CO), resulting from addition of methanol across the Fe–N bond of ($\text{^6\Pi PNP}$)Fe(H)(CO). This reversibly formed iron(II) methoxide complex is favored at mild temperatures but eliminates methanol upon heating.
Importance of Dispersion on the Stability of the Concave-Bound CpM (M = Fe, Ru, Os) Complexes of Sumanene

S. H. Martínez, S. Pan, J. L. Cabellos, E. Dzib, M. A. Fernández-Herrera, G. Merino

Organometallics 2017, 36, 2036.

Abstract

The preference for concave mode binding of the CpM unit with sumanene in CpM(η^6-sumanene)^+ (M = Fe, Ru, Os) over the convex mode is analyzed by various density functional theory based methods including (or not) dispersion and solvent effects. In the case of the iron complex, the concave-bound isomer becomes energetically more favorable than the convex form only after the proper inclusion of dispersion effects, highlighting the importance of such contributions to stabilize the former arrangement. For the ruthenium complex, both the dispersion and solvent effects should be taken into account to provide a correct trend. The noncovalent interaction index corroborates the role of dispersion in concave selectivity. Our computations also show that the presence of the counterion is not relevant for this selectivity, discarding the previously reported argument made by Okumura et al.
New Mode of Operation of Pd-NHC Systems Studied in a Catalytic Mizoroki–Heck Reaction


**Abstract**

Metal complexes bearing N-heterocyclic carbene (NHC) ligands are typically considered the system of choice for homogeneous catalysis with well-defined molecular active species due to their stable metal–ligand framework. A detailed study involving 19 different Pd-NHC complexes with imidazolium, benzimidazolium, and triazolium ligands has been carried out in the present work and revealed a new mode of operation of metal-NHC systems. The catalytic activity of the studied Pd-NHC systems is predominantly determined by the cleavage of the metal–NHC bond, while the catalyst performance is strongly affected by the stabilization of in situ formed metal clusters. In the present study, the formation of Pd nanoparticles was observed from a broad range of metal complexes with NHC ligands under standard Mizoroki–Heck reaction conditions. A mechanistic analysis revealed two different pathways to connect Pd-NHC complexes to “cocktail”-type catalysis: (i) reductive elimination from a Pd(II) intermediate and the release of NHC-containing byproducts and (ii) dissociation of NHC ligands from Pd intermediates. Metal-NHC systems are ubiquitously applied in modern organic synthesis and catalysis, while the new mode of operation revealed in the present study guides catalyst design and opens a variety of novel opportunities. As shown by experimental studies and theoretical calculations, metal clusters and nanoparticles can be readily formed from M-NHC complexes after formation of new M–C or M–H bonds followed by C–NHC or H–NHC coupling. Thus, a combination of a classical molecular mode of operation and a novel cocktail-type mode of operation, described in the present study, may be anticipated as an intrinsic feature of M-NHC catalytic systems.
**Enantioselective Intermolecular Addition of Aliphatic Amines to Acyclic Dienes with a Pd–PHOX Catalyst**

Nathan J. Adamson, Ethan Hull, and Steven J. Malcolmson


We report a method for the catalytic, enantioselective intermolecular addition of aliphatic amines to acyclic 1,3-dienes. In most cases, reactions proceed efficiently at or below room temperature in the presence of 5 mol % of a Pd catalyst bearing a PHOX ligand, generating allylic amines in up to 97:3 er. The presence of an electron-deficient phosphine within the ligand not only leads to a more active catalyst but also is critical for achieving high site selectivity in the transformation.

**Potassium tert-Butoxide-Catalyzed Dehydrogenative C–H Silylation of Heteroaromatics: A Combined Experimental and Computational Mechanistic Study**

Wen-Bo Liu et al.


We recently reported a new method for the direct dehydrogenative C–H silylation of heteroaromatics utilizing Earth-abundant potassium tert-butoxide. Herein we report a systematic experimental and computational mechanistic investigation of this transformation. Our experimental results are consistent with a radical chain mechanism. A trialkylsilyl radical may be initially generated by homolytic cleavage of a weakened Si–H bond of a hypercoordinated silicon species as detected by IR, or by traces of oxygen which can generate a reactive peroxide by reaction with [KOt-Bu]4 as indicated by density functional theory (DFT) calculations. Radical clock and kinetic isotope experiments support a mechanism in which the C–Si bond is formed through silyl radical addition to the heterocycle followed by subsequent β-hydrogen scission. DFT calculations reveal a reasonable energy profile for a radical mechanism and support the experimentally observed regioselectivity. The silylation reaction is shown to be reversible, with an equilibrium favoring products due to the generation of H2 gas. In situ NMR experiments with deuterated substrates show that H2 is formed by a cross-dehydrogenative mechanism. The stereochemical course at the silicon center was investigated utilizing a 2H-labeled silolane probe; complete scrambling at the silicon center was observed, consistent with a number of possible radical intermediates or hypercoordinate silicates.
B(C6F5)3-Catalyzed (Convergent) Disproportionation Reaction of Indoles

Yuxi Han, Sutao Zhang, Jianghua He, and Yuetao Zhang


A metal-free B(C6F5)3-catalyzed approach is developed for the disproportionation reaction of a series of indoles with various hydrosilanes, without any additives such as base and production of any small molecule such as dihydrogen. This boron catalyst system also exhibits excellent catalytic performance for practical application, such as catalyst loading as low as 0.01 mol % under solvent-free conditions, and a long-life catalytic performance highlighted by a constant catalytic activity being maintained and excellent yields being achieved for the desired products over 10 sequential additions of starting materials. On the basis of characterization of key intermediates through a series of in situ NMR reactions and detailed experimental data, we proposed a reaction mechanism which illustrated pathways for the formation of different products, including both major products and byproducts. Additional control experiments were conducted to support our proposed mechanism. Understanding the mechanism enables us to successfully suppress side reactions by choosing appropriate substrates and hydrosilanes. More importantly, the use of an elevated reaction temperature for continuous oxidation of the resulting indoline to indole makes the convergent disproportionation reaction an ideal atom-economical process. Near-quantitative conversions and up to 99% yields of C3-silylated indoles were achieved for various indoles with trisubstituted silanes, Ph3SiH (2b) or Ph2MeSiH (2d).

Ionic and Neutral Mechanisms for C–H Bond Silylation of Aromatic Heterocycles Catalyzed by Potassium tert-Butoxide

Shibdas Banerjee et al.


Exploiting C–H bond activation is difficult, although some success has been achieved using precious metal catalysts. Recently, it was reported that C–H bonds in aromatic heterocycles were converted to C–Si bonds by reaction with hydrosilanes under the catalytic action of potassium tert-butoxide alone. The use of Earth-abundant potassium cation as a catalyst for C–H bond functionalization seems to be
without precedent, and no mechanism for the process was established. Using ambient ionization mass spectrometry, we are able to identify crucial ionic intermediates present during the C–H silylation reaction. We propose a plausible catalytic cycle, which involves a pentacoordinate silicon intermediate consisting of silane reagent, substrate, and the tert-butoxide catalyst. Heterolysis of the Si–H bond, deprotonation of the heteroarene, addition of the heteroarene carbamion to the silyl ether, and dissociation of tert-butoxide from silicon lead to the silylated heteroarene product. The steps of the silylation mechanism may follow either an ionic route involving K+ and tBuO– ions or a neutral heterolytic route involving the [KOtBu]4 tetramer. Both mechanisms are consistent with the ionic intermediates detected experimentally. We also present reasons why KOtBu is an active catalyst whereas sodium tert-butoxide and lithium tert-butoxide are not, and we explain the relative reactivities of different (hetero)arenes in the silylation reaction. The unique role of KOtBu is traced, in part, to the stabilization of crucial intermediates through cation–π interactions.

**Periodic Trends in Olefin Epoxidation over Group IV and V Framework-Substituted Zeolite Catalysts: A Kinetic and Spectroscopic Study**

Daniel T. Bregante and David W. Flaherty


Group IV and V framework-substituted zeolites have been used for olefin epoxidation reactions for decades, yet the underlying properties that determine the selectivities and turnover rates of these catalysts have not yet been elucidated. Here, a combination of kinetic, thermodynamic, and in situ spectroscopic measurements show that when group IV (i.e., Ti, Zr, and Hf) or V (i.e., Nb and Ta) transition metals are substituted into zeolite *BEA*, the metals that form stronger Lewis acids give greater selectivities and rates for the desired epoxidation pathway and present smaller enthalpic barriers for both epoxidation and H2O2 decomposition reactions. In situ UV–vis spectroscopy shows that these group IV and V materials activate H2O2 to form pools of hydroperoxide, peroxide, and superoxide intermediates. Time-resolved UV–vis measurements and the isomeric distributions of Z-stilbene epoxidation products demonstrate that the active species for epoxidations on group IV and V transition metals are only M-OOH/(O2)– and M-(O2)– species, respectively. Mechanistic interpretations of kinetic data suggest that these group IV and V materials catalyze cyclohexene epoxidation and H2O2 decomposition through largely identical Eley–Rideal mechanisms that involve the irreversible activation of coordinated H2O2 followed by reaction with an olefin or H2O2. Epoxidation rates and selectivities vary over five- and two-orders of magnitude, respectively, among these catalysts and depend exponentially on the energy for ligand-to-metal charge transfer (LMCT) and the functional Lewis acid strength of the metal centers. Together, these observations show that more electrophilic active-oxygen species (i.e., lower-energy LMCT) are more reactive and selective for epoxidations of electron-rich olefins and explain why Ti-based catalysts have been identified as the most active among early transition metals for these reactions. Further, H2O2 decomposition (the undesirable reaction pathway) possesses a weaker dependence on Lewis acidity than epoxidation, which suggests that the design of catalysts with increased Lewis acid strength will simultaneously increase the reactivity and selectivity of olefin epoxidation.

**Enantioselective β-Protonation of Enals via a Shuttling Strategy**

Jiean Chen§, Pengfei Yuan§, Leming Wang, and Yong Huang

Remote asymmetric protonation is a longstanding challenge due to the small size of protons. Reactions involving electron-deficient olefins pose a further difficulty due to the electrophilic nature of these substrates. We report a shuttling system that delivers a proton in a highly enantioselective manner to the β-carbon of enals using a chiral N-heterocyclic carbene (NHC) catalyst. Choices of a Brønsted base shuttle and a Brønsted acid cocatalyst are critical for highly stereoselective β-protonation of the homoenolate intermediate and regeneration of the NHC catalyst results in functionalization of the carbonyl group. Thioesters with a β-chiral center were prepared in a redox-neutral transformation with an excellent yield and ee.

**Deoxygenation of Ethers To Form Carbon–Carbon Bonds via Nickel Catalysis**

Zhi-Chao Cao and Zhang-Jie Shi  

In this article a successful protocol was developed to construct carbon–carbon bonds by the extrusion of the O atom of ethers via nickel catalysis in the presence of reductants. This methodology is featured as a highly economic route to construct sp3–sp3 C–C bonds through dual C–O activation of ethers with good functional group tolerance.

**Measurement of Solvent OH−π Interactions Using a Molecular Balance**

Josef M. Maier, Ping Li, Erik C. Vik, Christopher J. Yehl, Sharon M. S. Strickland, and Ken D. Shimizu  

A molecular torsion balance was designed to study and measure OH−π interactions between protic solvents and aromatic surfaces. These specific solvent–solute interactions were measured via their influence on the folded–unfolded equilibrium of an N-arylimide rotor. Protic solvents displayed systematically weaker solvophobic interactions than aprotic solvents with similar solvent cohesion parameters. This was attributed to the formation of OH−π interactions between the protic solvents and the exposed aromatic surfaces in the unfolded conformer that offset the stronger solvophobic effects for protic solvents.
**Synthesis, Structure, and Catalysis of Palladium Complexes Bearing a Group 13 Metalloligand: Remarkable Effect of an Aluminum-Metalloligand in Hydrosilylation of CO2**

Jun Takaya and Nobuharu Iwasawa  

Efficient synthesis and catalysis of a series of palladium complexes having a group 13 metalloligand (Al, Ga, In) are reported utilizing 6,6''-bis(phosphino)terpyridine as a new scaffold for Pd–E bonds (E = Al, Ga, In). Systematic investigation revealed unique characteristics of the Al-metalloligand in both structure and reactivity, which exhibited the highest catalytic activity for hydrosilylation of CO2 ever reported (TOF = 19,300 h⁻¹). This study demonstrated fine-tuning of catalyst activity by the precisely designed metalloligand is a promising approach for new catalyst development in synthetic organometallic chemistry.

**Overcoming the Rate-Limiting Reaction during Photoreforming of Sugar Aldoses for H2-Generation**

Kai E. Sanwald, Tobias F. Berto, Wolfgang Eisenreich, Andreas Jentys, Oliver Y. Gutiérrez, and Johannes A. Lercher  
*ACS Catal.*, 2017, 7 (5), pp 3236–3244

Photoreforming of sugars on metalloadded semiconductors is an attractive process for H2-generation. However, the reaction proceeds typically with rapidly decreasing rates. We identified that this decrease is due to kinetic constraints rather than to catalyst deactivation. Thus, the nature of the rate-limiting reaction was elucidated by investigation of the reaction pathways and oxidation mechanisms during photoreforming of sugar aldoses on TiO2 decorated with Rh, Pd, or Pt. Using selective isotope labeling it is shown that ring opening of aldoses via direct hole transfer to the chemisorbed oxygenates yields primary formate esters. Under pH-neutral and acidic conditions, formates convert to the consecutive aldose intermediate through light-driven, redox-neutral hydrolysis. The slow kinetics of this step, which requires interaction with negative and positive photogenerated charges, leads to blocking of active sites at the photoanode and enhanced electron–hole recombination. Stable H2-evolution and sugar conversion over time is achieved through alkalinization of the aqueous-phase due to fast OH⁻-induced hydrolytic cleavage of formate intermediates.
Lignin Fragmentation onto Multifunctional Fe3O4@Nb2O5@Co@Re Catalysts: The Role of the Composition and Deposition Route of Rhenium

Cristina Opris et al.

Multifunctional Fe3O4@Nb2O5@Co@Re catalysts with metal loadings in the range of 2–7 wt % were prepared via a multistep process. Magnetic nanoparticles prepared by coprecipitation were covered with a niobia shell precipitated from an ammonium niobate–oxalate complex in the presence of hexadecyltrimethylammonium bromide. The deposition of cobalt was performed using a deposition/precipitation procedure. Finally, rhenium has been deposited following three different routes: (i) impregnation, (ii) deposition and precipitation of rhenium chloride (ImC and PP, respectively), and (iii) impregnation with ammonium perrhenate (ImA). The characterization of these catalysts was achieved by X-ray diffraction, Raman, H2 and NH3 temperature-programmed desorption, X-ray photoelectron spectroscopy, and transmission electron microscopy showing the influence of the preparation procedure, reduction, and Re/Co cooperation on the degree of dispersion and reduction. ImC and ImA routes led to more reduced catalysts, and the decrease in cobalt content corresponded to more reduced rhenium. An inverse relation between the acidity and the degree of reduction has been found. The screening of these catalysts in the fragmentation of the lignin confirmed the role of the structural characteristics and solvent. ImC catalysts exhibited better catalytic activity, especially for low metal loadings [2%Co@3%Re, 85% yield of LF, 15.5% yield of LR in tetrahydrofuran (THF), and 14.5% yield of insoluble LR in THF]. Although the extent was smaller, the PP catalysts allowed a more advanced fragmentation of the lignin to fragments with molecular weights between 200 and 400 Da. The catalysts were totally recovered by application of a magnetic field and recycled six times without any loss of activity or selectivity.

Promoting Lignin Depolymerization and Restraining the Condensation via an Oxidation–Hydrogenation Strategy

Chaofeng Zhang et al.
For lignin valorization, simultaneously achieving the efficient cleavage of ether bonds and restraining the condensation of the formed fragments represents a challenge thus far. Herein, we report a two-step oxidation–hydrogenation strategy to achieve this goal. In the oxidation step, the \( \text{O}_2/\text{NaNO}_2/\text{DDQ}/\text{NHPI} \) system selectively oxidizes \( \text{C}α\text{H}−\text{OH} \) to \( \text{C}α═\text{O} \) within the \( β-O-4 \) structure. In the subsequent hydrogenation step, the \( α-O-4 \) and the preoxidized \( β-O-4 \) structures are further hydrogenated over a \( \text{NiMo sulfide catalyst} \), leading to the cleavage of \( \text{C}β–\text{OPh} \) and \( \text{C}α–\text{OPh} \) bonds. Besides the transformation of lignin model compounds, the yield of phenolic monomers from birch wood is up to 32% by using this two-step strategy. The preoxidation of \( \text{C}α\text{H}−\text{OH} \) to \( \text{C}α═\text{O} \) not only weakens the \( \text{C}β–\text{OPh} \) ether bond but also avoids the condensation reactions caused by the presence of \( \text{C}α+ \) from dehydroxylation of \( \text{C}α\text{H}−\text{OH} \). Furthermore, the \( \text{NiMo sulfide} \) prefers to catalyze the hydrogenative cleavage of the \( \text{C}β–\text{OPh} \) bond connecting with a \( \text{C}α═\text{O} \) rather than catalyze the hydrogenation of \( \text{C}α═\text{O} \) back to the original \( \text{C}α\text{H}−\text{OH} \), which further ensures and utilizes the advantages of preoxidation.

**Selective Copper–N-Heterocyclic Carbene (Copper-NHC)-Catalyzed Aerobic Cleavage of \( β-1 \) Lignin Models to Aldehydes**

Zhong-zhen Zhou, Mingxin Liu, and Chao-Jun Li

*ACS Catal., 2017, 7 (5), pp 3344–3348*

As fossil resources are undergoing fast depletion, the harvesting of sustainable aromatic compounds from biorenewable lignin has become highly appealing nowadays. However, the development of efficient catalysts for lignin depolymerization to high value-added chemicals is challenging. In this paper, a selective copper–N-heterocyclic carbene (copper-NHC)-catalyzed aerobic cleavage is reported for \( β-1 \) lignin model compound, which represents an important family of natural wood lignin. Using this catalyst system, the cleavage of \( β-1 \) model compounds gave >99% conversions and satisfactory yields of the corresponding aldehydes, which can serve as versatile starting materials for the chemical industry.

**Au–Carbon Electronic Interaction Mediated Selective Oxidation of Styrene**

Ben Liu, Pu Wang§, Aaron Lopes, Lei Jin, Wei Zhong, Yong Pei, Steven L. Suib, and Jie He

*ACS Catal., 2017, 7 (5), pp 3483–3488*

The rational design of the Au–support electronic interaction is crucial for Au nanocatalysis. We herein report our observation of electronic perturbation at the Au–carbon interface and its application in controlling the reaction selectivity in styrene oxidation. Ultrasmall Au nanocatalysts were grown in situ...
on a nitrided carbon support where the nitrogen-doped carbon supports enriched the surface charge density and generated electron-rich Au surface sites. The Au–carbon interaction altered the binding behavior of C═C bonds to catalytic centers, leading to a solvent-polarity-dependent selectivity in C═C oxidation reactions. A high selectivity of 90% to benzaldehyde was achieved in an apolar solvent, and a selectivity of 95% to styrene epoxide was attained in a polar solvent. The Au–carbon electronic perturbation, originating from surface functional groups on the carbon support, may provide an alternative avenue to tune the selectivity and activity of more complex reactions in heterogeneous catalysis.

Direct Catalytic Alcoholysis of Unactivated 8-Aminoquinoline Amides

Toru Deguchi, Hai-Long Xin, Hiroyuki Morimoto, and Takashi Ohshima

Direct catalytic alcoholysis of unactivated amides is one of the most difficult challenges in organic chemistry, and an applicable method for cleaving amides used as directing groups in regioselective functionalization reactions has not been reported. Herein, we report direct catalytic alcoholysis of 8-aminoquinoline amides, which are highly effective directing groups in regioselective functionalization reactions. The reactions proceeded with a simple combination of substrates, air-stable catalysts, and alcohols, affording the corresponding esters in good yields with broad functional group tolerance. Highly chemoselective cleavage of the 8-aminoquinoline amides in the presence of related carbonyl functionalities and preliminary mechanistic studies are also described.

Understanding and Overcoming the Limitations of Bacillus badius and Caldalkalibacillus thermarum Amine Dehydrogenases for Biocatalytic Reductive Amination

Ahir Pushpanath, Elina Siirola, Amin Bornadel, David Woodlock, and Ursula Schell

The direct asymmetric reductive amination of ketones using ammonia as the sole amino donor is a growing field of research in both chemocatalysis and biocatalysis. Recent research has focused on the enzyme engineering of amino acid dehydrogenases (to obtain amine dehydrogenases), and this
technology promises to be a potentially exploitable route for chiral amine synthesis. However, the use of these enzymes in industrial biocatalysis has not yet been demonstrated with substrate loadings above 80 mM, because of the enzymes' generally low turnover numbers (kcat < 0.1 s−1) and variable stability under reaction conditions. In this work, a newly engineered amine dehydrogenase from a phenylalanine dehydrogenase (PheDH) from Caldalkalibacillius thermarum was recruited and compared against an existing amine dehydrogenase (AmDH) from Bacillus badius for both kinetic and thermostability parameters, with the former exhibiting an increased thermostability (melting temperature, Tm) of 83.5 °C, compared to 56.5 °C for the latter. The recruited enzyme was further used in the reductive amination of up to 400 mM of phenoxy-2-propanone (c = 96%, ee (R) < 99%) in a biphasic reaction system utilizing a lyophilized whole-cell preparation. Finally, we performed computational docking simulations to rationalize the generally lower turnover numbers of AmDHs, compared to their PheDH counterparts.
Gold(I)-Catalyzed [2 + 2 + 2] Cyclotrimerization of 1,3-Diarylpropargyl Acetals
Helgi Freyr Jónsson, Sigvart Evjen, and Anne Fiksdahl
Org. Lett., 2017, 19 (9), 2202

A gold-nitrone catalyzed [2 + 2 + 2] cyclotrimerization of 1,3-diarylpropargyl acetal into cyclohexenylidene products (up to 74% yield) is reported. The trimerization is proposed to proceed through allenic intermediates via gold-catalyzed 1,3-alkoxy rearrangement. The presence of catalytic amounts of different nitrones, tuning of the Au(I) catalyst activity, was essential for controlled regio-/chemoselective cyclotrimerization. A linear nitrone–O–Au(I)–P coordination mode was shown (X-ray analysis) for a catalytic active phosphane–gold–nitrone complex, representing a group of Au(I) catalysts with specific properties.

Benzene C–H Etherification via Photocatalytic Hydrogen-Evolution Cross-Coupling Reaction
Yi-Wen Zheng, Pan Ye, Bin Chen, Qing-Yuan Meng, Ke Feng, Wenguang Wang, Li-Zhu Wu, and Chen-Ho Tung
Org. Lett., 2017, 19 (9), 2206

Aryl ethers can be constructed from the direct coupling between the benzene C–H bond and the alcohol O–H bond with the evolution of hydrogen via the synergistic merger of photocatalysis and cobalt catalysis. Utilizing the dual catalyst system consisting of 3-cyano-1-methylquinolinum photocatalyst and cobaloxime, intermolecular etherification of arenes with various alcohols and intramolecular alkoxylation of 3-phenylpropanols with formation of chromanes are accomplished. These reactions proceed at remarkably mild conditions, and the sole byproduct is equivalent hydrogen gas.

One-Pot Synthesis of 3-Substituted 2-Arylpyrrole in Aqueous Media via Addition–Annulation of Arylboronic Acid and Substituted Aliphatic Nitriles
Md Yousuf and Susanta Adhikari
Org. Lett., 2017, 19 (9), 2214

Pd(II)-catalyzed C–C coupling reactions between substituted aliphatic nitriles and arylboronic acids followed by in situ cyclodehydration have been employed for the first time to synthesize a wide variety of 3-substituted 2-aryl-1H-pyrroles in aqueous acetic acid. This one-pot synthesis is green, and it conforms to atom economy. The structures of two representative pyrroles, 3k and 5f, were confirmed by X-ray crystallographic analysis.
Synthesis of Spirocyclohexadienones through Radical Cascade Reactions Featuring 3-Fold Carbon–Carbon Bond Formation
Nina Hegmann, Lea Prusko, and Markus R. Heinrich
Org. Lett., 2017, 19 (9), 2222

The radical 5-exo cyclization starting from 2-allyloxyphenyldiazonium ions can be employed for the diastereoselective synthesis of ortho-spirocyclohexadienones through a consecutive addition to alkynes. The spirocyclic systems are formed in a radical [2 + 2 + 1] cycloaddition comprising three carbon–carbon formations, of which the final one is an ipso attack onto the aromatic system at the original position of the diazonium-derived aryl radical.

Iron-Catalyzed Dehydrogenative sp3–sp2 Coupling via Direct Oxidative C–H Activation of Acetonitrile
Huimin Su, Luyao Wang, Honghua Rao, and Hao Xu
Org. Lett., 2017, 19 (9), 2226

An iron-catalyzed dehydrogenative sp3–sp2 coupling of acetonitrile and 2-arylimidazo[1,2-a]pyridine has been realized, which can serve as a novel approach toward heteroarylacetonitriles. The merit of this strategy is illustrated by the breadth of functional groups tolerated in the transformation and the fast access to pharmaceuticals (such as zolpidem) directly from the heteroarylacetonitriles.

Palladium(0)-Catalyzed Dearomative [3 + 2] Cycloaddition of 3-Nitroindoles with Vinylcyclopropanes: An Entry to Stereodefined 2,3-Fused Cyclopentannulated Indoline Derivatives
Maxime Laugeois, Johanne Ling, Charlène Fédard, Véronique Michelet, Virginie Ratovelomanana-Vidal, and Maxime R. Vitale
Org. Lett., 2017, 19 (9), 2266

The palladium(0)-catalyzed diastereoselective dearomative cyclopentannulation of 3-nitroindoles with vinylcyclopropanes is described. This straightforward and highly atom-economical method leads to a wide range of functionalized indolines in good yields and diastereoselectivities and represents an unprecedented entry toward the valuable 2,3-fused cyclopentannulated indoline scaffold.
Synthesis of Dihydropyridinone-Fused Indoles and α-Carbolines via N-Heterocyclic Carbene-Catalyzed \([3 + 3]\) Annulation of Indolin-2-imines and Bromoenals

Liang Yi, Yuyang Zhang, Zhao-Fei Zhang, Dequn Sun, and Song Ye

*Org. Lett.*, **2017**, 19 (9), 2286

The N-heterocyclic carbene catalyzed \([3 + 3]\) annulation of indolin-2-imines and bromoenals was developed to give dihydropyridinone-fused indoles in good to high yields, which were transformed to α-carbolines with different 2-substituents by a process of dehydrogenation, tosylation, and palladium catalyzed C–C or C–N coupling reaction.

Asymmetric Synthesis of Trisubstituted Tetrahydrothiophenes via in Situ Generated Chiral Fluoride-Catalyzed Cascade Sulfa-Michael/Aldol Reaction of 1,4-Dithiane-2,5-diol and α,β-Unsaturated Ketones

Mengying Duan, Yidong Liu, Jun Ao, Lu Xue, Shilong Luo, Yu Tan, Wenling Qin, Choong Eui Song, and Hailong Yan

*Org. Lett.*, **2017**, 19 (9), 2298

A chiral fluoride-catalyzed asymmetric cascade sulfa-Michael/aldol condensation reaction of 1,4-dithiane-2,5-diol and a series of α,β-unsaturated ketones is described to access chiral trisubstituted tetrahydrothiophene derivatives. The target products, including the spiro tetrahydrothiophene derivatives bearing a five-, six-, and seven-membered ring, were highly functionalized and showed high ee value. This established protocol realized a highly enantioselective reaction with a catalytic amount of KF and Song’s chiral oligoEG via in situ generated chiral fluoride to construct useful heterocyclic skeletons with great complexity.

Accessing Polyoxygenated Dibenzofurans via the Union of Phenols and o-Benzoquinones: Rapid Syntheses of Metabolites Isolated from *Ribes takare*

Meng Yao Zhang and Russell A. Barrow

*Org. Lett.*, **2017**, 19 (9), 2302

The construction of polyoxygenated dibenzo[b,d]furan frameworks from the union of substituted phenols/naphthols and o-benzoquinones via a Michael-oxidation-oxa-Michael cascade is reported. The power of this transformation is demonstrated in the generation of a library of highly substituted dibenzofurans, featuring specifically substituted molecules containing broad ranges of functionality. The utility of this method is showcased in the total syntheses of two dibenzofurans isolated from *Ribes takare*, assembling the carbon scaffold of both natural products in one operation.
Enantioselective Spirocyclopropanation of \textit{para}-Quinone Methides Using Ammonium Ylides

Lukas Roiser and Mario Waser

\textit{Org. Lett.}, \textbf{2017}, 19 (9), 2338

The use of Cinchona alkaloid-based chiral ammonium ylides allows for the first highly enantioselective and broadly applicable spirocyclopropanation reactions of \textit{para}-quinone methides. This strategy provides a straightforward protocol toward the chiral spiro[2.5]octa-4,7-dien-6-one skeleton, which is a frequently found structural motif in important biologically active molecules.

Rhodium-Catalyzed Asymmetric Conjugate Alkynylation of \textit{β,γ}- Unsaturated \textit{α}-Ketoesters

Yanle Zhi, Jianhang Huang, Na Liu, Tao Lu, and Xiaowei Dou

\textit{Org. Lett.}, \textbf{2017}, 19 (9), 2378

The first example of catalytic asymmetric conjugate alkynylation of \textit{β,γ}-unsaturated \textit{α}-ketoesters is reported. By using Rh(I)/(R)-DM-binap complex as the catalyst and diphenyl[(triisopropylsilyl)ethynyl]methanol as the alkynylation reagent, the alkynylation reaction proceeded smoothly to afford \textit{α}-ketoesters bearing a propargylic chiral center at \textit{γ} position in good yields with high enantioselectivities.


Jiaojiao Xing, Yu Lei, Yu-Ning Gao, and Min Shi

\textit{Org. Lett.}, \textbf{2017}, 19 (9), 2382

A [3 + 2] annulation of \textit{α}-substituted secondary \textit{β}-ketoamides with δ-acetoxy-modified allenoate has been developed in the presence of phosphine catalyst. In this spiroannulation reaction, \textit{β}-ketoamides were used as the bis-nucleophilic partner while the \textit{γ,δ}-carbon of 5-acetoxypenta-2,3-dienoate participated as a C2 synthon, affording the desired functionalized five-membered \textit{N}-heterocyclic derivatives in moderate to excellent yields and diastereoselectivities under mild conditions. Preliminary attempts on the asymmetric variant of this reaction have been also examined, giving the corresponding products with moderate ee values.
Regioselective Functionalization of Enamides at the α-Carbon via Unsymmetrical 2-Amidoallyl Cations
Mirza A. Saputra, Nitin S. Dange, Alexander H. Cleveland, Joshua A. Malone, Frank R. Fronczek, and Rendy Kartika
Org. Lett., 2017, 19 (9), 2414

A new method to functionalize enamides via an intermediacy of unsymmetrical 2-amidoallyl cations is reported. Generated under mild Brønsted acid catalysis, these reactive species were found to undergo addition with various nucleophiles at the less substituted α-carbon to produce highly substituted enamides in high yields with complete control of regioselectivity.

Enantioselective Synthesis of 1,2-Dihydronaphthalenes via Oxidative N-Heterocyclic Carbene Catalysis
Saima Perveen, Zhifei Zhao, Guoxiang Zhang, Jian Liu, Muhammad Anwar, and Xinqiang Fang
Org. Lett., 2017, 19 (10), 2470

1,2-Dihydronaphthalenes are important molecules in both medicinal and synthetic chemistry, but methods for the catalytic asymmetric construction of this class of molecules are limited. The diastereo- and enantioselective N-heterocyclic carbene-catalyzed cascade annulation reactions using benzodiketones and enals under oxidative conditions, which afford a variety of 1,2-dihydronaphthalenes with two adjacent stereocenters in up to 99% yield, with >20:1 dr, and up to 99% ee, are reported. Furthermore, the product can be easily transformed to a series of useful compounds such as alcohol, amide, and epoxide.

Gangam Srikanth Kumar, Pravin Kumar, and Manmohan Kapur
Org. Lett., 2017, 19 (10), 2494

A unique, ruthenium-catalyzed, [3 + 3] annulation of anilines with allyl alcohols in the synthesis of substituted quinolines is reported. The method employs a traceless directing group strategy in the proximal C–H bond activation and represents a one-pot Domino synthesis of quinolines from anilines.
**One-Pot, Metal-Free Conversion of Anilines to Aryl Bromides and Iodides**

Derek A. Leas, Yuxiang Dong, Jonathan L. Vennerstrom, and Douglas E. Stack  
*Org. Lett.*, 2017, 19 (10), 2518

A metal-free synthesis of aryl bromides and iodides from anilines via halogen abstraction from bromotrichloromethane and diiodomethane is described. This one-pot reaction affords aryl halides from the corresponding anilines in moderate to excellent yields without isolation of diazonium salts. The transformation has short reaction times, a simple workup, and insensitivity to moisture and air and avoids excess halogenation. DFT calculations support a SRN1 mechanism. This method represents a convenient alternative to the classic Sandmeyer reaction.

**Synthesis of Spiroketalts by Synergistic Gold and Scandium Catalysis**

Man Liang, Shuai Zhang, Jiong Jia, Chen-Ho Tung, Jianwu Wang, and Zhenghu Xu  
*Org. Lett.*, 2017, 19 (10), 2526

An ultrafast synthesis of spiroketalts by synergistic gold(I) and Sc(III) catalysis has been reported. Diverse 5,6-benzannulated spiroketalts were rapidly constructed by the diastereoselective [4 + 2] cycloaddition between gold-generated enol ether and Sc(III)-catalyzed o-quinone methide intermediates. Ultrafast reaction rate, ambient reaction temperature, general scope, high yields, excellent diastereoselectivity, and good scalability are attractive features of this method.

**P-Stereogenic Bicyclo[4.3.1]phosphite Boranes: Synthesis and Utility of Tunable P-Tether Systems for the Desymmetrization of C2-Symmetric 1,3-anti-Diols**

Jana L. Markley and Paul R. Hanson  
*Org. Lett.*, 2017, 19 (10), 2552

The development of P-stereogenic bicyclo[4.3.1]phosphite borane tether systems for the desymmetrization of C2-symmetric dienediols is reported. This report highlights preliminary studies including tether installation and removal as well as chemoselective functionalization of the exocyclic olefin via diimide reduction or cross-metathesis. Most notably, a divergent oxidation strategy allows for the transformation of the bicyclic phosphite borane complexes to the corresponding phosphate or thiophosphate systems, highlighting the electronic attenuation of this P-tether system.
**Brønsted Acid-Catalyzed Intramolecular Hydroarylation of β-Benzylstyrenes**

Xiao Cai, Amir Keshavarz, Justin D. Omaque, and Benjamin J. Stokes  
*Org. Lett.*, **2017**, 19 (10), 2626

Using triphenylmethylium tetrakis(pentafluorophenyl)borate as a convenient Brønsted acid precatalyst, β-(α,α-dimethylbenzyl)styrenes are shown to cyclize efficiently to afford a variety of new indanes that possess a benzylic quaternary center. The geminal dimethyl-containing quaternary center is proposed to be necessary to arm the substrate for cyclization through steric biasing.

**Photoinduced Vitamin B12-Catalysis for Deprotection of (Allyloxy)arenes**

Maciej Giedyk, Joanna Turkowska, Sandra Lepak, Marcin Marculewicz, Keith ó Proinsias, and Dorota Gryko  
*Org. Lett.*, **2017**, 19 (10), 2670

Vitamin B12 is a natural cobalt complex that, while reduced to the “supernucleophilic” Co(I) form, can easily react with electrophiles via an SN2 mechanism. It is also shown to react via an SN2′ mechanism with allylic compounds allowing for photochemical deprotection of (allyloxy)arenes. A sustainable alternative to commonly used noble metal-catalyzed deprotection reactions is presented.

**Alkali-Induced Ring-Opening of 2-Amidodihydrofuran and Manganese-Catalyzed Aerobic Dehydrogenation Annulation: Access to Functionalized Oxazole**

Pan Li, Jingjing Zhao, Xinjian Li, and Fuwei Li  
*J. Org. Chem.*, **2017**, 82 (9), 4569

A novel and efficient synthesis of functionalized oxazoles from 2-amidodihydrofurans has been achieved by alkali-induced intramolecular C–O bond cleavage and formation using air as a green oxidant. Moreover, these functionalized oxazoles could be readily transformed into the corresponding oxazole-substituted pyrazoles and 2H-azirines.
Bifunctional Quaternary Ammonium Salts Catalyzed Stereoselective Conjugate Addition of Oxindoles to Electron-Deficient β-Haloalkenes
Qiaowen Jin, Changwu Zheng, Gang Zhao, and Gang Zou
J. Org. Chem., 2017, 82 (9), 4840

A highly Z-selective asymmetric conjugate addition of 3-substituted oxindoles to β-haloalkene ketones/esters catalyzed by readily available chiral bifunctional quaternary ammonium salts is reported. This reaction provides efficient access to a range of 2-oxoindole derivatives bearing a thermodynamically unstable Z-olefin structure and a chiral quaternary carbon center in high yields (up to 90%) and with good to high stereoselectivities (up to >19:1 Z/E and 91% ee) under mild conditions.

Consecutive Sonogashira Coupling and Hydroamination Cyclization for the Synthesis of Isoindolo[1,2-b]quinazolin-10(12H)-ones Catalyzed by CuI/L-Proline
Jian-Quan Liu, Yong-Gang Ma, Mei-Mei Zhang, and Xiang-Shan Wang
J. Org. Chem., 2017, 82 (9), 4918

A consecutive Sonogashira coupling reaction, acetylene hydroamination cyclization of 2-(2-bromophenyl)quinazolin-4(3H)-ones and terminal alkynes, is described catalyzed by CuI/l-proline in the presence of Cs2CO3. This procedure provided a facile method for the synthesis of isoindolo[1,2-b]quinazolin-10(12H)-one derivatives in good yields.

Multiple Approaches to the In Situ Generation of Anhydrous Tetraalkylammonium Fluoride Salts for SNAr Fluorination Reactions
Megan A. Cismesia, Sarah J. Ryan, Douglas C. Bland, and Melanie S. Sanford

This article focuses on the development of practical approaches to the in situ generation of anhydrous fluoride salts for applications in nucleophilic aromatic substitution (SNAr) reactions. We report herein that a variety of combinations of inexpensive nucleophiles (e.g., tetramethylammonium cyanide and phenoxydine salts) and fluoride-containing electrophiles (e.g., acid fluoride, fluoroformate, benzenesulfonyl fluoride, and aryl fluorosulfonate derivatives) are effective for this transformation. Ultimately, we demonstrate that the combination of tetramethylammonium 2,6-dimethylphenoxy and sulfuryl fluoride (SO2F2) serves as a particularly practical route to anhydrous tetramethylammonium fluoride. This procedure is applied to the SNAr fluorination of a range of electron-deficient aryl and heteroaryl chlorides as well as nitroarenes.
Indium-Catalyzed Regioselective β-Alkylation of Pyrroles with Carbonyl Compounds and Hydrosilanes and Its Application to Construction of a Quaternary Carbon Center with a β-Pyrrolyl Group
Shota Nomiyama, Takahiro Ogura, Hiroaki Ishida, Kazuki Aoki, and Teruhisa Tsuchimoto

Treatment of N-substituted pyrroles with carbonyl compounds and nucleophiles under indium catalysis was found to be a promising method for preparing β-alkylpyrroles without contamination by α-alkylpyrroles. With this methodology, a variety of alkyl groups, which are primary, secondary, and tertiary as well as cyclic and functionalized types, can be introduced in place onto the pyrrole ring. The simplicity performable as a catalytic one-step process is one of the important features of this reaction. The substituent on the nitrogen atom of the product β-alkylpyrrole can be removed easily by literature procedures. Therefore, the indium-catalyzed β-alkylation plus the N-deprotection is a powerful system for all six variations, which are N-substituted and N-unsubstituted β-alkylpyrroles having primary, secondary, and tertiary alkyl groups. Our method is applicable to synthesizing, albeit in two steps, β-pyrrolyl-group-connected unsymmetrical tetraarylmethanes that have not been addressed thus far. Mechanistic studies showed the following three aspects: (1) dipyrrolylalkanes produced in situ from the pyrrole and carbonyl compound are key intermediates, (2) the selective β-alkylation is attributed to the selective elimination of an α-pyrrolyl group from the dipyrrolylalkane intermediates, and (3) the indium Lewis acid catalyst is indispensable for the progress of both stages.

Vinylogous Nucleophilic Substitution of the Hydroxy Group in Diarylmethanols with 3-Propenyl-2-silyloxyindoles: Towards the Synthesis of α-Alkylidene-δ-diaryl-2-oxindoles
Amol P. Jadhav, Amjad Ali and Ravi P. Singh

We report herein a highly stereoselective method for the indium triflate-catalyzed vinylogous substitution of the hydroxy group of diarylmethyl alcohols with 3-alkenyl-2-silyloxyindoles, which affords broadly substituted α-alkylidene-δ-diaryl-2-oxindole products with high efficiency and complete γ-site and Z-selectivity. The reaction displays very wide substrate scopes for both the reactants, benzhydryl alcohols and 3-alkenyl-2-silyloxyindoles. The utility of the substituted adducts is shown by their conversion to other useful derivatives.
Employing a green and efficient 2,2,2-trifluoroacetophenone-catalyzed oxidation of alkenes, which utilizes \( \text{H}_2\text{O}_2 \) as the green oxidant, a novel and sustainable synthesis of indolines and pyrrolidines was developed. This constitutes a cheap, general and environmentally-friendly protocol for the synthesis of substituted nitrogen-containing heterocycles. A variety of substitution patterns, both aromatic and aliphatic moieties, are well tolerated leading to the desired nitrogen heterocycles in good to excellent yields.

**Efficient Selenium-Catalyzed Selective C\(^{sp^3}\)-H Oxidation of Benzylpyridines with Molecular Oxygen**

Weiwei Jin, Poonnapa Zheng, Wing-Tak Wong and Ga-Lai Law


An efficient selenium-catalyzed direct oxidation of benzylpyridines in aqueous DMSO has been successfully developed by using molecular oxygen as the oxidant. A variety of benzoylpyridines with broad functional group tolerance were obtained in modest to excellent yields and with exclusive chemoselectivity.

**Synthesis of 2-Substituted Quinolines via Rhodium(III)-Catalyzed C–H Activation of Imidamides and Coupling with Cyclopropanols**

Xukai Zhou, Zisong Qi, Songjie Yu, Lingheng Kong, Yang Li, Wan-Fa Tian and Xingwei Li


An efficient synthesis of 2-substituted quinolines from readily available cyclopropanols and imidamides has been developed, where the cyclopropanol acts as a C3 synthon. With the assistance of a bifunctional imidamide directing group, the reaction occurred via sequential C–H/C–C cleavage and C–C/C–N bond formation.
Rhodium(III)-Catalyzed Cascade Redox-Neutral C–H Functionalization and Aromatization: Synthesis of Unsymmetrical ortho-Biphenols
Zhiyong Hu and Guixia Liu

An efficient rhodium(III)-catalyzed coupling reaction of N-aryloxyacetamides with 6-diazo-2-cyclohexenones through a cascade redox-neutral C–H functionalization and aromatization has been developed. This novel and scalable transformation provides a straightforward way to construct unsymmetrical ortho-biphenols with broad substrate scope under mild and redox-neutral conditions. The synthetic utility of this approach is demonstrated in the late-stage functionalization of bioactive compounds and the synthesis of an optically active ortho-biphenol.

Efficient Generation of C–S Bonds via a By-Product-Promoted Selective Coupling of Alcohols, Organic Halides, and Thiourea
Xiantao Ma, Lei Yu, Chenliang Su, Yaqi Yang, Huan Li and Qing Xu

A metal- and base-free three-component coupling of alcohols, heteroaryl halides, and thiourea has been developed for direct and selective synthesis of heteroaryl thioethers. This method can be easily scaled up to the gram scale and extended to dialkyl thioethers, heteroaryl selenides, benzothiazoles, and some antimycobacterially-active thioethers. Mechanistic studies revealed that a by-product-promoted in situ C–O activation of alcohols to more reactive alkyl halides and slow release of the thiol and alkyl halide intermediates are the key to the high selectivity and success of the reaction.

Exploration of A New Zwitterion: Phosphine-Catalyzed [2+1+2] Cycloaddition Reaction
Yu-Ning Gao, Qin Xu, Yin Wei and Min Shi

A new zwitterion generated from different electron-deficient alkenes and phosphines has been designed and its reactivity was explored. We demonstrated that this new zwitterion directed a novel [2+1+2] cycloaddition reaction between vinylpyridines and isatin-derived electron-deficient alkenes, affording spirocyclopentenedioxindole derivatives containing three stereocenters in moderate to good yields with good diastereoselectivities. A plausible mechanism has been proposed relying on preliminary mechanistic investigations and supported by theoretical calculations.
Copper-Catalyzed Asymmetric Allylic Alkylation of β-Keto Esters with Allylic Alcohols

Paz Trillo and Alejandro Baeza


The asymmetric allylic alkylation reaction of β-keto esters catalyzed by copper complex tBuBOX-Cu(OTf)2 employing allylic alcohols as environmentally friendly electrophilic partner, is herein described. This new protocol renders in general the corresponding allylic products with two consecutive all-carbon stereocenters in good both yields and enantioselectivities and with low to modest diastereoselection. The regioselectivity of the process seems to be governed by the formation of the most stable olefin according to the results obtained when non-symmetrically substituted alcohols were employed. The scope, limitations and mechanistic aspects of the process are also discussed.
Biomass-Derived Butadiene by Dehydra-Decyclization of Tetrahydrofuran

Omar A. Abdelrahman, Dae Sung Park, Katherine P. Vinter, Charles S. Spanjers, Limin Ren, Hong Je Cho, Dionisios G. Vlachos, Wei Fan, Michael Tsapatsis, and Paul J. Dauenhauer

ACS Sustainable Chemistry & Engineering 2017 5 (5), 3732-3736

Abstract
Catalytic ring-opening dehydration of tetrahydrofuran (THF), itself a product of decarbonylation and reduction of biomass-derived furfural, yields 1,3-butadiene, an important monomer in rubbers and elastomers. It is demonstrated that dehydra-decyclization of THF with phosphorus-containing siliceous self-pillared pentasil (SPP) or MFI structure exhibits high selectivity to butadiene (85–99%) at both low (9%) and high (89%) conversion of THF. High selectivity to pentadiene and hexadiene was also obtained from 2-methyl-tetrahydrofuran and 2,5-dimethyl-tetrahydrofuran, respectively, with phosphorus-containing, all-silica zeolites.

Efficient Method of Lignin Isolation Using Microwave-Assisted Acidolysis and Characterization of the Residual Lignin

Long Zhou, Vitaliy Budarin, Jiajun Fan, Raymond Sloan, and Duncan Macquarrie

ACS Sustainable Chemistry & Engineering 2017 5 (5), 3768-3774

Abstract
Microwave heating is characterized by high efficiency and selectivity in biomass treatment. Due to the high thermal stability and low polarity of lignin, isolation of lignin by high-temperature microwave treatment is a promising subject for investigation. In this paper, microwave treatment is applied to polysaccharide liquefaction and lignin isolation from softwood at 160–210 °C for 10 min with dilute sulfuric acid. Mass balance/element analysis/FTIR/TG/solid-state 13C NMR/Py-GC/MS are applied to investigate the processed residues (residual lignin). At 190 °C processing temperature, the residual lignin is a material rich in aromatics. High lignin purity (93 wt %) and yield (82 wt %) could be achieved by a simple protocol, which usually takes days or even weeks using conventional milled wood lignin protocols. The Py-GC/MS is applied to check the structure of lignin by a newly developed approach. The liquid phase after isolation is analyzed by GC-MS and liquid carbon NMR. Most chemicals in processed liquid are from cellulose and hemicellulose, suggesting that lignin is preserved well in the residue. By comparison, we found that microwave isolation causes less lignin degradation than conventional acidolysis under equivalent conditions. It is concluded that microwave treatment is potentially a promising tool for isolation of polysaccharide-free lignin with high efficiency.
Luminescent and Transparent Wood Composites Fabricated by Poly(methyl methacrylate) and \(\gamma\text{-Fe}_2\text{O}_3@\text{YVO}_4:\text{Eu}^3+\) Nanoparticle Impregnation

Wentao Gan, Shaoliang Xiao, Likun Gao, Runan Gao, Jian Li, and Xianxu Zhan

ACS Sustainable Chemistry & Engineering 2017 5 (5), 3855-3862

Abstract

Natural wood is functionalized using the index matching poly(methyl methacrylate) (PMMA) and luminescent \(\gamma\text{-Fe}_2\text{O}_3@\text{YVO}_4:\text{Eu}^3+\) nanoparticles to form a novel type of luminescent and transparent wood composite. First, the delignified wood template was obtained from natural wood through a lignin removal process, which can be used as a support for transparent polymer and phosphor nanoparticles. Then, the functionalization occurs in the lumen of wood, which benefits from PMMA that fills the cell lumen and enhances cellulose nanofiber interaction, leading to wood composites with excellent thermal properties, dimensional stability, and mechanical properties. More importantly, this wood composite displays a high optical transmittance in a broad wavelength range between 350 and 800 nm, magnetic responsiveness, and brightly colored photoluminescence under UV excitation at 254 nm. The unique properties and green nature of the luminescent wood composite have great potential in applications including green LED lighting equipment, luminescent magnetic switches, and anti-counterfeiting facilities.
Phytochemical Recovery for Valorization of Loblolly Pine and Sweetgum Bark Residues

Kalavathy Rajan, Andrew Nelson, Joshua P. Adams, and Danielle Julie Carrier

ACS Sustainable Chemistry & Engineering 2017 5 (5), 4258-4266

Abstract
Bark residues from forest products production using loblolly pine (LP) and sweetgum (SG) are currently combusted in pulp and paper mills. Hot water extraction (HWE) of phytochemicals from bark prior to combustion could be an effective method to valorize these biomass streams. On average, the LP and SG-HWE contained 12% monosaccharides, 33% polysaccharides, 21% total phenolics and 8% organic acids. Major phytochemicals recorded in LP and SG-HWE were shikimic acid (15%), gallic acid (7.5%), vanillic acid (5–7%) and vanillin. Antimicrobial and antioxidant activities of LP and SG-HWE were evaluated for LP and SG bark harvested in different months (January, April and September) and from different sized trees (diameter at breast height or DBH, ranging from 2 to 33 cm). All LP and SG-HWE inhibited a Staphylococcus aureus cocktail. LP-HWE harvested in April from DBH 27 and 33 cm also inhibited Listeria monocytogenes, Salmonella enterica and Escherichia coli. All SG-HWE preparations, at 12.5 μg, produced significant reduction in human low-density lipoprotein (LDL) peroxidation, as compared to the copper induced control; only LP-HWE prepared from January bark produced similar results. Knowledge of seasonal variations in bark phytochemical content would thus enhance the feasibility of phytochemical extraction.

Renewable High-Performance Polyurethane Bioplastics Derived from Lignin–Poly(ε-caprolactone)

Yan Zhang, Jianjun Liao, Xiangchen Fang, Fudong Bai, Kai Qiao, and Lingmin Wang

ACS Sustainable Chemistry & Engineering 2017 5 (5), 4276-4284

Abstract
Here, we report novel lignin-poly(ε-caprolactone)-based polyurethane bioplastics with high performance. The poly(ε-caprolactone) (PCL) was incorporated as a biodegradable soft segment to the lignin by the bridge of hexamethylene disocyanate (HDI) with long flexible aliphatic chains and high reactivity. The effects of -NCO/-OH molar ratio, content of lignin, and molecular weight of the PCL on the properties of the resultant polyurethane plastics were thoroughly evaluated. It is important that the polyurethane film still possessed high performance in the tensile strength, breaking elongation, and tear strength, which could reach 19.35 MPa, 188.36%, and 38.94 kN/m, respectively, when the content of lignin reached as high as 37.3%; moreover, it was very stable at 340.8 °C and presented excellent solvent-resistance. The results demonstrated that the modification of the lignin based on the urethane chemistry represents an effective strategy for developing lignin-based high-performance sustainable materials.
Zeolites as sustainable catalysts for the selective synthesis of renewable bisphenols from lignin-derived monomers

P. Ferrini, S.-F. Koelewijn, J. Van Aelst, N. Nuttens, B. F. Sels

ChemSusChem 2017, 10, 2249 - 2257

Abstract

Alternative biobased bisphenols from lignocellulosic biomass are not only favorable to reduce the environmental impact of current petroleum-derived plastics, but they can be simultaneously beneficial for health issues related to bisphenol A (BPA). Additionally, conventional BPA synthesis entails a large excess of unrecoverable homogeneous acid catalyst (e.g., HCl) or unrecyclable thermolabile sulfonated resins. In this report, zeolites are proposed as recoverable and thermally stable solid acids for the Brønsted-acid-catalyzed condensation between 4-methylguaiacol and formaldehyde to selectively produce renewable bisphenols. It is found that the Brønsted-acid-site density plays a pivotal role for catalyst performance. In particular, the cheap and environmentally friendly FAU 40 exhibits outstanding activity (turnover frequency of 496 h⁻¹) and selectivity (>95 %), outperforming even the best benchmark catalyst. Additionally, the zeolite can be easily recycled without activity loss after regeneration by coke burn-off. The catalytic zeolite system also seems very promising for other lignin-derived alkylphenols, alkylguaiacols, and alkylsyringols.
Nitrogen Fixation by Gliding Arc Plasma: Better Insight by Chemical Kinetics Modelling

W. Wang, B. Patil, S. Heijkers, V. Hessel, A. Bogaerts

ChemSusChem 2017, 10, 2145

Abstract
The conversion of atmospheric nitrogen into valuable compounds, that is, so-called nitrogen fixation, is gaining increased interest, owing to the essential role in the nitrogen cycle of the biosphere. Plasma technology, and more specifically gliding arc plasma, has great potential in this area, but little is known about the underlying mechanisms. Therefore, we developed a detailed chemical kinetics model for a pulsed-power gliding-arc reactor operating at atmospheric pressure for nitrogen oxide synthesis. Experiments are performed to validate the model and reasonable agreement is reached between the calculated and measured NO and NO2 yields and the corresponding energy efficiency for NOx formation for different N2/O2 ratios, indicating that the model can provide a realistic picture of the plasma chemistry. Therefore, we can use the model to investigate the reaction pathways for the formation and loss of NOx. The results indicate that vibrational excitation of N2 in the gliding arc contributes significantly to activating the N2 molecules, and leads to an energy efficient way of NOx production, compared to the thermal process. Based on the underlying chemistry, the model allows us to propose solutions on how to further improve the NOx formation by gliding arc technology. Although the energy efficiency of the gliding-arc-based nitrogen fixation process at the present stage is not comparable to the world-scale Haber–Bosch process, we believe our study helps us to come up with more realistic scenarios of entering a cutting-edge innovation in new business cases for the decentralised production of fertilisers for agriculture, in which low-temperature plasma technology might play an important role.
Remarkably Efficient Microwave-Assisted Cross-Metathesis of Lipids under Solvent-Free Conditions

A. Ullah, M. Arshad

ChemSusChem 2017, 10, 2167

Abstract
Catalytic transformation of renewable feedstocks into fine chemicals is in high demands and olefin metathesis is a sophisticated tool for biomass conversion. Nevertheless, the large-scale viability of such processes depends on the conversion efficiency, energy efficiency, catalytic activity, selective conversion into desired products, and environmental footprint of the process. Therefore, conversions of renewables by using simple, swift, and efficient methods are desirable. A microwave-assisted ethenolysis and alkenolysis (using 1,5-hexadiene) of canola oil and methyl esters derived from canola oil (COME) and waste/recycled cooking oil (WOME) was carried out by using ruthenium-based catalytic systems. A systematic study using 1st and 2nd generation Grubbs and Hoveyda–Grubbs catalysts was carried out. Among all ruthenium catalysts, 2nd generation Hoveyda–Grubbs catalyst was found to be highly active in the range of 0.002–0.1 mol % loading. The conversions proved to be rapid providing unprecedented turnover frequencies (TOFs). High TOFs were achieved for ethenolysis of COME (21 450 min⁻¹), direct ethenolysis of canola oil (19 110 min⁻¹), for WOME (15 840 min⁻¹) and for cross-metathesis of 1,5-hexadiene with COME (10 920 min⁻¹). The ethenolysis of commercial methyl oleate was also performed with a TOF of 8000 min⁻¹ under microwave conditions.
Flow chemistry and polymer-supported pseudoenantiomeric acylating agents enable parallel kinetic resolution of chiral saturated N-heterocycles

Imants Kreituss and Jeffrey W. Bode

*Nature Chemistry* 2017, 9, 446–452, (10.1038/nchem.2681)

Abstract

Kinetic resolution is a common method to obtain enantioenriched material from a racemic mixture. This process will deliver enantiopure unreacted material when the selectivity factor of the process, $s$, is greater than 1; however, the scalemic reaction product is often discarded. Parallel kinetic resolution, on the other hand, provides access to two enantioenriched products from a single racemic starting material, but suffers from a variety of practical challenges regarding experimental design that limit its applications. Here, we describe the development of a flow-based system that enables practical parallel kinetic resolution of saturated N-heterocycles. This process provides access to both enantiomers of the starting material in good yield and high enantiopurity; similar results with classical kinetic resolution would require selectivity factors in the range of $s = 100$. To achieve this, two immobilized quasienantiomeric acylating agents were designed for the asymmetric acylation of racemic saturated N-heterocycles. Using the flow-based system we could efficiently separate, recover and reuse the polymer-supported reagents. The amide products could be readily separated and hydrolysed to the corresponding amines without detectable epimerization.
Tuning underwater adhesion with cation–π interactions

Matthew A. Gebbie¹,², Wei Wei², Alex M. Schrader²,³, Thomas R. Cristiani¹, Howard A. Dobbs⁴, Matthew Idso⁵, Bradley F. Chmelka⁴, J. Herbert Waite²,³* and Jacob N. Israelachvili¹,²,⁴*


Abstract

Cation–π interactions drive the self-assembly and cohesion of many biological molecules, including the adhesion proteins of several marine organisms. Although the origin of cation–π bonds in isolated pairs has been extensively studied, the energetics of cation–π-driven self-assembly in molecular films remains uncharted. Here we use nanoscale force measurements in combination with solid-state NMR spectroscopy to show that the cohesive properties of simple aromatic and lysine-rich peptides rival those of the strong reversible intermolecular cohesion exhibited by adhesion proteins of marine mussel. In particular, we show that peptides incorporating the amino acid phenylalanine, a functional group that is conspicuously sparing in the sequences of mussel proteins, exhibit reversible adhesion interactions significantly exceeding that of analogous mussel-mimetic peptides. More broadly, we demonstrate that interfacial confinement fundamentally alters the energetics of cation–π-mediated assembly: an insight that should prove relevant for diverse areas, which range from rationalizing biological assembly to engineering peptide-based biomaterials.
Photoredox activation of carbon dioxide for amino acid synthesis in continuous flow

Hyowon Seo, Matthew H. Katcher and Timothy F. Jamison *


Abstract

Although carbon dioxide (CO$_2$) is highly abundant, its low reactivity has limited its use in chemical synthesis. In particular, methods for carbon–carbon bond formation generally rely on two-electron mechanisms for CO$_2$ activation and require highly activated reaction partners. Alternatively, radical pathways accessed via photoredox catalysis could provide new reactivity under milder conditions. Here we demonstrate the direct coupling of CO$_2$ and amines via the single-electron reduction of CO$_2$ for the photoredox-catalysed continuous flow synthesis of α-amino acids. By leveraging the advantages of utilizing gases and photochemistry in flow, a commercially available organic photoredox catalyst effects the selective α-carboxylation of amines that bear various functional groups and heterocycles. The preliminary mechanistic studies support CO$_2$ activation and carbon–carbon bond formation via single-electron pathways, and we expect that this strategy will inspire new perspectives on using this feedstock chemical in organic synthesis.
Organocatalytic stereoselective [8+2] and [6+4] cycloadditions
Rasmus Mose, Gert Preegel, Jesper Larsen, Sofie Jakobsen, Eva Høgh Iversen and Karl Anker Jørgensen*


Abstract

Cycloadditions that involve more than six $\pi$ electrons are termed higher-order cycloadditions and are an excellent tool for solving complex synthetic challenges, as they provide direct access to polycyclic scaffolds that contain medium-sized rings. They have interesting synthetic potential for the discovery of new bioactive molecules and in natural product synthesis. It is peculiar that stereocontrolled [8+2] and [6+4] cycloadditions have been largely neglected for the past 50 years. Here we demonstrate a cross-dienamine activation of 2-cyclopentenone and the unprecedented endocyclic linear-dienamine activation of 2-cyclohexenones and 2-cycloheptenones. These dienamine intermediates undergo aminocatalytic stereoselective [8+2], [6+4] and formal [4+2] cycloadditions with various heptafulvenes. The periselectivities of the cycloadditions are controlled based on the ring size of the 2-cycloalkenones and the substitution patterns of the heptafulvenes. The chiral products obtained undergo various chemical and photochemical single-step transformations that give access to other classes of all-carbon polycyclic scaffolds.
Liubi Wu, Lulu Li, Bolong Li and Chen Zhao. Selective conversion of coconut oil to fatty alcohols in methanol over a hydrothermally prepared Cu/SiO$_2$ catalyst without extraneous hydrogen. *Chem. Commun.*, 2017, 53, 6152
DOI: [10.1039/C7CC01126A](https://doi.org/10.1039/C7CC01126A)

A novel one-pot approach selects a hydrothermally synthesized Cu/SiO$_2$ catalyst (consisting of Cu$_2$O·SiO$_2$ and Cu$^0$ surface species) to catalyze the reduction of a series of fatty esters, fatty acids, and coconut oil to fatty alcohols at 240 °C in methanol without extraneous hydrogen, attaining around 85% conversion and 100% selectivity.
A supported PdO nanocatalyst prepared by a facile in situ reduction process followed by an oxidation step showed significantly enhanced activity for the removal of pollutants from natural gas vehicles. The excellent catalytic performance is mainly due to high dispersion of the uniform PdO nanoparticles generated during the novel two-step method.
DOI: [10.1039/C7CC02050C](http://dx.doi.org/10.1039/C7CC02050C)

In this communication, we report a palladium-catalyzed decarboxylative allenylation of benzyl carbonates and tert-butyl carbonates of 2,3-allenols with 3-oxocarboxylic acids. The reaction provides a new and straightforward approach to 3,4-dienyl ketones under mild conditions.
Inexpensive copper catalysts enabled direct C–H chalcogenations at ambient temperature by means of photo-induced catalysis. The expedient copper catalysis set the stage for C–S and C–Se bond formation from readily accessible non-volatile elemental chalcogens. The photo-assisted copper catalysis manifold proved suitable for a wide range of substrates with good functional group tolerance and exhibited high catalytic efficacy even at a reaction temperature of 25 °C.
Mickaël Henrion, Thierry Roisnel, Jean-Luc Couturier, Jean-Luc Dubois, Jean-Baptiste Sortais, Christophe Darcel, Jean-François Carpentier. **Ruthenium complexes bearing amino-bis(phosphinite) or amino-bis(aminophosphine) ligands: Application in catalytic ester hydrogenation.**

Molecular Catalysis, 2017, **432**, 15

DOI: [10.1016/j.mcat.2017.01.025](http://dx.doi.org/10.1016/j.mcat.2017.01.025)

**Highlights**

- Synthesis and full characterization of new ruthenium complexes derived from tridentate amino-bis(aminophosphine) ligands.
- Catalytic performance of these new complexes and of Stephan’s Ru-{amino-bis(phosphinite)} complexes have been investigated in the hydrogenation of simple and fatty unsaturated esters.
- The Ru-{amino-bis(aminophosphine)} complexes are more efficient than their corresponding Ru-{amino-bis(phosphinite)} analogues.

**Abstract**

Mononuclear hydrido and dinuclear chloro ruthenium(II) complexes derived from readily available amino-bis(phosphinite) and amino(bisaminophosphine) tridentate ligands were applied in the catalytic hydrogenation of ester derivatives. Notably, the cationic ruthenium dimer **2c** proved to be an efficient pre-catalyst when used in combination with KO'Bu in THF at 120 °C and 50 bar H₂ with aromatic and aliphatic esters.
Efficient solvent-free fixation of $\text{CO}_2$ into cyclic carbonates catalyzed by Bi(III) porphyrin/TBAI at atmospheric pressure.

*Molecular Catalysis,* 2017, **432**, 37
DOI: [10.1016/j.mcat.2017.01.019](https://doi.org/10.1016/j.mcat.2017.01.019)

**Highlights**

- A series of new Bi (III) porphyrin complexes were synthesized as the catalyst for the cycloaddition of $\text{CO}_2$ and epoxides.
- The $2a$/TBAI catalytic system could catalyze the cycloaddition of many epoxides with $\text{CO}_2$ into corresponding cyclic carbonates with good activities (up to 98%) and selectivities (>99%) at atmospheric pressure (0.1 MPa) within 6 h.
- The easy self-polymerized glycidyl methacrylate could be converted into its corresponding cyclic carbonate selectively in high yield of 94.8% with $2a$/TBAI as catalyst at room temperature and 0.1 MPa.
- The optimized catalytic conditions were screened as (90 °C, 1 h, 2 MPa) and a very high TOF value (37,900 h$^{-1}$) was achieved via adjusting reaction factors.
- Kinetic studies gave out an inferred mechanism.
Mingli Lan, Bin Zhang, Haiyang Cheng, Xiaoru Li, Qifan Wu, Zhong Ying, Yaxi Zhu, Yan Li, Xiangchun Meng, Fengyu Zhao. **Chemoselective hydrogenation of 3-nitrostyrene to 3-aminostyrene over Pt-Bi/TiO₂ catalysts.** *Molecular Catalysis*, 2017, **432**, 23

**Highlights**
- Pt-Bi/TiO₂ was first time developed for the hydrogenation of NS to AS.
- A high selectivity to AS of 96% was achieved over Pt-Bi/TiO₂-1.5.
- The terraces Pt sites transferred to low coordinated Pt sites with addition of Bi.
- The low-coordinated Pt sites were responsible for the chemoselectivity of Pt-Bi/TiO₂.
Marlena Musik, Eugeniusz Milchert. **Selective epoxidation of sesame oil with peracetic acid.**  
*Molecular Catalysis,* 2017, **433**, 170  

**Highlights**
- The aim of this study was to determine the influence of technological parameters of epoxidation of sesame oil.
- The optimal conditions for selective epoxidation of sesame oil are:
  - 90 °C, stirring speed at least 700 rpm, reaction time 4 h.
  - CH$_3$COOH/C=C molar ratio 0.8:1, H$_2$O$_2$/C=C molar ratio 3.5:1, amount of catalyst as H$_2$SO$_4$/H$_2$O$_2$ + CH$_3$COOH) 3.0 wt %.

**Abstract**
The course of epoxidation of sesame oil (SO) with peracetic acid formed “in situ” by the reaction of 30 wt% hydrogen peroxide and acetic acid in the presence of sulfuric acid(VI) as a catalyst was studied. The iodine number (IN), epoxy number (EN), a relative conversion to oxirane and oxirane oxygen content were determined every hour during the reaction. Under optimal conditions the selectivity of transformation of ethylenic unsaturation to oxirane rings is $S = 93.5\%$, conversion of ethylenic unsaturation $C_{SO} = 77.2\%$, relative conversion to oxirane $RCO = 78.1\%$, oxirane oxygen content $EOe = 5.1\%$, IN = 0.03 mol/100 g, EN = 0.33 mol/100 g. Decreasing of the selectivity of transformation to oxirane rings is mainly caused by their hydration to glycols.
Cellulose and lignin colocalization at the plant cell wall surface limits microbial hydrolysis of Populus biomass

Alexandru Dumitrache, Allison Tolbert, Jace Natzke, Steven D. Brown, Brian H. Davison and Arthur J. Ragauskas

Green Chem., 2017, 19, 2275

Abstract

Biorefining of plant feedstocks into fuels and specialty chemicals, using biological conversion, requires the solubilization of lignocellulosics into simpler oligomeric compounds. However, non-pretreated woody biomass has shown high resistance to hydrolysis by cellulolytic microbes or purified cellulases. We investigate the limited solubilization of Populus deltoides by the cellulolytic thermophile Clostridium thermocellum in the absence of solute inhibitors. Compared to control samples, fermented poplar revealed that the hydrolysis of carbohydrates in secondary cell walls ceased prematurely as the presence of lignin increased at the surface. In quantitative fluorescence colocalization analysis by confocal laser scanning microscopy, the Manders’ coefficient of the fractional overlap between lignin and cellulose signals increased from an average of 0.67 to a near-maximum of 0.92 in fermented tissue. Chemical imaging by time-of-flight secondary ion mass spectrometry revealed a 49% decline in surface cellulose and a compensatory 30% and 11% increase in surface S- and G-lignin, respectively. Although 72% of the initial glucan was still present in the lignocellulose matrix of this feedstock, subsequent treatments with cell-free purified cellulases did not significantly restore hydrolysis. This confirmed that biomass surfaces had become non-productive for the C. thermocellum hydrolytic exoproteome. This study provides direct evidence for an explicit definition of feedstock recalcitrance, whereby depletion of surface carbohydrate increases lignin exposure which leads to inhibition of enzyme activity, while the bulk residual biomass retains significant undigested carbohydrate content. The analysis presented here establishes a novel method for the quantitation of lignocellulose recalcitrance.
Rapid and productive extraction of high purity cellulose material via selective depolymerization of the lignin-carbohydrate complex at mild conditions

Jiming Yang, Xingmei Lu, Xiaomin Liu, Junli Xu, Qing Zhou and Suojiang Zhang

Green Chem., 2017, 19, 2234

Abstract

A new green cellulose extraction method – the selective degradation dissolution extraction (SDDE) method based on the [Bmim]Cl–AS (i.e. amino sulfonic acid (AS)) solvent system – was found which could rapidly extract a high yield and purity of cellulose from cornstalk at relatively low temperatures in a remarkably short time. In the SDDE method, the lignin-carbohydrate complex protective layer (LCCPL), which wraps around the cellulose, was selectively depolymerized into small molecules; as a result, the rapid dissolution of lignocellulose biomass and the efficient removal of lignin and hemicellulose from the regenerated material (RM) were successfully achieved. The cellulose content of the RM could reach 99.16 ± 0.15%, which is the highest purity of cellulose extracted from the lignocellulose biomass in one step by IL solvent systems. The delignification rate could reach 97.56 ± 0.29% while the hemicellulose was completely removed in only 1 h after the cornstalk powder was dissolved in [Bmim]Cl–AS (the AS content was 1.5 wt%) at 100 °C. The result showed that the addition of AS not only improved the purity of cellulose in the RM but also increased its yield. The yield of cellulose increased from 19.94 ± 0.45% to 71.04 ± 0.78% after the addition of AS. As the mild fractionation conditions reduced consumption of energy greatly as well as that the additive was cheap and environmentally friendly, the SDDE might be able to provide a feasible path to achieve an efficient cellulose extraction from lignocellulose biomass. In addition, utilization of the lignocellulose biomass mostly focused on the preparation of bioethanol via hydrolysis and fermentation. This work provided an alternative that high purity cellulose derivatives and cellulose composites could be produced from the lignocellulose biomass.
A Pd-Catalyzed in situ domino process for mild and quantitative production of 2,5-dimethylfuran directly from carbohydrates

Hu Li, Wenfeng Zhao, Anders Riisager, Shunugavel Saravanamurugan, Zhongwei Wang, Zhen Fang and Song Yang

Green Chem., 2017, 19, 2101

Abstract

An in situ domino process has been developed to be highly efficient for direct and mild conversion of various hexose sugars to the biofuel 2,5-dimethylfuran in almost quantitative yields, without separation of unstable intermediates at 120 °C in n-butanol, by using polymethylhydrosiloxane and hydrophobic Pd/C as a H-donor and a bifunctional catalyst, respectively. Among the cascade reactions, the hydrosilylation process was confirmed by deuterium-labeling and kinetic studies to be favorable for sugar dehydration and exclusively acts on deoxygenation of in situ formed intermediates including furanic alcohols and aldehydes to DMF via a hydride transfer process that was facilitated by an alcoholic solvent. The catalytic system is more selective than the H2-participated counterpart, and could be scaled up with only 0.04 mol% catalyst loading, giving DMF in a comparable yield of 85%. Moreover, Pd(0) was demonstrated to be the active species for deoxygenation, and the heterogeneous catalyst exhibited good recyclability with little elemental leaching.
Induction of lignin solubility for a series of polar ionic liquids by the addition of a small amount of water

Takashi Akiba, a,b Akiko Tsurumakia,b and Hiroyuki Ohno

Green Chem., 2017, 19, 2260

Abstract

Addition of a small amount of water was found to induce the lignin solubilizing ability in several polar ionic liquids which showed no lignin solubility in the absence of water. Similarly, addition of water was found to enhance lignin solubility in many polar ionic liquids. Though addition of water lowered the proton accepting ability of these ionic liquids, their proton donating ability was found to increase. The lignin dissolution by ionic liquids was newly found to be a function of both the proton accepting ability and proton donating ability of the ionic liquids. Water is a poor solvent for polysaccharides, and water addition has therefore been confirmed to be effective to improve the selective extraction yield of lignin from cedar powder under mild conditions.
Silica-based nanocatalysts in the C–C and C-heteroatom bond forming cascade reactions for the synthesis of biologically active heterocyclic scaffolds

E. Pérez Mayoral, E. Soriano, V. Calvino-Casilda, M.L. Rojas-Cervantes, R.M. Martín-Aranda


The design and development of hybrid materials with application in catalysis science is an interesting researching field, especially in the chemical industry for fine chemicals production. The properties of nanostructured catalysts can be changed by tuning the interaction between the support and the active phases. Silica nanoparticles are very convenient solid supports for the synthesis of organic-inorganic hybrid nanocatalysts, endowing them of the required features to optimize activity and selectivity, stability and recyclability. In this review, we analyze the latest developments and give a perspective concerning the recent applications of silica-based nanocatalysts for the synthesis of heterocyclic scaffolds, biologically active, via cascade reactions.

Heterocyclic rings often are the structural cores responsible of the biological activities in natural products and synthetic compounds. These systems are frequently synthesized by multicomponent reactions (MCRs), through cascade reactions. Such versatile catalytic systems have been successfully applied in a great variety of organic transformations for the synthesis of complex molecules and would play a key role in establishing new and more efficient sustainable technologies.
Hydrodeoxygenation reactions were studied with model compounds on sulfided hydrotreating CoMo/γ-Al₂O₃ and NiMo/γ-Al₂O₃ catalysts with and without adding a sulfur-containing compound into the reaction mixtures. Clear differences were observed in the behaviour of the model compounds. The addition of H₂S improved the reactivity of methyl heptanoate and guaiacol with the formation of methanethiol but decreased that of phenol. The presence of sulfur compounds in the gas phase affected also the selectivities reducing the hydrogenation activity of the catalysts and shifting the C₇/C₆ hydrocarbon distribution from methyl heptanoate. Thus sulfur groups present on the catalyst surface form the key components for the reactions. The reaction network of methyl heptanoate can be described with two types of reactions: reactions with only hydrogen addition and reactions with the contribution of the surface SH⁻ groups. We propose that the ability of the nucleophilic SH⁻ groups to interact with model compounds is a primary factor influencing the initial overall reactivity of the starting compounds. Furthermore, the increasing amount of ___SH⁻ groups directed the distribution of hydrocarbons towards C₆ instead of C₇ hydrocarbons from methyl heptanoate by accelerating the decarbonylation/decarboxylation reaction and the 1-hexanethiol formation.
A reaction mode of carbene-catalysed aryl aldehyde activation and induced phenol OH functionalization


*Nature Communications 8, 2017, 15598*

The research in the field of asymmetric carbene organic catalysis has primarily focused on the activation of carbon atoms in non-aromatic scaffolds. Here we report a reaction mode of carbene catalysis that allows for aromatic aldehyde activation and remote oxygen atom functionalization. The addition of a carbene catalyst to the aldehyde moiety of 2-hydroxyl aryl aldehyde eventually enables dearomatization and remote OH activation. The catalytic process generates a type of carbene-derived intermediate with an oxygen atom as the reactive centre. Inexpensive achiral urea co-catalyst works cooperatively with the carbene catalyst, leading to consistent enhancement of the reaction enantioselectivity. Given the wide presence of aromatic moieties and heteroatoms in natural products and synthetic functional molecules, we expect our reaction mode to significantly expand the power of carbene catalysis in asymmetric chemical synthesis.

Construction of hierarchically porous metal–organic frameworks through linker labilization

Shuai Yuan, Lanfang Zou, Jun-Sheng Qin, Jialuo Li, Lan Huang, Liang Feng, Xuan Wang, Mathieu Bosch, Ali Alsalme, Tahir Cagin & Hong-Cai Zhou

*Nature Communications 8, 2017, 15356*

A major goal of metal–organic framework (MOF) research is the expansion of pore size and volume. Although many approaches have been attempted to increase the pore size of MOF materials, it is still a challenge to construct MOFs with precisely customized pore apertures for specific applications. Herein, we present a new method, namely linker labilization, to increase the MOF porosity and pore size, giving rise to hierarchical-pore architectures. Microporous MOFs with robust metal nodes and pro-labile linkers were initially synthesized. The mesopores were subsequently created as crystal defects through the splitting of a pro-labile-linker and the removal of the linker fragments by acid treatment. We demonstrate that linker labilization method can create controllable hierarchical porous structures in stable MOFs, which facilitates the diffusion and adsorption process of guest molecules to improve the performances of MOFs in adsorption and catalysis.

Controllable cyanation of carbon-hydrogen bonds by zeolite crystals over manganese oxide catalyst

Liang Wang, Guoxiong Wang, Jian Zhang, Chaoqun Bian, Xiangju Meng & Feng-Shou Xiao

*Nature Communications 8, 2017, 15240*

The synthesis of organic nitriles without using toxic cyanides is in great demand but challenging to make. Here we report an environmentally benign and cost-efficient synthesis of nitriles from the direct oxidative cyanation of primary carbon-hydrogen bonds with easily available molecular oxygen and urea. The key to this success is to design and synthesize manganese oxide catalysts fixed inside zeolite crystals, forming a manganese oxide catalyst with zeolite sheath (MnO$_x$@S-1), which exhibits high selectivity for producing nitriles by efficiently facilitating the oxidative cyanation reaction and hindering the side hydration reaction. The work delineates a sustainable strategy for synthesizing nitriles while avoiding conventional toxic cyanide, which might open a new avenue for selective transformation of carbon-hydrogen bonds.
Nickel-catalysed retro-hydroamidocarbonylation of aliphatic amides to olefins

Jiefeng Hu, Minyan Wang, Xinghui Pu & Zhuangzhi Shi
Nature Communications 8, 2017, 14993

Amide and olefins are important synthetic intermediates with complementary reactivity which play a key role in the construction of natural products, pharmaceuticals and manmade materials. Converting the normally highly stable aliphatic amides into olefins directly is a challenging task. Here we show that a Ni/NHC-catalytic system has been established for decarbonylative elimination of aliphatic amides to generate various olefins via C–N and C–C bond cleavage. This study not only overcomes the acyl C–N bond activation in aliphatic amides, but also encompasses distinct chemical advances on a new type of elimination reaction called retro-hydroamidocarbonylation. This transformation shows good functional group compatibility and can serve as a powerful synthetic tool for late-stage olefination of amide groups in complex compounds.

Directly converting CO₂ into a gasoline fuel

Jian Wei, Qingjie Ge, Ruwei Yao, Zhiyong Wen, Chuanyan Fang, Lisheng Guo, Hengyong Xu & Jian Sun
Nature Communications 8, 2017, 15174

The direct production of liquid fuels from CO₂ hydrogenation has attracted enormous interest for its significant roles in mitigating CO₂ emissions and reducing dependence on petrochemicals. Here we report a highly efficient, stable and multifunctional Na–Fe₃O₄/HZSM-5 catalyst, which can directly convert CO₂ to gasoline-range (C₅–C₁₁) hydrocarbons with selectivity up to 78% of all hydrocarbons while only 4% methane at a CO₂ conversion of 22% under industrial relevant conditions. It is achieved by a multifunctional catalyst providing three types of active sites (Fe₃O₄, Fe₅C₂ and acid sites), which cooperatively catalyse a tandem reaction. More significantly, the appropriate proximity of three types of active sites plays a crucial role in the successive and synergetic catalytic conversion of CO₂ to gasoline. The multifunctional catalyst, exhibiting a remarkable stability for 1,000 h on stream, definitely has the potential to be a promising industrial catalyst for CO₂ utilization to liquid fuels.
Predictive compound accumulation rules yield a broad-spectrum antibiotic

Michelle F. Richter, Bryon S. Drown, Andrew P. Riley, Alfredo Garcia, Tomohiro Shirai, Riley L. Svec and Paul J. Hergenrother


Abstract

Most small molecules are unable to rapidly traverse the outer membrane of Gram-negative bacteria and accumulate inside these cells, making the discovery of much-needed drugs against these pathogens challenging. Current understanding of the physicochemical properties that dictate small-molecule accumulation in Gram-negative bacteria is largely based on retrospective analyses of antibacterial agents, which suggest that polarity and molecular weight are key factors. Here we assess the ability of over 180 diverse compounds to accumulate in *Escherichia coli*. Computational analysis of the results reveals major differences from the retrospective studies, namely that the small molecules that are most likely to accumulate contain an amine, are amphiphilic and rigid, and have low globularity. These guidelines were then applied to convert deoxynybomycin, a natural product that is active only against Gram-positive organisms, into an antibiotic with activity against a diverse panel of multi-drug-resistant Gram-negative pathogens. We anticipate that these findings will aid in the discovery and development of antibiotics against Gram-negative bacteria.
Submillihertz magnetic spectroscopy performed with a nanoscale quantum sensor

Simon Schmitt, Tuvia Gefen, Felix M. Stürner, Thomas Unden, Gerhard Wolff, Christoph Müller, Jochen Scheuer, Boris Naydenov, Matthew Markham, Sebastien Pezzagna, Jan Meijer, Ilai Schwarz, Martin Plenio, Alex Retzker, Liam P. McGuinness, * Fedor Jelezko

Science 2017, (356) 6340, 832.

Abstract

Precise timekeeping is critical to metrology, forming the basis by which standards of time, length, and fundamental constants are determined. Stable clocks are particularly valuable in spectroscopy because they define the ultimate frequency precision that can be reached. In quantum metrology, the qubit coherence time defines the clock stability, from which the spectral linewidth and frequency precision are determined. We demonstrate a quantum sensing protocol in which the spectral precision goes beyond the sensor coherence time and is limited by the stability of a classical clock. Using this technique, we observed a precision in frequency estimation scaling in time $T$ as $T^{-3/2}$ for classical oscillating fields. The narrow linewidth magnetometer based on single spins in diamond is used to sense nanoscale magnetic fields with an intrinsic frequency resolution of 607 micro hertz, which is eight orders of magnitude narrower than the qubit coherence time.
Cluster Size Effects in Ethylene Hydrogenation over Palladium

Alvaro Posada-Borbon, Christopher J. Heard, and Henrik Grönbeck*


Abstract

Density functional theory calculations are used to investigate ethylene hydrogenation over palladium clusters in the range from Pd$_{13}$ to Pd$_{116}$. A comparison is made to single crystal surfaces, which exemplifies several novel aspects of clusters. We find that the adsorption energies are always higher for the clusters, even if the comparison is made to adsorption on stepped surfaces in the low-coverage regime. Clusters are found to accommodate higher adsorbate coverages than extended surfaces. The saturation coverage for Pd$_{13}$ is unity, whereas it is 0.33 on Pd(111). The activation energies for hydrogenation of C$_2$H$_4$ to C$_2$H$_5$ over Pd$_{38}$ are clearly different from Pd(111) and Pd(211), which stresses the limitation of extended surfaces as models for nanoparticles.
Ruthenium Cluster Structure Change Induced by Hydrogen Adsorption: Ru$_{19}^-$

Dennis Bumüller, Anna-Sophia Hehn, Eugen Waldt, Reinhart Ahlrichs, Manfred M. Kappes, and Detlef Schooss*


Abstract

The effect of hydrogenation on the structure of Ru$_{19}^-$ has been studied using a combination of trapped ion electron diffraction and density functional computations. While the bare Ru$_{19}^-$ cluster has a closed-shell octahedral geometry, hydrogenation of the cluster changes the structure type of the ruthenium core toward an icosahedral motif. The experiments show a gradual structural transition depending on the number of adsorbed hydrogen atoms. Density functional theory computations reveal the driving force behind this process to be the larger hydrogen adsorption energies for the bi-icosahedral structure and predict a corresponding structural rearrangement at around 20 adsorbed hydrogen atoms, which is consistent with the experimental findings. Additionally, the computations provide insight into the hydrogen-binding situation. They show that hydrogen is preferentially atomically bound only to surface Ru atoms. H$_2$ binding is predicted only at high hydrogen loadings.
General Structure–Reactivity Relationship for Oxygen on Transition-Metal Oxides

Victor Fung, Franklin Feng Tao, and De-en Jiang*


Abstract

Despite many recent developments in designing and screening catalysts for improved performance, transition-metal oxides continue to prove to be challenging due to the myriad inherent complexities of the systems and the possible morphologies that they can exhibit. Herein we propose a structural descriptor, the adjusted coordination number (ACN), which can generalize the reactivity of the oxygen sites over the many possible surface facets and defects of a transition-metal oxide. We demonstrate the strong correlation of this geometric descriptor with the electronic and energetic properties of the active sites on five facets of four transition-metal oxides. We then use the structural descriptor to predict C–H activation energies to show the great potential of using ACN for the prediction of catalytic performance. This study presents a first look into quantifying the relation between active site structure and reactivity of transition-metal-oxide catalysts.