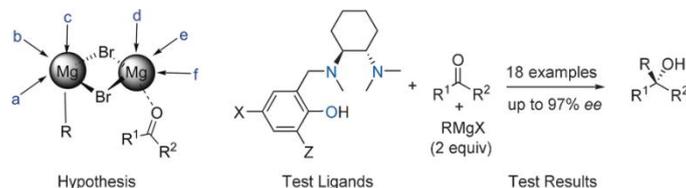


Asymmetric Grignard Synthesis of Tertiary Alcohols through Rational Ligand Design

Bartosz Bieszczad and Declan G. Gilheany

[Angew. Chem. Int. Ed. 2017, 56\(15\), 4272](#)



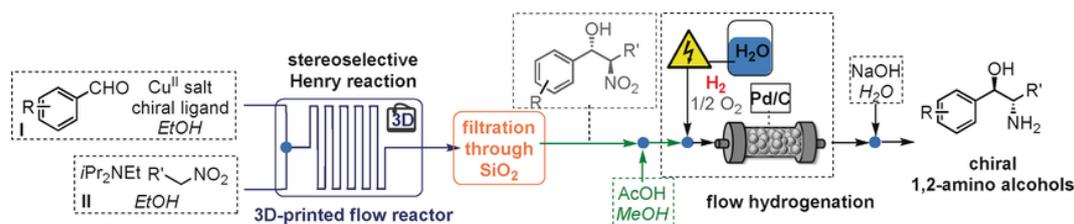
Abstract

A simple, general and practical method is reported for highly enantioselective construction of tertiary alcohols through the direct addition of organomagnesium reagents to ketones. Discovered by rational ligand design based on a mechanistic hypothesis, it has an unprecedented broad scope. It utilizes a new type of chiral tridentate diamine/phenol ligand that is easily removed from the reaction mixture. It is exemplified by application to a formal asymmetric synthesis (>95:5 d.r.) of vitamin E.

Stereoselective Catalytic Synthesis of Active Pharmaceutical Ingredients in Homemade 3D-Printed Mesoreactors

Sergio Rossi, Riccardo Porta, Davide Brenna, Alessandra Puglisi and Maurizio Benaglia

[Angew. Chem. Int. Ed. 2017, 56\(15\), 4290](#)



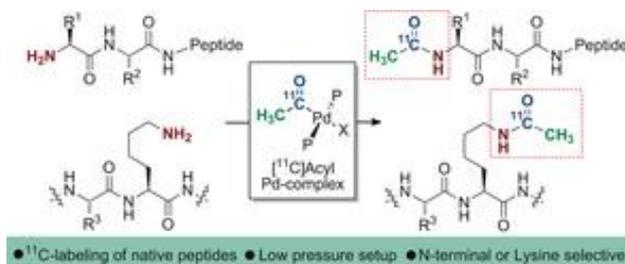
Abstract

3D-printed flow reactors were designed, fabricated from different materials (PLA, HIPS, nylon), and used for a catalytic stereoselective Henry reaction. The use of readily prepared and tunable 3D-printed reactors enabled the rapid screening of devices with different sizes, shapes, and channel dimensions, aimed at the identification of the best-performing reactor setup. The optimized process afforded the products in high yields, moderate diastereoselectivity, and up to 90 % ee. The method was applied to the continuous-flow synthesis of biologically active chiral 1,2-amino alcohols (norephedrine, metamaminol, and methoxamine) through a two-step sequence combining the nitroaldol reaction with a hydrogenation. To highlight potential industrial applications of this method, a multistep continuous synthesis of norephedrine has been realized. The product was isolated without any intermediate purifications or solvent switches.

Application of Methyl Bisphosphine-Ligated Palladium Complexes for Low Pressure N-11C-Acetylation of Peptides

Thomas L. Andersen, Patrik Nordeman, Heidi F. Christoffersen, H el ene Audrain, Gunnar Antoni and Troels Skrydstrup

[Angew. Chem. Int. Ed. 2017, 56\(16\), 4549](#)



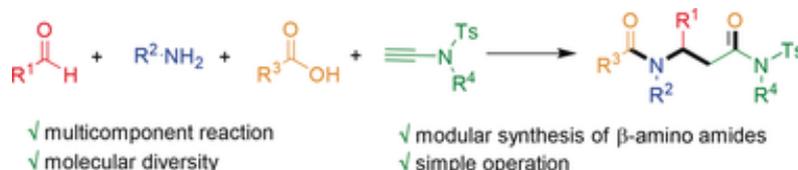
Abstract

A mild and effective method is described for ¹¹C-labeling of peptides selectively at the N-terminal nitrogen or at internal lysine positions. The presented method relies on the use of specific biphosphine palladium–methyl complexes and their high reactivity towards amino-carbonylation of amine groups in the presence [¹¹C]carbon monoxide. The protocol facilitates the production of native N-¹¹C-acetylated peptides, without any structural modifications and has been applied to a selection of bioactive peptides.

One-Pot Multicomponent Synthesis of β-Amino Amides

Bo Huang, Linwei Zeng, Yangyong Shen and Sunliang Cui

[Angew. Chem. Int. Ed. 2017, 56\(16\), 4565](#)



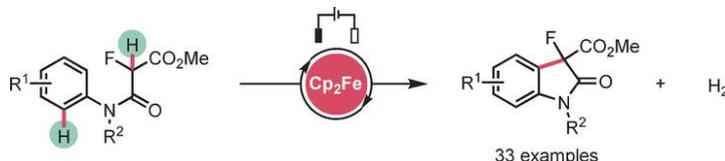
Abstract

Multicomponent reactions are excellent tools for rapid generation of small molecules with broad chemical diversity and molecular complexity. Herein, a novel one-pot multicomponent synthesis of β-amino amides from aldehydes, anilines, carboxylic acids and ynamides has been successfully developed. This process is practical and efficient to unravel synthetic utility and scalability. Moreover, an isotope labeling reaction was conducted to elucidate a plausible reaction mechanism.

Synthesis of C3-Fluorinated Oxindoles through Reagent-Free Cross-Dehydrogenative Coupling

Zheng-Jian Wu and Hai-Chao Xu

[Angew. Chem. Int. Ed. 2017, 56\(17\), 4734](#)



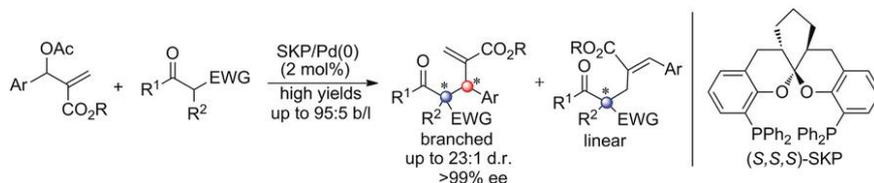
Abstract

Reported herein is an unprecedented synthesis of C3-fluorinated oxindoles through cross-dehydrogenative coupling of C(sp³)-H and C(sp²)-H bonds from malonate amides. Under the unique and mild electrochemical conditions, the requisite oxidant and base are generated in a continuous fashion, allowing the formation of the base- and heat-sensitive 3-fluorooxindoles in high efficiency with broad substrate scope. The synthetic usefulness of the electrochemical method is further highlighted by its easy scalability and the diverse transformations of the electrolysis product.

Palladium-Catalyzed Asymmetric Construction of Vicinal Tertiary and All-Carbon Quaternary Stereocenters by Allylation of β -Ketocarboxyls with Morita–Baylis–Hillman Adducts

Jiawang Liu, Zhaobin Han, Xiaoming Wang, Fanye Meng, Zheng Wang and Kailing Ding

[Angew. Chem. Int. Ed. 2017, 56\(18\), 5050](#)



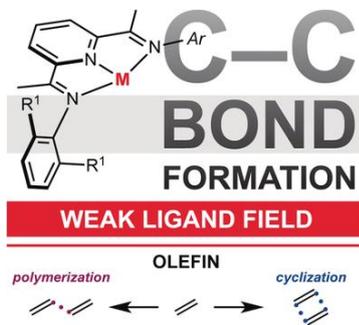
Abstract

Palladium-catalyzed regio-, diastereo-, and enantioselective allylic alkylation of β -ketocarboxyls with Morita–Baylis–Hillman adducts has been developed using a spiroketal-based diphosphine (SKP) as the ligand, thus affording a range of densely functionalized products bearing vicinal tertiary and all-carbon quaternary stereocenters in high selectivities. The utility of the protocol was demonstrated by the facile synthesis of some complex molecules by simple product transformations.

Carbon–Carbon Bond Formation in a Weak Ligand Field: Leveraging Open-Shell First-Row Transition-Metal Catalysts

Prof. Dr. Paul J. Chirik

[Angew. Chem. Int. Ed. 2017, 56\(19\), 5170](#)



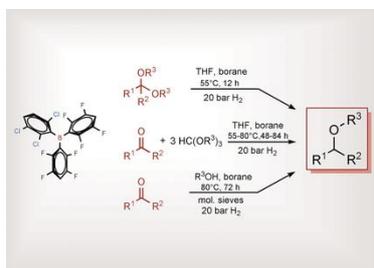
Abstract

Unique features of earth-abundant transition-metal catalysts are reviewed in the context of catalytic carbon–carbon bond-forming reactions. Aryl-substituted bis(imino)pyridine iron and cobalt dihalide compounds, when activated with alkyl aluminum reagents, form highly active catalysts for the polymerization of ethylene. Open-shell iron and cobalt alkyl complexes have been synthesized that serve as single-component olefin polymerization catalysts. Reduced bis(imino)pyridine iron and cobalt dinitrogen compounds have also been discovered that promote the unique [2+2] cycloaddition of unactivated terminal alkenes. Studies of the electronic structure support open-shell intermediates, a deviation from traditional strong-field organometallic compounds that promote catalytic C–C bond formation.

Auto-Tandem Catalysis with Frustrated Lewis Pairs for Reductive Etherification of Aldehydes and Ketones

Mária Bakos, Dr.  Gy, Dr. Attila Domj and Dr. Tibor So

[Angew. Chem. Int. Ed. 2017, 56\(19\), 5217](#)



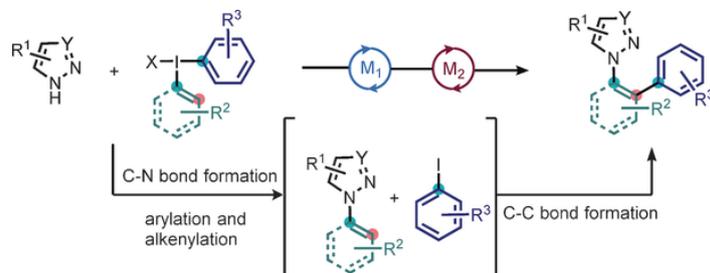
Abstract

Herein we report that a single frustrated Lewis pair (FLP) catalyst can promote the reductive etherification of aldehydes and ketones. The reaction does not require an exogenous acid catalyst, but the combined action of FLP on H₂, R-OH or H₂O generates the required Brnsted acid in a reversible, “turn on” manner. The method is not only a complementary metal-free reductive etherification, but also a niche procedure for ethers that would be either synthetically inconvenient or even intractable to access by alternative synthetic protocols.

Domino N/C-Arylation via In Situ Generation of a Directing Group: Atom-Efficient Arylation Using Diaryliodonium Salts (pages 5263–5266)

Dr. Christopher J. Teskey, Dr. Shariar M. A. Sohel, Danielle L. Bunting, Dr. Sachin G. Modha and Prof. Dr. Michael F. Greaney

[Angew. Chem. Int. Ed. 2017, 56\(19\), 5263](#)



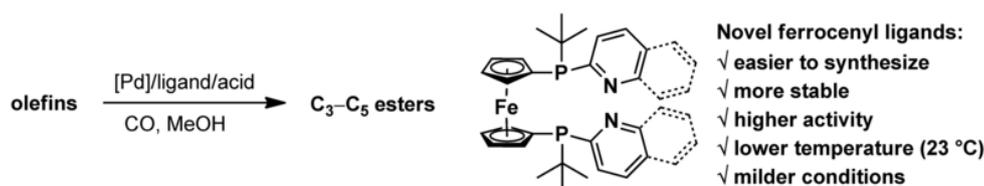
Abstract

Both aryl components of diaryliodonium salts can be used in a domino one-pot reaction via in situ generation of a directing group. A number of heterocycles undergo N-arylation which is followed by ruthenium-catalyzed C-arylation. Notably the reaction extends well to unsymmetrical diaryliodonium salts with a number of highly selective examples shown.

Efficient Palladium-Catalyzed Alkoxy carbonylation of Bulk Industrial Olefins Using Ferrocenyl Phosphine Ligands

Dr. Kaiwu Dong, Rui Sang, Dr. Xianjie Fang, Prof. Dr. Robert Franke, Dr. Anke Spannenberg, Dr. Helfried Neumann, Dr. Ralf Jackstell and Prof. Dr. Matthias Beller

[Angew. Chem. Int. Ed. 2017, 56\(19\), 5267](#)



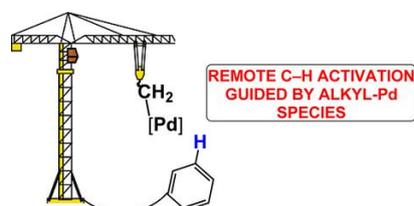
Abstract

The development of ligands plays a key role and provides important innovations in homogeneous catalysis. In this context, we report a novel class of ferrocenyl phosphines for the alkoxy carbonylation of industrially important alkenes. A basic feature of our ligands is the combination of sterically hindered and amphoteric moieties on the P atoms, which leads to improved activity and productivity for alkoxy carbonylation reactions compared to the current industrial state-of-the-art ligand 1,2-bis((di-tert-butylphosphino)methyl)benzene). Advantageously, palladium catalysts with these novel ligands also enable such transformations without additional acid under milder reaction conditions. The practicability of the optimized ligand was demonstrated by preparation on >10 g scale and its use in palladium-catalyzed carbonylations on kilogram scale.

σ -Alkyl-Pd^{II} Species for Remote C–H Functionalization

Vaibhav P. Mehta and José-Antonio García-López

[ChemCatChem 2017, 9\(7\), 1149](#)



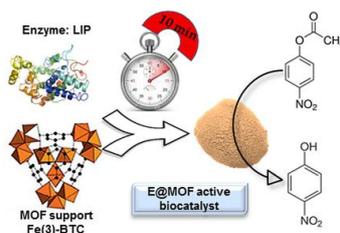
Abstract

The transition-metal-directed C–H activation processes have traditionally required the installation of suitable coordinating groups to place the metal in close proximity to an specific neighboring or remote C(sp²)-H or C(sp³)-H moiety of the molecular structure. Alternatively, substitution of C–H bonds at positions previously thought inaccessible are now performed through domino processes via in situ generated σ -alkyl-Pd^{II} species. This Concept article highlights on recent developments which utilize these σ -alkyl-Pd^{II}-species for remote C–H functionalization to reinvigorate new C–C bond formation in cascade fashion via use of catalytic palladium metal.

Rapid In Situ Immobilization of Enzymes in Metal–Organic Framework Supports under Mild Conditions

Victoria Gascón, Cristina Carucci, Mayra B. Jiménez, Rosa M. Blanco, Manuel Sánchez-Sánchez and Edmond Magner

[ChemCatChem 2017, 9\(7\), 1182](#)

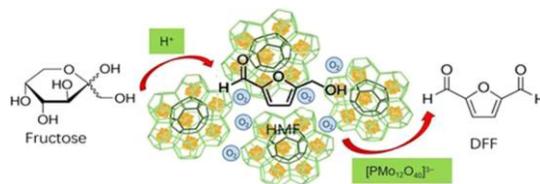


Abstract

The use of a metal–organic framework (MOF) as a support for the in situ immobilization of enzymes was explored. The MOF support, a Basolite F300-like material, was prepared from FeCl₃ and the tridentate linker trimesic acid. Immobilization of alcohol dehydrogenase, lipase, and glucose oxidase was performed in situ under mild conditions (aqueous solution, neutral pH, and at room temperature) in a rapid and facile manner with retention of activity for at least 1 week. The catalytic activities of lipase and glucose oxidase were similar to the activities of the free enzymes; with alcohol dehydrogenase, there was a substantial decrease in activity on immobilization that may arise from diffusion limitations. The approach demonstrates that a MOF material, prepared from cheap and commercially available materials, can be successively utilized to prepare stable and catalytically active biocatalysts in a rapid and facile manner.

Cr-MIL-101-Encapsulated Keggin Phosphomolybdic Acid as a Catalyst for the One-Pot Synthesis of 2,5-Diformylfuran from Fructose

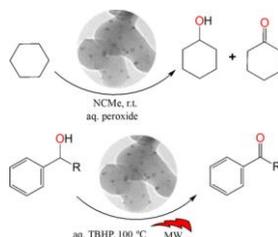
Jun Zhao, Jayakumar Anjali, Yibo Yan and Jong-Min Lee

[ChemCatChem 2017, 9\(7\), 1187](#)**Abstract**

The conversion of fructose into 2,5-diformylfuran (DFF) is a tandem reaction that consists of the dehydration of fructose to 5-hydroxymethylfurfural (HMF) catalyzed by an acid catalyst and subsequent oxidation of HMF to DFF by a redox catalyst. Phosphomolybdic acid encapsulated in MIL-101 (PMA-MIL-101), with high Brønsted acidity and moderate redox potential, was evaluated as a promising catalyst for the one-pot synthesis of DFF directly from fructose. The results demonstrated that PMA-MIL-101 was an efficient and recyclable bifunctional catalyst for the production of DFF from fructose in DMSO; it showed high activity and selectivity towards the direct transformation of fructose into DFF, and it could be reused. A satisfactory DFF yield of 75.1 % was obtained over 2 PMA-MIL-101 in a one-pot, one-step reaction under optimal reaction conditions.

Supported Gold Nanoparticles as Reusable Catalysts for Oxidation Reactions of Industrial Significance

Luísa Margarida Dias Ribeiro de Sousa Martins, Sónia Alexandra Correia Carabineiro, Jiawei Wang, Bruno Gonçalo Martins Rocha, Francisco José Maldonado-Hódar and Armando José Latourrette de Oliveira Pombeiro

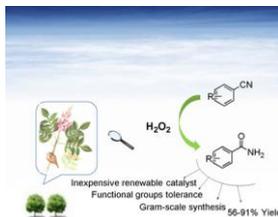
[ChemCatChem 2017, 9\(7\), 1211](#)**Abstract**

The efficient single-pot oxidative functionalisation of alkanes and alcohols under mild conditions was catalysed by Au nanoparticles supported on Al_2O_3 , Fe_2O_3 , ZnO and TiO_2 . The obtained materials were tested for cyclohexane oxidation under mild conditions (60 °C, atmospheric pressure) using an environmentally friendly oxidant (H_2O_2). The materials were also tested in the oxidation of benzyl alcohol and methylbenzyl alcohol in the presence of *tert*-butylhydroperoxide as the oxidant under microwave irradiation. With regard to cyclohexane oxidation, all materials were highly selective towards the formation of cyclohexanol and cyclohexanone. No traces of byproducts were detected under the optimised conditions. Au on Fe_2O_3 led to the best results (13.5 % yield). This system showed an interesting almost exclusive formation of cyclohexanol at 4 h reaction time. Catalyst recycling was tested in up to five cycles, and the catalyst maintained almost the original level of activity after three cycles with no significant leaching. With regard to oxidation of benzyl alcohol and methylbenzyl alcohol, all materials were highly selective towards the formation of benzaldehyde or acetophenone, respectively. No traces of byproducts were detected. Addition of Au increased alcohol conversion from 5 (TiO_2) to 91 % (Au/TiO_2). The recycling of Au/TiO_2 was tested in up to 10 cycles, and the catalytic activity remained high in the first four cycles.

Efficient Hydration of Nitriles Promoted by Gallic Acid Derived from Renewable Bioresources

Tao Deng and Cheng-Zhang Wang

[ChemCatChem 2017, 9\(7\), 1349](#)



Abstract

An efficient gallic acid promoted nitriles hydration at room temperature with ethanol/water as a solvent has been developed. The present protocol offers a wide range of amides in moderate to good yields. Moreover, galla chinensis extract can serve as the promoter to perform the hydration, which also shows the potential utilization of natural feedstocks.

Renewable Surfactants through the Hydroaminomethylation of Terpenes

Thiemo A. Faßbach, Tom Gaide, Michael Terhorst, Prof. Dr. Arno Behr and Dr. Andreas J. Vorholt

[ChemCatChem 2017, 9\(8\), 1359](#)

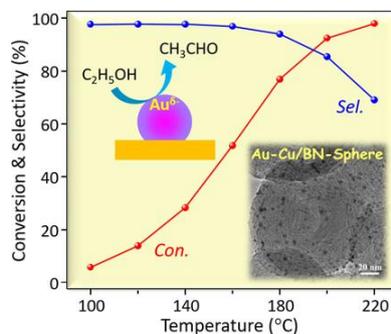


Abstract

A catalytic system was developed to enable the use of industrially available terpenes (e.g., β -myrcene, β -farnesene) in hydroaminomethylation to obtain renewable building blocks for surfactants in two steps. This homogeneously catalyzed tandem reaction includes both hydroformylation and enamine condensation steps, followed by hydrogenation. Under the optimized conditions, the Rh/1,2-bis(diphenylphosphino)ethane catalytic system delivers products in high yields (70%) after short reaction times (3 h) with unprecedentedly high turnover frequency (TOF) values for the hydroformylation of 1,3-dienes of over $739 \text{ mol mol}^{-1} \text{ h}^{-1}$. This is the highest TOF reported to date for the hydroformylation of a 1,3-diene. Furthermore, regioselectivities of 97% and above were observed in the hydroformylation step, which is extraordinarily high for the conversion of 1,3-dienes. The terpene-derived amines obtained were further functionalized to quaternary ammonium compounds that were found to show surface activity quite similar to that of industrially available quaternary ammonium compounds. The hydroaminomethylation of terpenes achieves higher step efficiency than industrial means and makes use of an alternative, renewable feedstock to synthesize more environmentally friendly surfactants.

Spherical Boron Nitride Supported Gold–Copper Catalysts for the Low-Temperature Selective Oxidation of Ethanol

Dr. Yang Wang, Dr. Lei Shi, Dr. Wenduo Lu, Dr. Qiang Sun, Dr. Zifeng Wang, Prof. Chunyi Zhi and Prof. An-Hui Lu

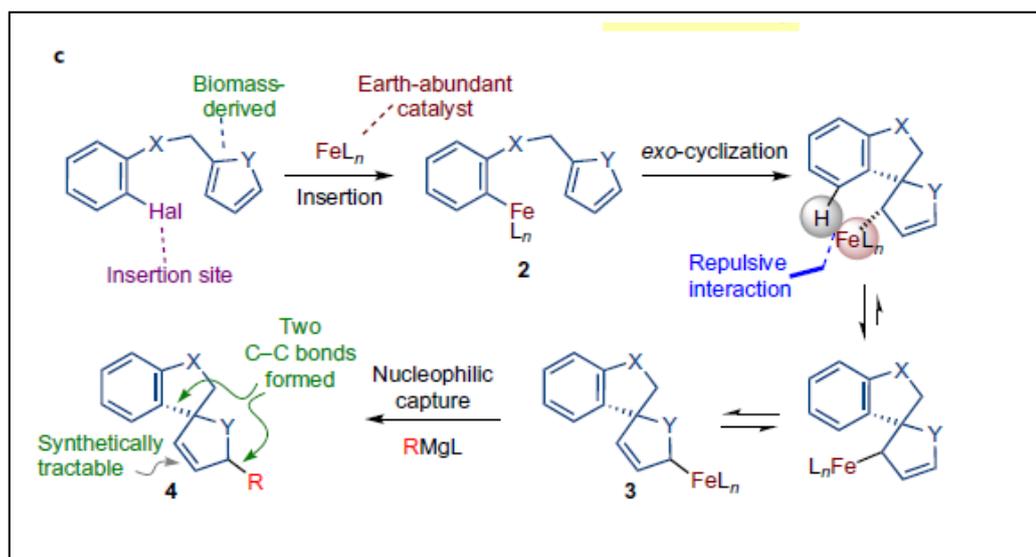
[ChemCatChem 2017, 9\(8\), 1363](#)**Abstract**

The oxidation of ethanol to acetaldehyde in the fine-chemical industry is a burgeoning process that requires leading-edge technology. A major challenge is to find a catalyst with high ethanol conversion and high acetaldehyde selectivity at a high gas hourly space velocity (GHSV) and a low operation temperature. Boron nitride nanosphere supported Au–Cu nanoparticles offer much opportunity for low-temperature ethanol oxidation. A catalytic ethanol conversion of 77 % and a selectivity of 94 % towards acetaldehyde were achieved at a temperature of 180 °C and a high GHSV of 100 000 mL_{g_{cat}}⁻¹ h⁻¹, values that far exceed those obtained with Au–Cu/SiO₂. The immobilized Au–Cu nanoparticles have an average size of approximately 3 nm, and the majority of Au species are assigned Au⁰. The weak interaction of acetaldehyde with both Au–Cu active phases and the boron nitride support facilitates the adsorption–desorption behavior of acetaldehyde. As a result, the progression of secondary reactions is slowed and the degree of coverage of the active sites is minimized.

An iron-catalysed C–C bond-forming spirocyclization cascade providing sustainable access to new 3D heterocyclic frameworks

Kirsty Adams, Anthony K. Ball, James Birkett, Lee Brown, Ben Chappell, Duncan M. Gill, P. K. Tony Lo, Nathan J. Patmore, Craig. R. Rice, James Ryan, Piotr Raubo and Joseph B. Sweeney*

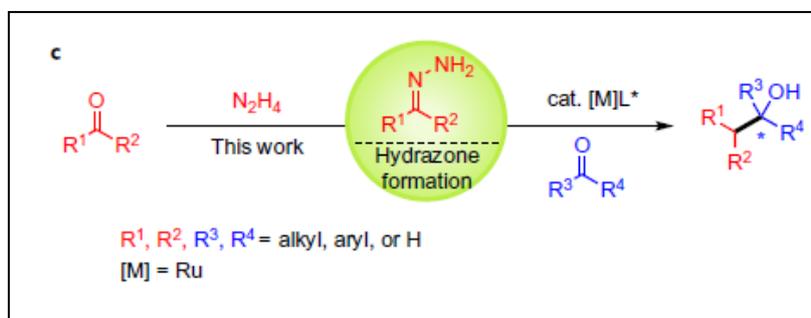
[NATURE CHEMISTRY, 2017, 9, 396](#)

**Abstract**

Heterocyclic architectures offer powerful creative possibilities to a range of chemistry end-users. This is particularly true of heterocycles containing a high proportion of sp^3 -carbon atoms, which confer precise spatial definition upon chemical probes, drug substances, chiral monomers and the like. Nonetheless, simple catalytic routes to new heterocyclic cores are infrequently reported, and methods making use of biomass-accessible starting materials are also rare. Here, we demonstrate a new method allowing rapid entry to spirocyclic bis-heterocycles, in which inexpensive iron(III) catalysts mediate a highly stereoselective C–C bond-forming cyclization cascade reaction using (2-halo)aryl ethers and amines constructed using feedstock chemicals readily available from plant sources. $Fe(acac)_3$ mediates the deiodinative cyclization of (2-halo)aryloxy furfuryl ethers, followed by capture of the intermediate metal species by Grignard reagents, to deliver spirocycles containing two asymmetric centres. The reactions offer potential entry to key structural motifs present in bioactive natural products.

Aldehydes as alkyl carbanion equivalents for additions to carbonyl compounds

Haining Wang, Xi-Jie Dai and Chao-Jun Li *

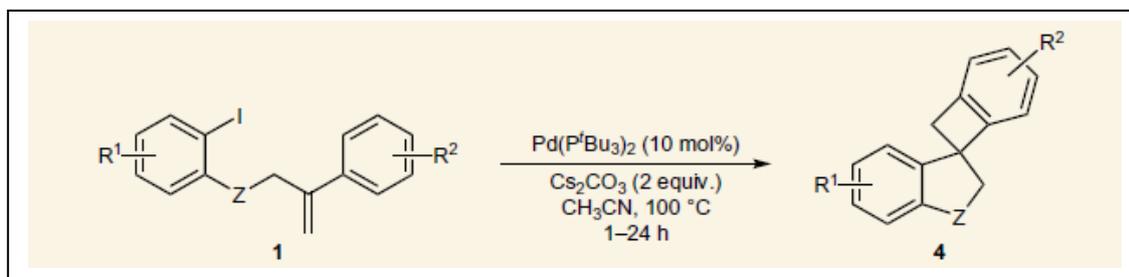
[NATURE CHEMISTRY, 2017, 9, 374](#)**Abstract**

Nucleophilic addition reactions of organometallic reagents to carbonyl compounds for carbon–carbon bond construction have played a pivotal role in modern chemistry. However, this reaction’s reliance on petroleum-derived chemical feedstocks and a stoichiometric quantity of metal have prompted the development of many carbanion equivalents and catalytic metal alternatives. Here, we show that naturally occurring carbonyls can be used as latent alkyl carbanion equivalents for additions to carbonyl compounds, via reductive polarity reversal. Such ‘umpolung’ reactivity is facilitated by a ruthenium catalyst and diphosphine ligand under mild conditions, delivering synthetically valuable secondary and tertiary alcohols in up to 98% yield. The unique chemoselectivity exhibited by carbonyl-derived carbanion equivalents is demonstrated by their tolerance to protic reaction media and good functional group compatibility. Enantioenriched tertiary alcohols can also be accessed with the aid of chiral ligands, albeit with moderate stereocontrol. Such carbonyl-derived carbanion equivalents are anticipated to find broad utility in chemical bond formation.

Remote C–H alkylation and C–C bond cleavage enabled by an in situ generated palladacycle

Juntao Ye, Zhihao Shi, Theresa Sperger, Yoshifumi Yasukawa, Cian Kingston, Franziska Schoenebeck* and Mark Lautens

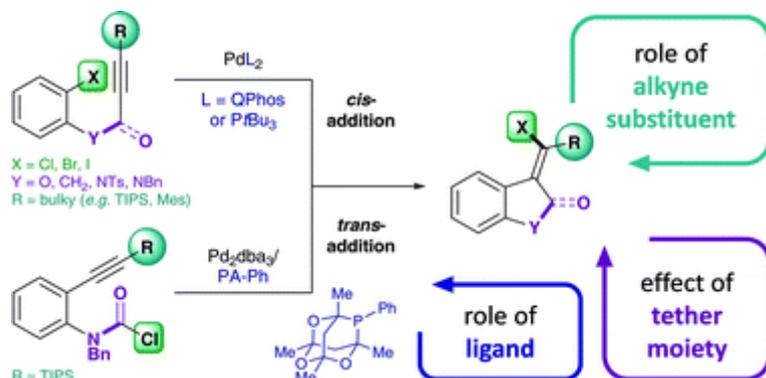
[NATURE CHEMISTRY, 2017, 9, 361](#)

**Abstract**

The direct and selective functionalization of C–H bonds of arenes is one of the most challenging yet valuable aims in organic synthesis. Despite notable recent achievements, a pre-installed directing group proved to be essential in most of the methodologies reported so far. In this context, the use of a transient directing group that can be generated in situ has attracted attention and demonstrated the great potential of this strategy. Here we report the use of an in situ generated palladacycle to accomplish remote-selective C–H alkylation reactions of arenes. Following the C–H functionalization event, the alkylated aryl ring undergoes a formal migration to provide diversely substituted benzofuran and indole scaffolds. Computational studies revealed that a palladium(IV) intermediate is not involved in the alkylation step. The aryl migration was found to proceed through a sequential C–C bond cleavage, insertion and β-hydride-elimination process. The increasing steric bulk that builds up during the C–H functionalization step drives the unusual C–C bond cleavage in a non-strained system.

Mechanistic insights on the Pd-catalyzed addition of C-X bonds across alkynes – a combined experimental and computational study

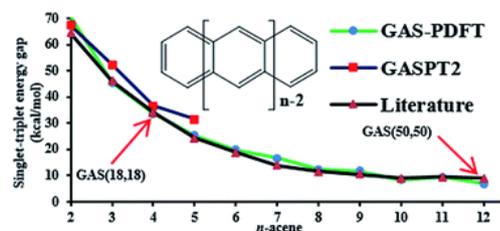
T. Sperger, C. M. Le, M. Lautens, F. Schoenebeck

[Chemical Science 2017, 8, 2914](#)**Abstract**

The Pd-catalyzed intramolecular addition of carbamoyl chlorides and aryl halides across alkynes is investigated by means of DFT calculations and mechanistic test experiments. The data suggest a mechanistic pathway that involves oxidative addition, alkyne insertion, *cis* \rightarrow *trans* isomerization and reductive elimination. Our data indicate that oxidative addition is the reactivity limiting step in the addition of aryl chlorides and bromides across alkynes. However, for the corresponding addition of carbamoyl chlorides, alkyne insertion is found to be limiting. Full energetic reaction pathways for the intramolecular additions across alkynes are presented herein and the role of ligands, alkyne substituents and tether moieties are discussed. Notably, the calculations could rationalize a pronounced effect of the alkyne substituent, which accounts for the exceptional reactivity of TIPS-substituted alkynes. In particular, the bulky silyl moiety is shown to significantly destabilize the formed Pd(II)-intermediates, thus facilitating both *cis* \rightarrow *trans* isomerization and reductive elimination, which overall results in a flatter energetic landscape and a therefore increased catalytic efficiency.

Generalized-active-space pair-density functional theory: an efficient method to study large, strongly correlated, conjugated systems

S. Gosh, C. J. Cramer, D. G. Truhlar, L. Gagliardi

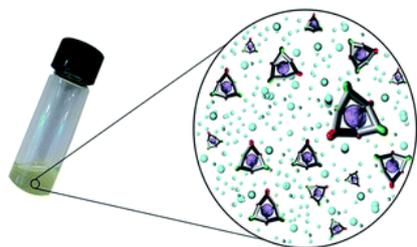
[Chemical Science 2017, 8, 2741](#)**Abstract**

Predicting ground- and excited-state properties of open-shell organic molecules by electronic structure theory can be challenging because an accurate treatment has to correctly describe both static and dynamic electron correlation. Strongly correlated systems, *i.e.*, systems with near-degeneracy correlation effects, are particularly troublesome. Multiconfigurational wave function methods based on an active space are adequate in principle, but it is impractical to capture most of the dynamic correlation in these methods for systems characterized by many active electrons. We recently developed a new method called multiconfiguration pair-density functional theory (MC-PDFT), that combines the advantages of wave function theory and density functional theory to provide a more practical treatment of strongly correlated systems. Here we present calculations of the singlet–triplet gaps in oligoacenes ranging from naphthalene to dodecacene. Calculations were performed for unprecedentedly large orbitally optimized active spaces of 50 electrons in 50 orbitals, and we test a range of active spaces and active space partitions, including four kinds of frontier orbital partitions. We show that MC-PDFT can predict the singlet–triplet splittings for oligoacenes consistent with the best available and much more expensive methods, and indeed MC-PDFT may constitute the benchmark against which those other models should be compared, given the absence of experimental data.

Understanding gas capacity, guest selectivity, and diffusion in porous liquids

R. L. Greenaway, D. Holden, E. G. B. Eden, A. Stephenson, C. W. Yong, M. J. Bennison, T. Hasell, M. E. Briggs, S. L. James, A. I. Cooper

[Chemical Science 2017, 8, 2640](#)



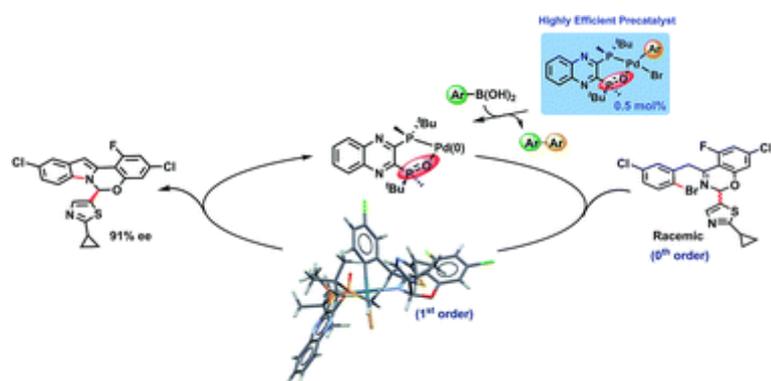
Abstract

Porous liquids are a new class of material that could have applications in areas such as gas separation and homogeneous catalysis. Here we use a combination of measurement techniques, molecular simulations, and control experiments to advance the quantitative understanding of these liquids. In particular, we show that the cage cavities remain unoccupied in the absence of a suitable guest, and that the liquids can adsorb large quantities of gas, with gas occupancy in the cages as high as 72% and 74% for Xe and SF₆, respectively. Gases can be reversibly loaded and released by using non-chemical triggers such as sonication, suggesting potential for gas separation schemes. Diffusion NMR experiments show that gases are in dynamic equilibrium between a bound and unbound state in the cage cavities, in agreement with recent simulations for related porous liquids. Comparison with gas adsorption in porous organic cage solids suggests that porous liquids have similar gas binding affinities, and that the physical properties of the cage molecule are translated into the liquid state. By contrast, some physical properties are different: for example, solid homochiral porous cages show enantioselectivity for chiral aromatic alcohols, whereas the equivalent homochiral porous liquids do not. This can be attributed to a loss of supramolecular organisation in the isotropic porous liquid.

A rational pre-catalyst design for bis-phosphine mono-oxide palladium catalyzed reactions

Y. Ji, H. Li, A. M. Hyde, Q. Chen, K. M. Belyk, K. W. Lexa, J. Yin, E. C. Sherer, R. T. Williamson, A. Brunskill, S. Ren, L.-C. Campeau, I. W. Davies, R. T. Ruck

[Chemical Science 2017, 8, 2841](#)



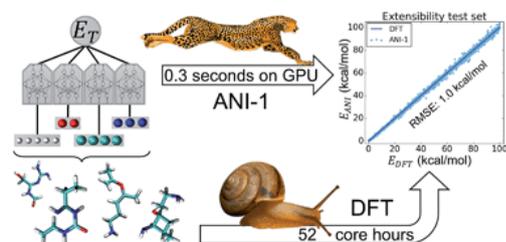
Abstract

Significant catalyst loading reduction and increased reaction robustness have been achieved for a Pd-catalyzed asymmetric intramolecular C–N coupling through comprehensive mechanistic studies. Detailed kinetic, spectroscopic, and crystallographic analyses revealed that the mono-oxidation of the bis-phosphine ligand is critical for a successful transformation. ^{31}P NMR studies provided an understanding of the inefficient activation of the $\text{Pd}(\text{OAc})_2/(\text{R},\text{R})\text{-QuinoxP}^*$ pre-catalyst to form the active bis-phosphine mono-oxide–Pd(0) catalyst with competitive formation of a less active $(\text{R},\text{R})\text{-QuinoxP}^*\cdot\text{PdBr}_2$ complex. Based on these detailed mechanistic studies, a new series of bis-phosphine mono-oxides (BPMO)-ligated Pd(II) pre-catalysts have been rationally developed that allow for reliable and complete catalyst activation which should have general utility in academic and industrial settings.

ANI-1: an extensible neutral network potential with DFT accuracy at force field computational cost

J. S. Smith, O. Isayev, A. E. Roitberg

[Chemical Science 2017, 8, 3192](#)

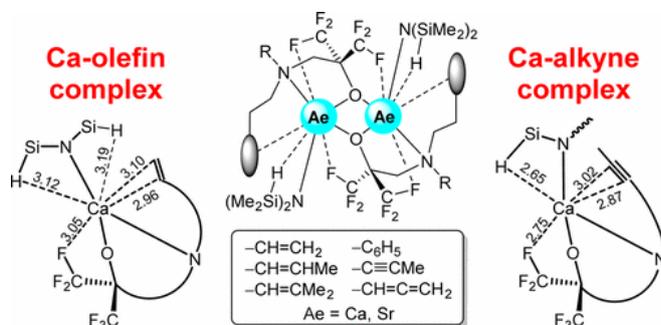


Abstract

Deep learning is revolutionizing many areas of science and technology, especially image, text, and speech recognition. In this paper, we demonstrate how a deep neural network (NN) trained on quantum mechanical (QM) DFT calculations can learn an accurate and transferable potential for organic molecules. We introduce ANAKIN-ME (Accurate Neural network engine for Molecular Energies) or ANI for short. ANI is a new method designed with the intent of developing transferable neural network potentials that utilize a highly-modified version of the Behler and Parrinello symmetry functions to build single-atom atomic environment vectors (AEV) as a molecular representation. AEVs provide the ability to train neural networks to data that spans both configurational and conformational space, a feat not previously accomplished on this scale. We utilized ANI to build a potential called ANI-1, which was trained on a subset of the GDB databases with up to 8 heavy atoms in order to predict total energies for organic molecules containing four atom types: H, C, N, and O. To obtain an accelerated but physically relevant sampling of molecular potential surfaces, we also proposed a Normal Mode Sampling (NMS) method for generating molecular conformations. Through a series of case studies, we show that ANI-1 is chemically accurate compared to reference DFT calculations on much larger molecular systems (up to 54 atoms) than those included in the training data set.

π Ligands in Alkali Earth Complexes

S.-C. Rosca, E. Caytan, V. Dorcet, T. Roisnel, J.-F. Carpentier, Y. Sarazin

[Organometallics 2017, 36, 1269](#)

Abstract

π ligands such as olefins and alkynes bind intramolecularly to the metal atom in d^0 complexes of the large alkaline earths (Ae) calcium and strontium supported by fluoroalkoxy ligands with dangling unsaturated C=C or C \equiv C bonds, and having the amide N(SiMe₂H)₂⁻ as the coligand. These O-bridged dinuclear complexes are further stabilized by secondary C-F \rightarrow Ae and β -Si-H \cdots Ae interactions. In a set of structurally related Ca-olefin complexes, the strength of these interactions gradually increases as the coordination of the olefin onto Ca²⁺ becomes weaker (from η^2 -coordinated to η^1 to fully dissociated) upon increasing steric congestion, thus ensuring that overwhelming electronic depletion does not occur at calcium. NMR data imply that the olefins are metal-bound in [D₈]toluene solutions. The Ae \cdots C π , C-F \rightarrow Ae, and β -Si-H \cdots Ae noncovalent interactions are also strong in the parent Ae-alkyne complexes, the first examples of non-acetylide Ae-alkynes compounds. Calcium-arene complexes could not be made, as the aromatic tether did not bind to the metal atom. Instead, a trinuclear complex with noninteracting C₆H₅ groups was obtained. It exhibits exceptionally strong C-F \rightarrow Ca and β -Si-H \cdots Ca interactions. NMR data indicate that the congeneric calcium-allene complex can be made, but it spontaneously isomerizes toward the more stable Ca-alkyne via an unusual 1,3-hydride shift intramolecular process.

Experimental and Theoretical Studies on the Mechanism of the C-S Bond Activation of Pd^{II} Thiolate /Thioether Complexes

S. Kumar, F. Guyon, M. Knorr, S. Labat, K. Miqueu, C. Golz, C. Strohmann

[Organometallics 2017, 36, 1303](#)



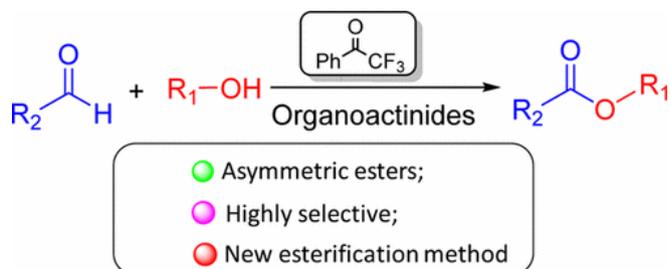
Abstract

Two equivalents of **L** (**L** = 4-methylthio-2-thioxo-1,3-dithiole-5-thiolate or Medmit) react with *cis*-Pd(PR₃)₂Cl₂ (R = Ph and Et) to afford Pd(PR₃)(η¹-**L**)(η²-**L**) (R = Et: **1**; R = Ph: **2**) complexes, which have been characterized by X-ray crystallography. These compounds are dynamic in solution due to an exchange of the thiomethyl groups on palladium. Variable-temperature ¹H NMR spectroscopy reveals a low coalescence temperature (173 K). Treatment of Pd(*diphos*)Cl₂ (*diphos* = dppe or dppm) with 2 equiv of **L** affords thiolato complexes Pd(dppe)(η¹-**L**)₂ (**3**) and Pd(dppm)(η¹-**L**)₂ (**4**). Whereas **3** is rigid in solution with firm η²-coordination of dppe and η¹-coordination of the thiolate, two linkage isomers Pd(η²-dppm)(η¹-**L**)₂ and Pd(η¹-dppm)(η¹-**L**)(η²-**L**) coexist in a solution of **4**. **L** coordinated on Pd^{II} undergoes a S-demethylation reaction leading to dithiolene complexes and Me**L**. This transformation requires high temperature, and its efficiency depends on the nature of the phosphines as well as the nature of the metal (Pd vs Pt). DFT calculations reveal that the most likely mechanism depends on the lability of phosphines. Starting from M(PR₃)₂(η¹-**L**)₂ (M = Pd and Pt; R = Ph and Et), the favored sequence implies decooordination of one triethyl phosphine (M(PEt₃)(η¹-**L**)(η²-**L**)₂ as intermediate) or two triphenylphosphines (Pd(η²-**L**)₂ as intermediate) followed by oxidative addition and reductive elimination (OA/RE) reactions. In the case of PEt₃, this OA/RE sequence can also compete with an intramolecular nucleophilic addition (A_N), which can be described as an attack of a thiolate sulfur atom on a CH₃⁺ carbocation. An intramolecular S_N2 process was found to be the most feasible, starting from M(dppe)(η¹-**L**)₂ (M = Pd and Pt), with the nucleophile approaching the thiomethyl group at an angle of 180° with respect to the C_{CH₃}-S bond. The influence of the coligand has also been studied experimentally. Structurally characterized disulfide **L-L** dimer has been isolated upon reaction of 2 equiv of **L** with MCl₂ (M = Pd and Pt).

Selective Actinide-Catalyzed Tandem Proton-Transfer Esterification of Aldehydes with Alcohols for the Production of Asymmetric Esters

H. Liu, M. S. Eisen

[Organometallics 2017, 36, 1461](#)



Abstract

Actinide-catalyzed tandem proton-transfer esterification between aldehydes and alcohols is presented herein for the first time. It represents a novel convenient and external-oxidant-free methodology in the preparation of asymmetric ester compounds. Various kinds of aldehydes and alcohols can be applied to this reaction, affording the corresponding ester product in moderate to high yields. A plausible mechanism was proposed on the basis of the kinetic, stoichiometric, and deuterium-labeling studies.

Intramolecular Aminoalkoxylation of Unfunctionalized Olefins via Intramolecular Iodoamination and Aziridinium Ion Ring-Opening Sequence

Hui Sun, Bin Cui, Lili Duan, and Yue-Ming Li

Org. Lett., **2017**, 19 (7), 1520

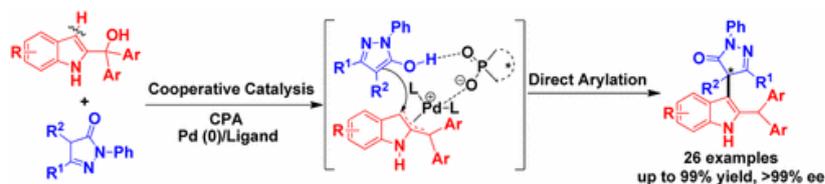


The preparation of prolinol ether type compounds was realized via MnI_2 -catalyzed intramolecular iodoamination of unfunctionalized olefins and subsequent ring opening of an aziridinium ion intermediate with alcohols/phenols. In the presence of a catalytic amount of MnI_2 and 2 equiv of NaI , intramolecular aminoalkoxylation of different *N*-benzyl-5-methylhex-4-en-1-amine substrates proceeded readily in alcoholic solvents, leading to 2-(alkoxyalkyl)pyrrolidine products in up to 90% isolated yields.

Enantioselective Direct α -Arylation of Pyrazol-5-ones with 2-Indolylmethanols via Organo-Metal Cooperative Catalysis

Zi-Qi Zhu, Yang Shen, Jin-Xi Liu, Ji-Yu Tao, and Feng Shi

Org. Lett., **2017**, 19 (7), 1542

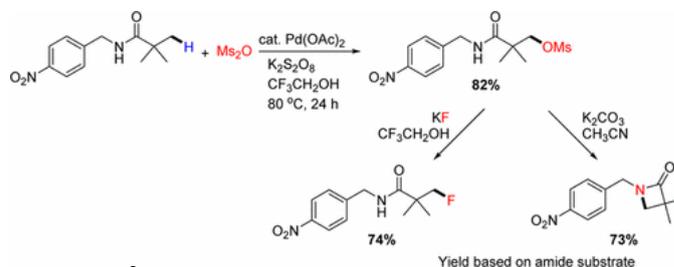


The first catalytic asymmetric α -arylation of pyrazol-5-ones has been established by using 2-indolylmethanols as direct electrophilic arylation reagents under the cooperative catalysis of $Pd(0)$ and a chiral phosphoric acid, which afforded the α -arylation products of pyrazol-5-ones in generally high yields and good enantioselectivities (up to 99% yield, >99% ee).

Palladium-Catalyzed β -Mesylation of Simple Amide via Primary sp^3 C–H Activation

Ren Zhao and Wenjun Lu

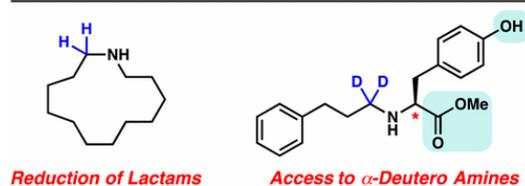
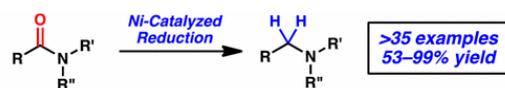
Org. Lett., **2017**, 19 (7), 1768



A β -mesylation of primary sp^3 C–H bonds from simple amides with methanesulfonic anhydride (Ms_2O) has been established successfully at 80 °C in a $Pd(OAc)_2$ (catalyst)/ $K_2S_2O_8$ (oxidant)/ CF_3CH_2OH (solvent) system. These amide substrates involve *N*-monosubstituted linear, branch, or cyclic alkanes, and electron-deficient benzyl compounds. The β -mesylated amide products can be converted easily to β -fluoroamides or β -lactams through inter- or intramolecular S_N2 processes.

Nickel-Catalyzed Reduction of Secondary and Tertiary Amides

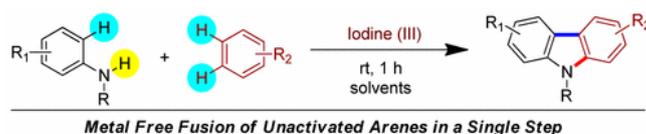
Bryan J. Simmons, Marie Hoffmann, Jaeyeon Hwang, Moritz K. Jackl, and Neil K. Garg

Org. Lett., **2017**, 19 (7), 1910

The nickel-catalyzed reduction of secondary and tertiary amides to give amine products is reported. The transformation is tolerant of extensive variation with respect to the amide substrate, proceeds in the presence of esters and epimerizable stereocenters, and can be used to achieve the reduction of lactams. Moreover, this methodology provides a simple tactic for accessing medically relevant α -deuterated amines.

An Organic Intermolecular Dehydrogenative Annulation Reaction

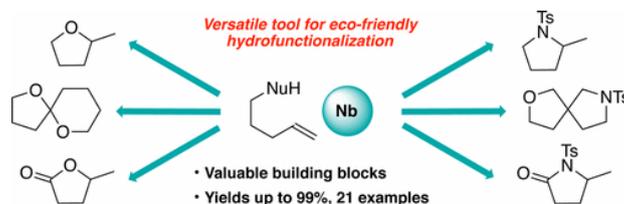
Saikat Maiti, Tapas Kumar Achar, and Prasenjit Mal

Org. Lett., **2017**, 19 (8), 2006

The discovery of a direct method for the synthesis of three-ring heterocyclic carbazoles from unactivated arenes and anilides by a metal-free (organic) intermolecular dehydrogenative annulation reaction under ambient laboratory conditions is reported. Iodine(III) was used as the sole reagent either stoichiometrically from inexpensive phenyliodine diacetate or organocatalytically by in situ generation from PhI-*m*CPBA. In a single step, three C(sp²)-H bonds and one N(sp³)-H bond are functionalized from two different arenes for tandem C-C and C-N bond formation reactions.

Niobium-Catalyzed Intramolecular Addition of O-H and N-H Bonds to Alkenes: A Tool for Hydrofunctionalization

Laura Ferrand, Yue Tang, Corinne Aubert, Louis Fensterbank, Virginie Mouriès-Mansuy, Marc Petit, and Muriel Amatore

Org. Lett., **2017**, 19 (8), 2062

A convenient, versatile, and easy to handle intramolecular hydrofunctionalization of alkenes (C-O and C-N bonds formation) is reported using a novel niobium-based catalytic system. This atom economic and eco-friendly methodology provides an additional synthetic tool for the straightforward formation of valuable building blocks enabling molecular complexity. Various pyran, furan, pyrrolidine, piperidine,

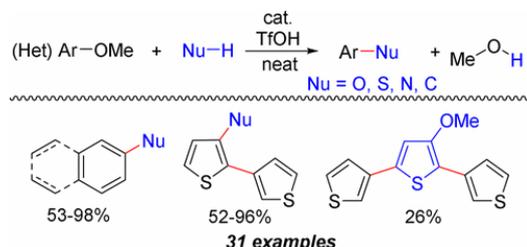
lactone, and lactam derivatives as well as spirocyclic compounds are produced in high yields and selectivities.

Nucleophilic *ipso*-Substitution of Aryl Methyl Ethers through Aryl C–OMe Bond Cleavage:

Access to Functionalized Bisthiophenes

Abhishek Kumar Mishra, Ajay Verma, and Srijit Biswas

J. Org. Chem., 2017, 82 (7), 3403

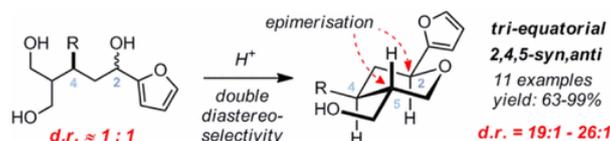


A metal and solvent free strategy to functionalize aryl methyl ethers through direct nucleophilic substitution of aryl C–OMe bond has been described. A wide range of O, S, N, and C-centered uncharged nucleophiles has been successfully employed. Using this protocol, functional derivatives of bisthiophene have been synthesized in a straightforward way. The reactions are highly atom-efficient and generate methanol as the only byproduct.

Furanyl Cyclic Ethers: Single and Double Diastereoselectivity in the Synthesis of 2,4-Di and 2,4,5-Trisubstituted Tetrahydropyrans

Dennis A. Cooper, Emma Robbins, Graham J. Tizzard, Simon J. Coles, and Matthew O'Brien

J. Org. Chem., 2017, 82 (7), 3441

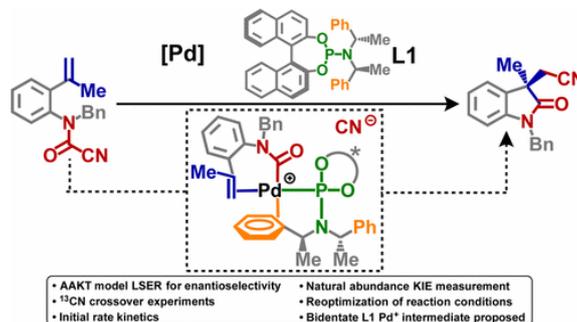


Combining the desymmetrization of a prochiral bis-hydroxymethyl group with the epimerization of a chiral furanyl ether in a single transformation, high levels of double diastereoselectivity have been achieved in a synthesis of 2,4,5-trisubstituted tetrahydropyrans, which proceeds under thermodynamic control.

Mechanistic Model for Enantioselective Intramolecular Alkene Cyanoamidation via Palladium-Catalyzed C–CN Bond Activation

Grant B. Frost, Nicholas A. Serratore, Jodi M. Ogilvie, and Christopher J. Douglas

J. Org. Chem., 2017, 82 (7), 3721

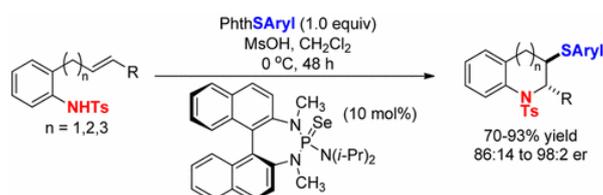


We studied key aspects of the mechanism of Pd-catalyzed C–CN bond activation and intramolecular enantioselective alkene cyanoamidation. An Abboud–Abraham–Kamlet–Taft (AAKT) linear solvation energy relationship (LSER) model for enantioselectivity was established. We investigated the impact of Lewis acid (BPh₃), Lewis base (DMPU), and no additives. BPh₃ additive led to diminished enantioselectivity and differing results in ¹³CN crossover experiments, initial rate kinetics, and natural abundance ¹²C/¹³C kinetic isotope effect measurements. We propose two catalytic mechanisms to account for our experimental results. We propose that the DMPU/nonadditive pathway passes through a κ^2 -phosphoramidite-stabilized Pd⁺ intermediate, resulting in high enantioselectivity. BPh₃ prevents the dissociation of CN[–], leading to a less rigid κ^2 -phosphoramidite-neutral Pd intermediate.

Catalytic, Enantioselective, Intramolecular Sulfenoamination of Alkenes with Anilines

Scott E. Denmark and Hyung Min Chi

J. Org. Chem., **2017**, *82* (7), 3826



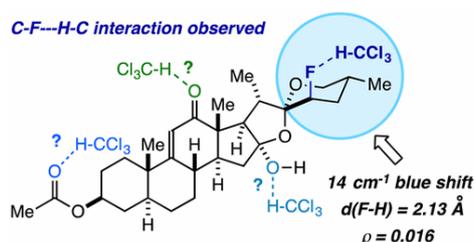
A method for the catalytic, enantioselective, intramolecular sulfenoamination of alkenes with aniline nucleophiles has been developed. The method employs a chiral, Lewis basic selenophosphoramidate catalyst and a Brønsted acid co-catalyst to promote stereocontrolled C–N and C–S bond formation by activation of an achiral sulfenylating agent. Benzoannulated nitrogen-containing heterocycles such as indolines, tetrahydroquinolines, and tetrahydrobenzazepines were prepared with high to excellent enantioselectivities. The impact of tether length and electron density of both the nucleophile and olefin on the reactivity, site selectivity, and enantioselectivity were investigated and interpreted in terms of substrate-dependent stereodetermining thiiranium ion formation or capture.

Intermolecular Aliphatic C–F...H–C Interaction in the Presence of “Stronger” Hydrogen Bond

Acceptors: Crystallographic, Computational, and IR Studies

Cody Ross Pitts, Maxime A. Siegler, and Thomas Lectka

J. Org. Chem., **2017**, *82* (7), 3996



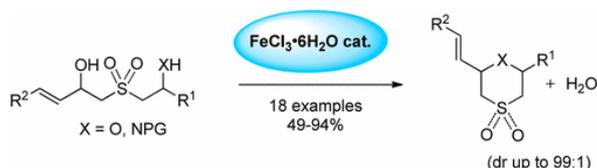
An unprecedented intermolecular aliphatic C–F...H–C interaction was observed in the X-ray crystal structure of a fluorinated triterpenoid. Despite the notion of fluorine being a poor acceptor, computational and IR studies revealed this interaction to be a weak to moderate hydrogen bond with a C–H stretch vibration frequency blue-shifted by 14 cm^{–1} and d(F–H) = 2.13 Å. In addition, the aliphatic

C–F bond is the preferred acceptor in the presence of multiple, traditionally stronger oxygen-based hydrogen bond acceptors.

Iron-Catalyzed Synthesis of Sulfur-Containing Heterocycles

Cyril Bosset, Gauthier Lefebvre, Patrick Angibaud, Ian Stansfield, Lieven Meerpoel, Didier Berthelot, Amandine Guérinot, and Janine Cossy

J. Org. Chem., **2017**, *82* (8), 4020

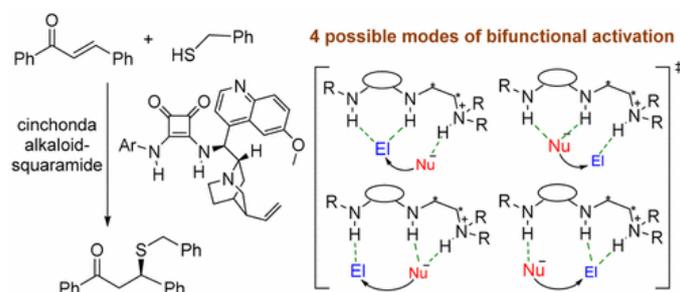


An iron-catalyzed synthesis of sulfur- and sulfone-containing heterocycles is reported. The method is based on the cyclization of readily available substrates and proceeded with high efficiency and diastereoselectivity. A variety of sulfur-containing heterocycles bearing moieties suitable for subsequent functionalization are prepared. Illustrative examples of such postcyclization modifications are also presented.

Cinchona Alkaloid-Squaramide Catalyzed Sulfa-Michael Addition Reaction: Mode of Bifunctional Activation and Origin of Stereinduction

Jinlong Guo and Ming Wah Wong

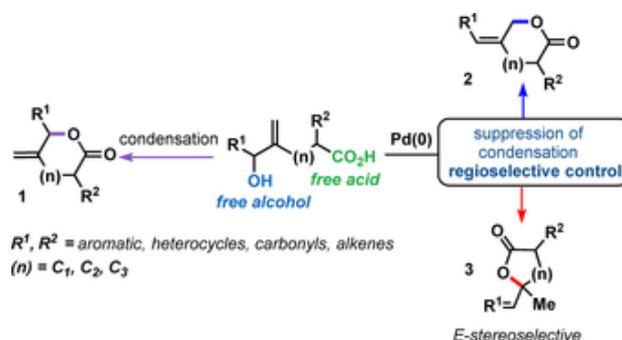
J. Org. Chem., **2017**, *82* (8), 4362



The mechanism of the enantioselective sulfa-Michael addition reaction catalyzed by a cinchona alkaloid-squaramide bifunctional organocatalyst was studied using density functional theory (DFT). Four possible modes of dual activation mechanism via hydrogen bonds were considered. Our study showed that Houk's bifunctional Brønsted acid–hydrogen bonding model, which works for cinchonidine or cinchona alkaloid-urea catalyzed sulfa-Michael addition reactions, also applies to the catalytic system under investigation. In addition, we examined the origin of the stereoselectivity by identifying stereocontrolling transition states. Distortion–interaction analysis revealed that attractive interaction between the substrates and catalyst in the C–S bond forming transition state is the key reason for stereoselection in this catalytic reaction. Noncovalent interaction (NCI) analysis showed that a series of more favorable cooperative noncovalent interactions, namely, hydrogen bond, π -stacking, and C–H \cdots π interaction and C–H \cdots F interactions, in the major R-inducing transition state. The predicted enantiometric excess is in good accord with the observed value.

Palladium-Catalyzed Cyclization of Free Hydroxyalkenoic Acids: Regio- and Chemoselective Access to Methylene Lactones

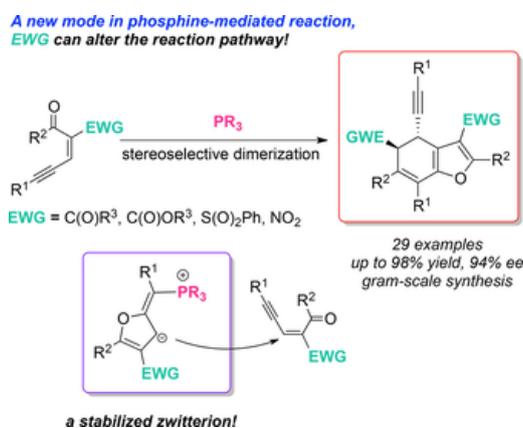
Yelena Mostinski, Ramesh Kotikalapudi, Viviana Valerio, Riva Nataf and Dmitry Tselikhovsky
Adv.Synth. Catal. **2017**, 359,1164



A general and collective synthesis of medium-sized methylene lactones via controlled cyclizations of easily accessible collective precursors is described. The rapid composition of key-hydroxyalkenoic acid scaffold yields an assembly of oxocanones, oxepanones, and pyranones in a regioselective and stereodirected fashion via palladium-catalyzed cyclization.

Phosphine-Mediated Dimerization of Conjugated Ene-Yne Ketones: Stereoselective Construction of Dihydrobenzofurans

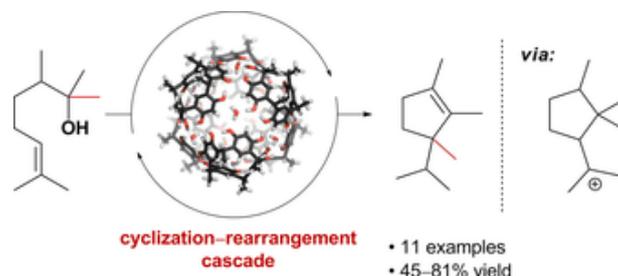
Cheng-Zhi Zhu, Yao-Liang Sun, Yin Wei and Min Shi
Adv.Synth. Catal. **2017**, 359,1263



A new strategy for the phosphine-mediated dimerization of conjugated ene-yne ketones to produce functionalized dihydrobenzofurans has been developed, affording diversified 4,5-dihydrobenzofurans in moderate to excellent yields with high diastereoselectivities under mild conditions. This new synthetic method can tolerate a variety of functional groups and can be performed on a gram scale and in an asymmetric variant using the chiral phosphine Xyl-BINAP to give the desired products with up to 94% ee.

Host-Catalyzed Cyclodehydration–Rearrangement Cascade Reaction of Unsaturated Tertiary Alcohols

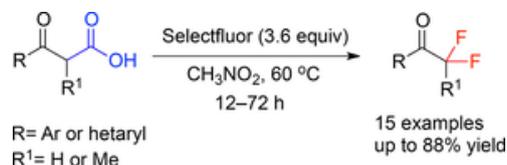
Lorenzo Catti, Alexander Pöthig and Konrad Tiefenbacher
Adv.Synth. Catal. **2017**, 359,1331



The Brønsted acidic resorcin[4]arene hexamer can be applied as an effective catalyst in the dehydrative cyclization and subsequent rearrangement of unsaturated tertiary alcohols. This is the first report on catalyzing such a reaction with a Brønsted acid. Scope and limitations of this cyclopentene-forming reaction sequence are presented. Furthermore, substrate-selective conversion as well as competitive inhibition are described and provide evidence that the reactions proceed within the cavity of the self-assembled structure. Additionally, a cyclobutanone-forming intramolecular hydride transfer of an encapsulated cyclopropyl acetate is reported.

Practical Access to Difluoromethyl Ketones via Straightforward Decarboxylative Difluorination of β -Ketoacids

Yin-Long Li, Jian Li and Jun Deng
Adv.Synth. Catal. **2017**, 359,1407

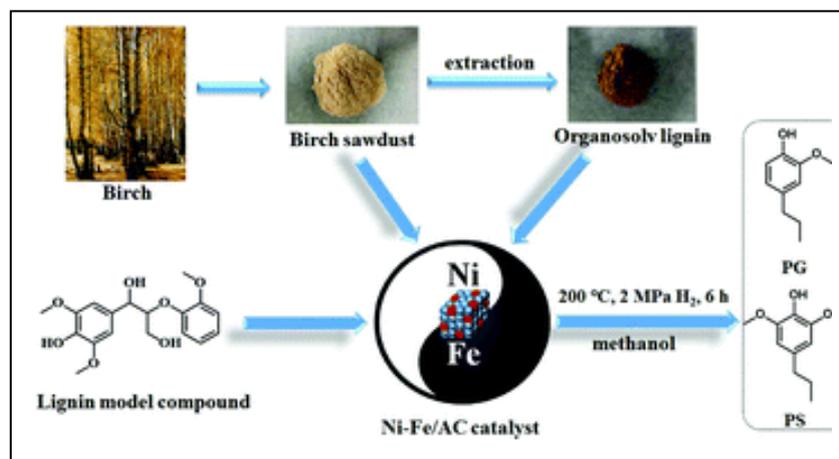


A facile synthetic approach to a series of difluoromethyl ketones from β -ketoacids has been described. This transformation is achieved through the straightforward decarboxylative difluorination of β -ketoacids in the absence of any catalyst. Furthermore, the resulted difluoromethyl ketones can be easily converted into corresponding difluoromethylated building blocks for pharmaceuticals and materials.

Depolymerization of lignin via a non-precious Ni–Fe alloy catalyst supported on activated carbon

Yongxiang Zhai, Chuang Li, Guangyue Xu, Yanfu Ma, Xiaohao Liu and Ying Zhang

Green Chem., 2017, 19,1895

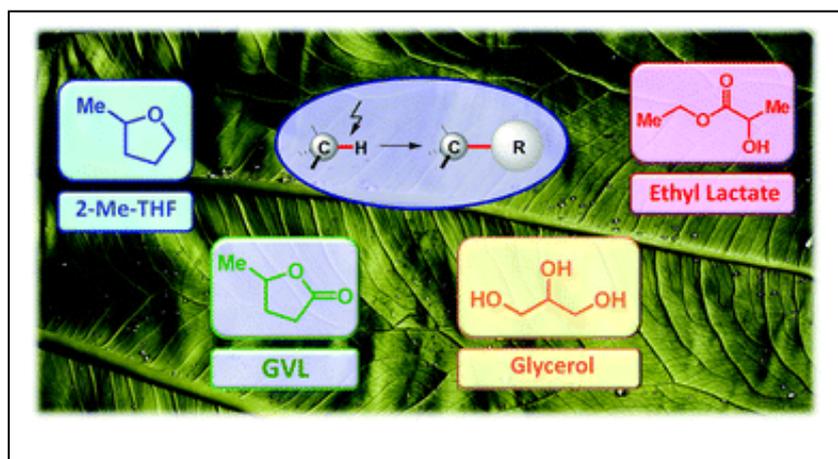
**Abstract**

Lignin primarily composed of methoxylated phenylpropanoid subunits is an abundant biomass that can be used to produce aromatics. Herein, a series of non-precious bimetallic Ni–Fe/AC catalysts were prepared for efficiently depolymerizing lignin. When organosolv birch lignin was used to determine the efficiency of the catalysts in methanol solvent, the Ni₁–Fe₁/AC (the ratio of Ni and Fe was 1 : 1) achieved the highest total yield of monomers (23.2 wt%, mainly propylguaiacol and propylsyringol) at 225 °C under 2 MPa H₂ for 6 h. From GPC analysis, it is also proved that lignin was efficiently depolymerized. The Ni–Fe alloy structure was formed according to XRD, HRTEM, H₂-TPR and XPS characterization. Based on the model compounds' tests, the Ni₁–Fe₁/AC catalyst showed high efficiency in ether bond cleavage without hydrogenation of aromatic rings which could be attributed to the synergistic effect of Ni and Fe on the alloy structure. The total yield of monomers by using the Ni₁–Fe₁/AC catalyst reached 39.5 wt% (88% selectivity to PG and PS) when birch wood sawdust was used as the substrate.

Biomass-derived solvents as effective media for cross-coupling reactions and C–H functionalization processes

Stefano Santoro, Francesco Ferlin, Lorenzo Luciani,^a Lutz Ackermann and Luigi Vaccaro

Green Chem., 2017, 19, 1601



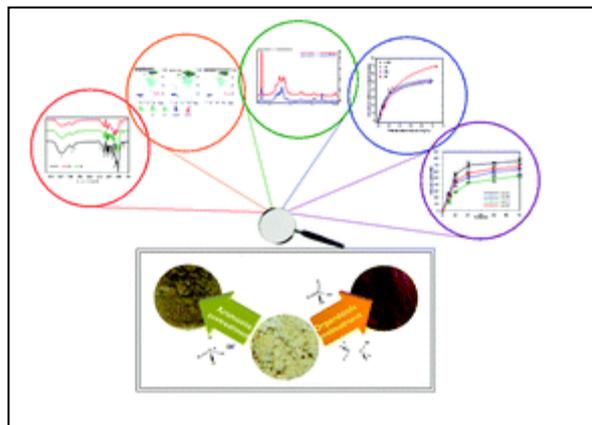
Abstract

Palladium-catalyzed cross-coupling reactions are indispensable tools in molecular syntheses with numerous applications in academia and for the practitioners in the chemical and pharmaceutical industries. Recent years have witnessed the increasing use of biomass-derived solvents as green reaction media in the palladium-, copper- and nickel-catalyzed cross-coupling technology, the key advances until January 2017 being summarized in this review. In addition, very recent first examples of transition metal-catalyzed C–H activations in biomass-originated solvents, such as γ -valerolactone and 2-MeTHF, are discussed as well.

Effects of organosolv and ammonia pretreatments on lignin properties and its inhibition for enzymatic hydrolysis

Chang Geun Yoo, Mi Li, Xianzhi Meng, Yunqiao Pu and Arthur J. Ragauskas

Green Chem., 2017, 19, 2006



Abstract

Lignin offers structural support and protection for plant cell walls; however, it also contributes to biomass

recalcitrance and the costs of biofuel production via the biological pathway. Organosolv and ammonia pretreatments have been developed to reduce biomass recalcitrance and improve sugar release performance during enzymatic hydrolysis. It is believed that lignin properties are related to its inhibition on enzymatic hydrolysis; therefore, understanding the characteristics of lignin is a key for effective biomass conversion to biofuels. In this study, an organosolv pretreatment using 60% ethanol with 1.25% H₂SO₄ significantly deconstructed poplar lignin and reduced its molecular weights due to the cleavage of lignin inter-unit linkages. The organosolv pretreatment increased the contents of phenolic OH units and the lignin residue showed a high cellulase maximum adsorption capacity. Ammonia pretreatment with 5% ammonium hydroxide was not as effective as organosolv pretreatment on lignin deconstruction.

Organosolv lignin residue had lower lignin S/G ratio than the untreated one. Compared to the organosolv

lignin residue and untreated lignin, ammonia lignin residue had a higher cellulase adsorption affinity. In addition, the effects of lignin on cellulose hydrolysis was investigated and the results suggested that the

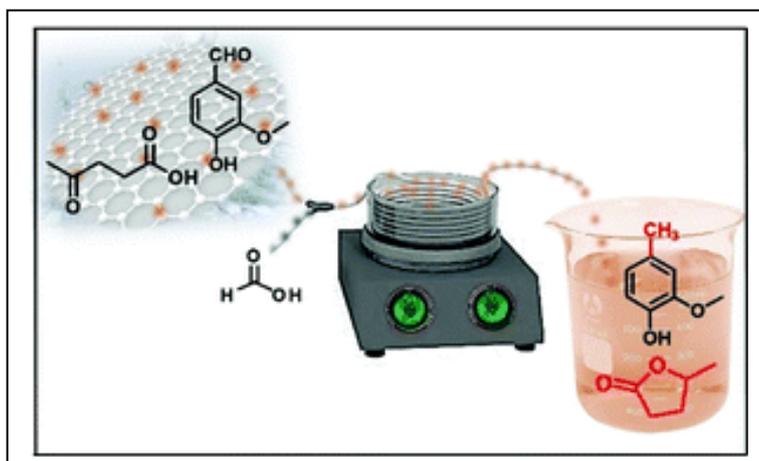
presence of lignin with cellulose substrates reduced cellulose hydrolysis, and its inhibitory effect was primarily determined by the lignin properties after each pretreatment. The organosolv pretreatment resulted in a slightly lower cellulase binding strength (249.7 mL g⁻¹) on poplar lignin than that on untreated samples (261.1 mL g⁻¹), while ammonia lignin residue showed a higher cellulase binding strength (402.8 mL g⁻¹) and had more significant inhibition effect on cellulose hydrolysis. These

results demonstrated that the binding strength significantly affected the lignin-derived inhibition on enzymatic hydrolysis of cellulose in the cellulose-lignin mixtures.

A sustainable approach to empower the bio-based future: upgrading of biomass via process Intensification

Kidus Tadele, Sanny Verma, Michael A. Gonzalezb and Rajender S. Varma

Green Chem., 2017, 19, 1624

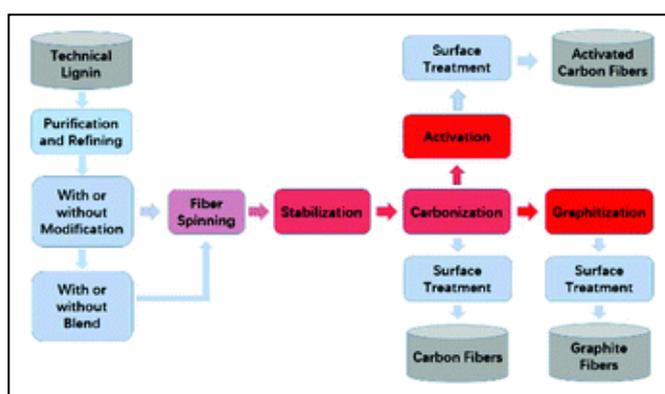


An economically viable and environmentally benign continuous flow intensified process has been developed that demonstrates its ability to upgrade biomass into potential biofuels, solvents, and pharmaceutical feedstocks using a bimetallic AgPd@g-C₃N₄ catalyst.

Manufacture and application of lignin-based carbon fibers (LCFs) and lignin-based carbon nanofibers (LCNFs)

Wei Fang, Sheng Yang, Xi-Luan Wang, Tong-Qi Yuan* and Run-Cang Sun

Green Chem., 2017, 19, 1794

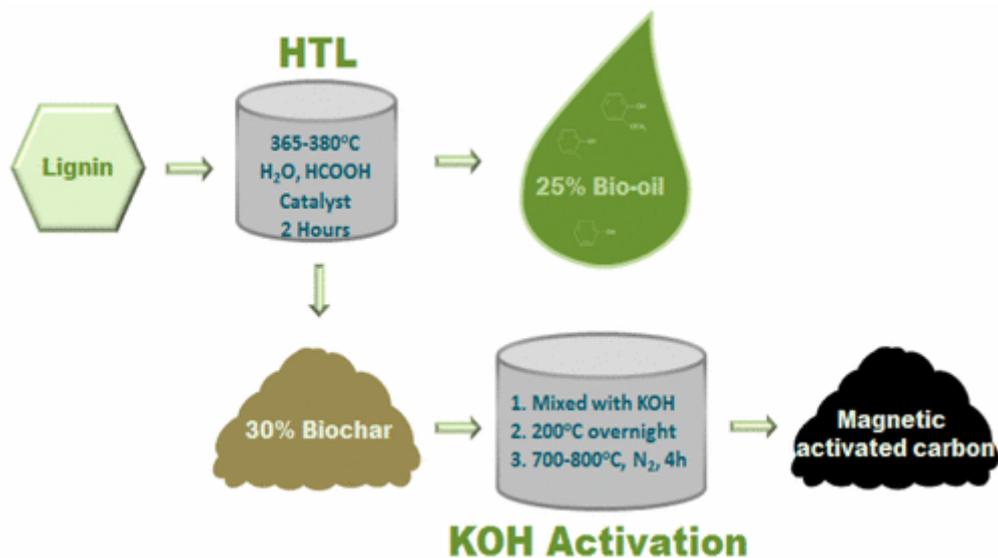


Environmental issues and constantly diminishing petroleum resources are considerable barriers inhibiting modernization, and vast efforts have been exerted to address these problems. Carbon fibers (CFs) are carbon materials with high mechanical strength and functionality for applications in construction, electronics, transportation, and aviation. Currently, most CFs are produced from polyacrylonitrile, a petroleum-based, unsustainable, and non-renewable chemical of relatively high price. Interestingly, lignin is an inexpensive, highly accessible, and renewable resource. It has been utilized to fabricate lignin-based carbon fibers (LCFs), which have met rapid development during the past two decades. In this review, LCFs are generalized by focusing on their steps of manufacture. Resource types and corresponding pretreatments ensure the processability of spinning and thermal treatments. Fibers are formed via spinning methods, including melt-spinning, wet-spinning, dry-spinning, and electrospinning. The next step is the most significant process of stabilization, in which fibers are oxidized, crosslinked, and thermally stabilized for pyrolysis. Subsequent to carbonization and/or additional processes (activation and graphitization), LCFs are obtained. Each step can influence the terminal performance of LCFs, which is discussed in detail. Recently produced LCFs of sub-micron size, also known as lignin-based carbon nanofibers (LCNFs), are detailed. Furthermore, attributed to the excellent performance and low cost of LCFs and LCNFs, they have been applied in various fields, predominantly for electronic devices such as batteries and supercapacitors. Our review is concluded with opinions on the potential for further advancement of this promising material.

High-Performance Magnetic Activated Carbon from Solid Waste from Lignin Conversion Processes. 1. Their Use As Adsorbents for CO₂

W. Hao, F. Björnerbäck, Y. Trushkina, M. Oregui Bengoechea, G. Salazar-Alvarez, T. Barth and N. Hedin.

[ACS Sustainable Chem. Eng.](#), 2017, 5, 3087–3095.



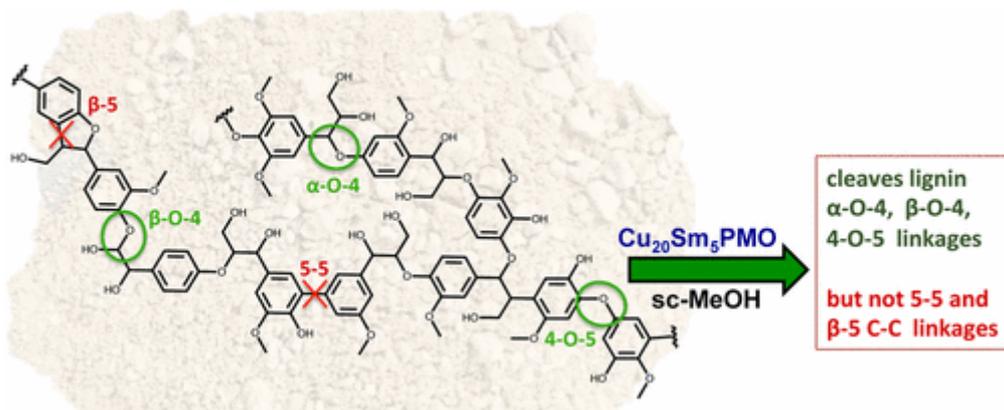
Abstract:

Lignin is naturally abundant and a renewable precursor with the potential to be used in the production of both chemicals and materials. As many lignin conversion processes suffer from a significant production of solid wastes in the form of hydrochars, this study focused on transforming hydrochars into magnetic activated carbons (MAC). The hydrochars were produced via hydrothermal treatment of lignins together with formic acid. The activation of the hydrochars was performed chemically with KOH with a focus on the optimization of the MACs as adsorbents for CO₂. MACs are potentially relevant to carbon capture and storage (CCS) and gas purification processes. In general, the MACs had high specific surface areas (up to 2875 m²/g), high specific pore volumes, and CO₂ adsorption capacities of up to 6.0 mmol/g (1 atm, 0 °C). The textual properties of the MACs depended on the temperature of the activation. MACs activated at a temperature of 700 °C had very high ultramicropore volumes, which are relevant for potential adsorption-driven separation of CO₂ from N₂. Activation at 800 °C led to MACs with larger pores and very high specific surface areas. This temperature-dependent optimization option, combined with the magnetic properties, provided numerous potential applications of the MACs besides those of CCS. The hydrochar was derived from eucalyptus lignin, and the corresponding MACs displayed soft magnetic behavior with coercivities of <100 Oe and saturation magnetization values of 1–10 emu/g.

Probing the Lignin Disassembly Pathways with Modified Catalysts Based on Cu-Doped Porous Metal Oxides

M. Chui, G. Metzker, C. M. Bernt, A. T. Tran, A. C. B. Burtoloso and P. C. Ford,

[ACS Sustainable Chem. Eng.](#), 2017, 5, 3158–3169.



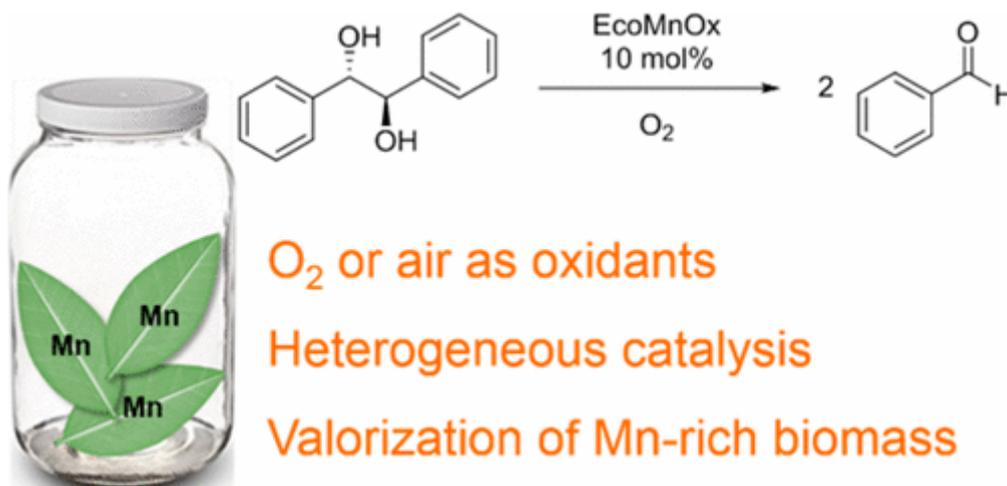
Abstract:

Described are the selectivities observed for reactions of lignin model compounds with modifications of the copper-doped porous metal oxide (CuPMO) system previously shown to be a catalyst for lignin disassembly in supercritical methanol (Matson et al., *J. Amer. Chem. Soc.* 2011, 133, 14090–14097). The models studied are benzyl phenyl ether, 2-phenylethyl phenyl ether, diphenyl ether, biphenyl, and 2,3-dihydrobenzofuran, which are respective mimetics of the α -O-4, β -O-4, 4-O-5, 5-5, and β -5 linkages characteristic of lignin. Also, briefly investigated as a substrate is poplar organosolv lignin. The catalyst modifications included added samarium(III) (both homogeneous and heterogeneous) or formic acid. The highest activity for the hydrogenolysis of aryl ether linkages was noted for catalysts with Sm(III) incorporated into the solid matrix of the PMO structure. In contrast, simply adding Sm^{3+} salts to the solution suppressed the hydrogenolysis activity. Added formic acid suppressed aryl ether hydrogenolysis, presumably by neutralizing base sites on the PMO surface but at the same time improved the selectivity toward aromatic products. Acetic acid induced similar reactivity changes. While these materials were variously successful in catalyzing the hydrogenolysis of the different ethers, there was very little activity toward the cleavage of the 5-5 and β -5 C-C bonds that represent a small, but significant, percentage of the linkages between monolignol units in lignins.

EcoMnOx, a Biosourced Catalyst for Selective Aerobic Oxidative Cleavage of Activated 1,2-Diols

V. Escande, C. H. Lam, C. Grison and P. T. Anastas.

[ACS Sustainable Chem. Eng.](#), 2017, 5 (4), pp 3214–3222



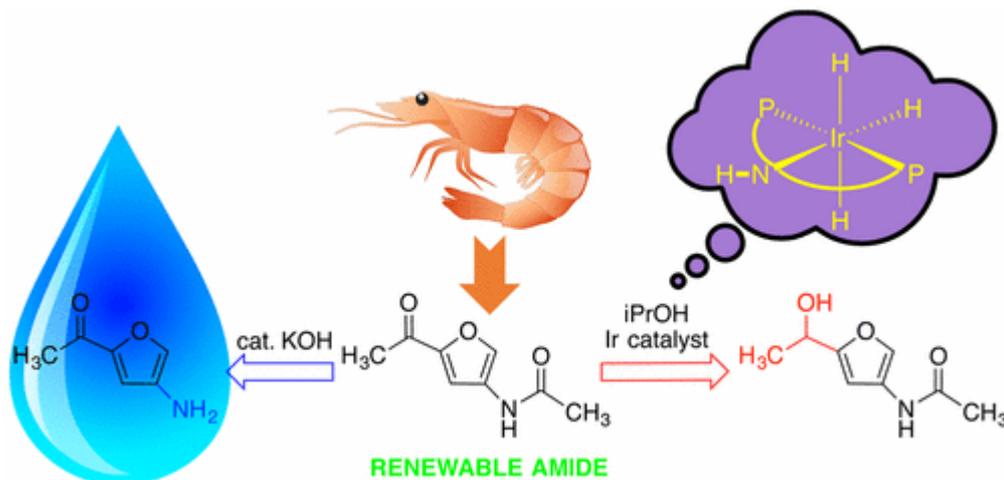
Abstract:

A novel catalyst, EcoMnOx, was prepared from waste biomass of Mn-hyperaccumulating plants. The valorization of this Mn-rich biomass is an alternative to its costly usual disposing and provides a new source of Mn. Extracted metal ions, including Mn²⁺, were oxidized in mild conditions by H₂O₂/NaOH to afford EcoMnOx, as a polymetallic oxide material containing from 8.9 to 14.1 wt % Mn. Spectroscopic studies of this material revealed the presence of Mn layered mixed oxides, rich in Mn^{IV} along with Mn^{III} and Mn^{II} species. EcoMnOx catalytic properties were assessed in the aerobic oxidative cleavage of 1,2-diols, under atmospheric pressure of O₂ or air. With only 10 mol % Mn, up to complete conversions were obtained on activated benzylic and allylic diols, with excellent selectivity toward aldehydes or ketones (98–99%). Moreover, because of its heterogeneous nature, the catalyst can be removed easily by filtration, and reapplied for a minimum of six successive runs without any loss of activity. Finally, E-factor analysis showed the EcoMnOx generates 4 to 17 times less waste compared to classical reagents such as NaIO₄ and Pb(OAc)₄, respectively, highlighting the sustainable assets of this new heterogeneous catalyst.

Formation of a Renewable Amine and an Alcohol via Transformations of 3-Acetamido-5-acetylfuran

Y. Liu, C. Stähler, J. N. Murphy, B. J. Furlong and F. M. Kerton.

[ACS Sustainable Chem. Eng.](#) 2017, Article ASAP



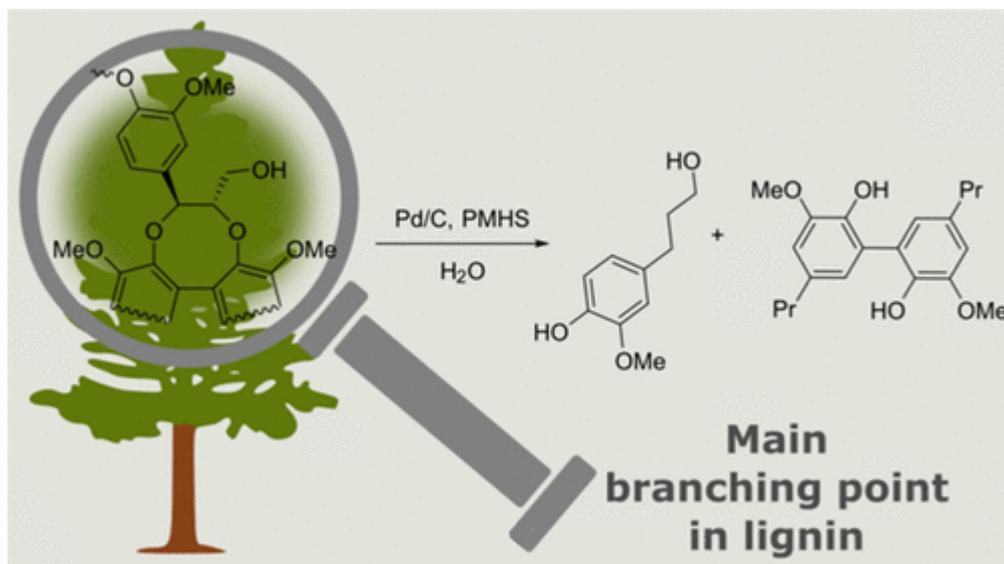
Abstract:

The reactivity of the renewable amide 3-acetamido-5-acetylfuran (3A5AF) was explored. Hydrolysis of the amido group to yield the amino-substituted furan, 2-acetyl-4-aminofuran (1), was achieved via NaOH catalysis. Reduction of the acetyl group could be achieved stoichiometrically using NaBH₄ or catalytically via transfer hydrogenation using an Ir catalyst. The product alcohol, 3-acetamido-5-(1-hydroxyethyl)furan (2), underwent dehydration during analysis via GC-MS to yield an alkene (3). The potential reactivity of 3A5AF and 1 toward carbon dioxide was studied, but no reaction was observed due to the inherent acidity of 3A5AF and 1 despite the latter being an amine. The computationally determined pK_a values for 3A5AF and 1 are reported. Interestingly, in this work, tautomerism of 3A5AF was observed in CD₃OD as evidenced by H–D exchange within the acetyl group.

Pd/C-Catalyzed Hydrogenolysis of Dibenzodioxocin Lignin Model Compounds Using Silanes and Water as Hydrogen Source

E. Subbotina, M. V. Galkin and J. S. M. Samec

[ACS Sustainable Chem. Eng.](#), 2017, Article ASAP



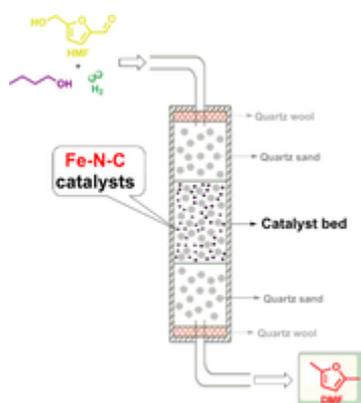
Abstract:

A mild Pd/C-catalyzed hydrogenolysis of the C–O bond of model compounds representing the dibenzodioxocin motif in lignin using polymethylhydrosiloxane (PMHS) and water as hydrogen sources was developed. The efficiency of the reaction is highly dependent on both water concentration and the addition of a base. The results from mechanistic studies showed that the benzylic C–O bond is cleaved faster than the terminal C–O bond, which only cleaves upon the presence of the neighboring phenol. We propose a hydrogen bond formation between an oxygen atom of an ether group and a proton of a neighboring phenol under the employed mild reaction conditions, which facilitates cleavage of the C–O bond.

Selective Hydrodeoxygenation of 5-Hydroxymethylfurfural to 2,5-Dimethylfuran over Heterogeneous Iron Catalysts

Dr. Jiang Li, Jun-ling Liu, He-yang Liu, Guang-yue Xu, Jun-jie Zhang, Jia-xing Liu, Dr. Guang-lin Zhou, Qin Li, Zhi-hao Xu, Prof. Dr. Yao Fu

[ChemSusChem](#), 2017, 10, 1436.



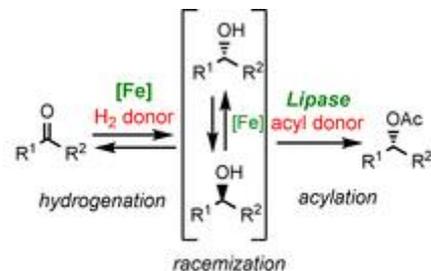
Abstract:

This work provided the first example of selective hydrodeoxygenation of 5-hydroxymethylfurfural (HMF) to 2,5-dimethylfuran (DMF) over heterogeneous Fe catalysts. A catalyst prepared by the pyrolysis of an Fe-phenanthroline complex on activated carbon at 800 °C was demonstrated to be the most active heterogeneous Fe catalyst. Under the optimal reaction conditions, complete conversion of HMF was achieved with 86.2 % selectivity to DMF. The reaction pathway was investigated thoroughly, and the hydrogenation of the C=O bond in HMF was demonstrated to be the rate-determining step during the hydrodeoxygenation, which could be accelerated greatly by using alcohol solvents as additional H-donors. The excellent stability of the Fe catalyst, which was probably a result of the well-preserved active species and the pore structure of the Fe catalyst in the presence of H₂, was demonstrated in batch and continuous flow fixed-bed reactors.

Asymmetric Chemoenzymatic Reductive Acylation of Ketones by a Combined Iron-Catalyzed Hydrogenation–Racemization and Enzymatic Resolution Cascade

O. El-Sepelgy, A. Brzozowska and M. Rueping

[ChemSusChem](#), 2017, 10, 1664.



The first example of noble-metal free cascade reductive acylation of ketones

Abstract:

A general and practical process for the conversion of prochiral ketones into the corresponding chiral acetates has been realized. An iron carbonyl complex is reported to catalyze the hydrogenation–dehydrogenation–hydrogenation of prochiral ketones. By merging the iron-catalyzed redox reactions with enantioselective enzymatic acylations a wide range of benzylic, aliphatic and (hetero)aromatic ketones, as well as diketones, were reductively acylated. The corresponding products were isolated with high yields and enantioselectivities. The use of an iron catalyst together with molecular hydrogen as the hydrogen donor and readily available ethyl acetate as acyl donor make this cascade process highly interesting in terms of both economic value and environmental credentials.

Efficient Cleavage of Lignin–Carbohydrate Complexes and Ultrafast Extraction of Lignin Oligomers from Wood Biomass by Microwave-Assisted Treatment with Deep Eutectic Solvent

Y. Liu, W. Chen, Q. Xia, B. Guo, Q. Wang, S. Liu, Y. Liu, J. Li, H. Yu.

[ChemSusChem](#), 2017, 10, 1692.



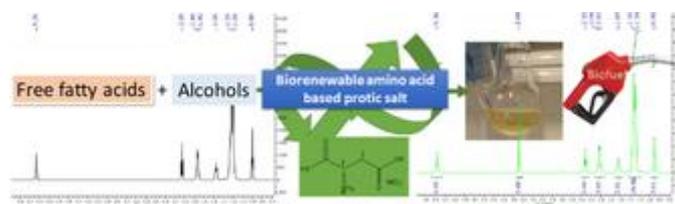
Abstract:

Lignocellulosic biomass is an abundant and renewable resource for the production of biobased value-added fuels, chemicals, and materials, but its effective exploitation by an energy-efficient and environmentally friendly strategy remains a challenge. Herein, a facile approach for efficiently cleaving lignin–carbohydrate complexes and ultrafast fractionation of components from wood by microwave-assisted treatment with deep eutectic solvent is reported. The solvent was composed of sustainable choline chloride and oxalic acid dihydrate, and showed a hydrogen-bond acidity of 1.31. Efficient fractionation of lignocellulose with the solvent was realized by heating at 80 °C under 800 W microwave irradiation for 3 min. The extracted lignin showed a low molecular weight of 913, a low polydispersity of 1.25, and consisted of lignin oligomers with high purity (ca. 96 %), and thus shows potential in downstream production of aromatic chemicals. The other dissolved matter mainly comprised glucose, xylose, and hydroxymethylfurfural. The undissolved material was cellulose with crystal I structure and a crystallinity of approximately 75 %, which can be used for fabricating nanocellulose. Therefore, this work promotes an ultrafast lignin-first biorefinery approach while simultaneously keeping the undissolved cellulose available for further utilization. This work is expected to contribute to improving the economics of overall biorefining of lignocellulosic biomass.

Catalytic Biodiesel Production Mediated by Amino Acid-Based Protic Salts

J. Li, Z. Guo

[ChemSusChem](#), 2017, 10, 1792.



Abstract:

Hetero- and homogeneous acid catalysts are effective catalysts for the production of biodiesel from oils containing high free fatty acids. The protic salts synthesized from natural amino acids were examined for catalytic activity and efficiency for the esterification of oleic acid after structural identification and characterization. In the esterification reaction of oleic acid with methanol, [Asp][NO₃] was the best catalyst, and its high activity correlated to its high Hammett acidity. The optimal reaction conditions for the esterification of oleic acid to achieve 97 % biodiesel yield were: 70 °C, 10 % catalyst loading (w/w, on oleic acid basis), methanol/oleic acid ratio 7.5:1, and 5 h. Generally, [Asp][NO₃] could be a good catalyst for the esterification of oleic acid with alcohols with chain lengths of up to six. The biodiesel yield of 93.86 % obtained from palm fatty acid distillate implies that the catalyst has potential for industrial application. A study of the kinetics indicated that the reaction followed pseudo-first-order kinetics with an activation energy and pre-exponential of 57.36 kJ mol⁻¹ and 44.24 × 10⁵ min⁻¹, respectively. The aspartic acid-derived protic salt is a promising, operationally simple, sustainable, renewable, and possibly biodegradable catalyst for the conversion of free fatty acids into biodiesel.

Solvent- and Halogen-Free Modification of Biobased Polyphenols to Introduce Vinyl Groups: Versatile Aromatic Building Blocks for Polymer Synthesis

A. Duval, L. Avérous.

[ChemSusChem](#), 2017, 10, 1813.



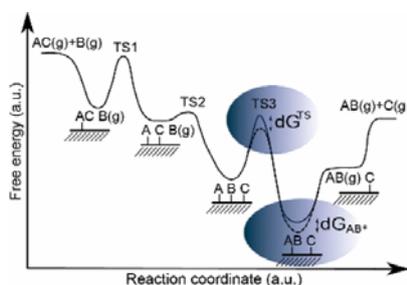
Abstract:

Various biobased polyphenols (lignins and condensed tannins) were derivatized with vinyl ethylene carbonate, a functional cyclic carbonate, to obtain multifunctional aromatic polymers bearing vinyl groups. The reaction was optimized on a condensed tannin and soda lignin. In both cases, full conversion of the phenol groups was achieved in only 1 h at 150 °C without solvent and with K₂CO₃ as a cheap and safe catalyst. This reaction was later applied to other condensed tannins and technical lignins (Kraft and organosolv), showing only little dependence on the chemical structure of the polyphenols. The obtained derivatives were thoroughly characterized by ¹H and ³¹P NMR spectroscopy, FTIR spectroscopy, and size-exclusion chromatography. The developed method was compared with previously published protocols for the introduction of vinyl groups on lignin, and shows promising advances toward the modification of biobased polyphenols according to green chemistry principles. The obtained macromolecules show great potential as highly versatile biobased aromatic building blocks for the synthesis of polymers through, for example, radical, metathesis, or thiol–ene reactions.

The Degree of Rate Control: A Powerful Tool for Catalysis Research

Charles T. Campbell

[ACS Catal. 2017, 7, 2770.](#)

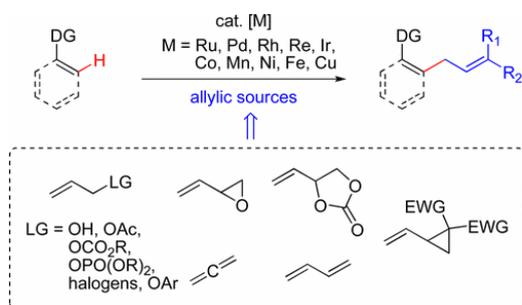


The “degree of rate control” (DRC) is a mathematical approach for analyzing multistep reaction mechanisms that has proven very useful in catalysis research. It identifies the “rate-controlling transition states and intermediates” (i.e., those whose DRCs are large in magnitude). Even in mechanisms with over 30 intermediates and transition states, these are generally just a few distinct chemical species whose energies, if they could be independently changed, would achieve a faster net reaction rate to the product of interest. For example, when there is a single “rate-determining step”, the DRC for its transition state (TS) is 1, which means (by definition) that if this TS’s energy could be decreased by kBT (where kB is Boltzmann’s constant and T is temperature), the net rate would increase by a factor of e . Because the (relative) energies of these key adsorbed intermediates and transition states can be adjusted by modifying the catalyst or solvent, or even a reactant’s molecular structure, the DRC values provide important ideas for catalyst improvement. The species with large DRCs are also the ones whose energetics must be most accurately measured or calculated to achieve an accurate kinetic model for any reaction mechanism. A tutorial on DRC analysis, the calculation of DRCs, and examples of the applications of DRCs in catalysis research is presented here. Applications of DRC analysis include the following: clarifying reaction kinetics, improving the accuracy of computational models, improving reaction conditions, improving choice of oxidant in selective oxidation, incorporation in algorithms which calculate net reaction rates of multistep mechanisms without solving the differential equations involved, and high-throughput computational screening of catalyst materials. Because DRC values can be determined experimentally, a full microkinetic model is not required to take advantage of DRC analysis.

Recent Advances in Catalytic C(sp²)-H Allylation Reactions

Neeraj Kumar Mishra, Satyasheel Sharma, Jihye Park, Sangil Han, In Su Kim

[ACS Catal. 2017, 7, 2821.](#)



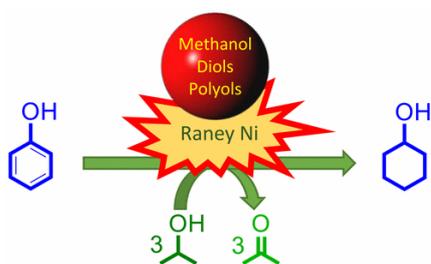
The linear or branched allyl moieties on aromatic rings are well-known as ubiquitous structural motifs found in a range of natural products and medicinally relevant molecules. They also represent an important class of organic intermediates for the transformation of an olefin group into many useful functional groups. Established methods for the installation of allylic groups rely primarily on nucleophilic substitution or transmetalation of aryl metal complexes to allyl electrophiles, Lewis acid-mediated Friedel–Crafts allylation of electron-rich arenes, and Tsuji–Trost allylation reactions with π -allyl species. Complementing previous protocols, the transition metal-catalyzed allylation reactions via

C–H activation strategy using various allylic surrogates like allylic acetates, allylic carbonates, allylic phosphonates, allylic halides, allylic alcohols, vinyl oxiranes, allenes, 1,3-dienes, and others have recently emerged as a powerful tool for creating the corresponding allyl, crotyl and prenyl moieties. This review, which includes all reported methods in the literature until the beginning of 2017, focuses on recent progress on direct allylation reactions of aromatic and vinylic C(sp²)–H bonds with allylic sources and various transition metal catalysts.

Liquid-Phase H-Transfer from 2-Propanol to Phenol on Raney Ni: Surface Processes and Inhibition

Marco Kennema, Ilton Barros Dalto de Castro, Fabian Meemken, Roberto Rinaldi

[ACS Catal. 2017, 7, 2437.](#)

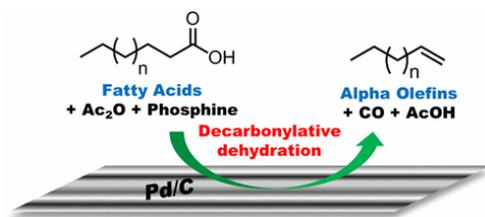


Raney Ni is perhaps the most widely used catalyst for the transformation of biogenic molecules in industrial practice (e.g., as in the production of sugar alcohols and hardening of vegetable oils). Currently, Raney Ni has found another key application; the catalytic upstream biorefining (CUB) of lignocellulose in which the soluble products released from the lignocellulosic matrix undergo reductive processes, rendering depolymerized lignin oils in addition to high-quality holocellulosic pulps. Despite the industrial importance of Raney Ni, its surface chemistry is poorly understood. In this study, using the H-transfer reaction between 2-propanol (2-PrOH) and phenol as a model reaction, we studied the influence of various alcohols on the catalytic performance of Raney Ni. For the H-transfer hydrogenation of phenol to cyclohexanol, the inhibition of the catalyst increases in the order of secondary alcohols < primary alcohols < polyols at 130 °C. To better understand the observed inhibition, we also studied the molecular interactions of the various alcohols at the catalytic solid–liquid interface using in situ attenuated total reflection infrared (ATR-IR) spectroscopy. The in situ spectroscopic data revealed that 2-PrOH adsorbs on at least two chemically different sites on the surface of Raney Ni. One of these two adsorption sites was attributed to the Ni site responsible for the saturation of the phenolic ring. The ATR-IR spectroscopic data also shows that the adsorption of phenol involves its hydroxyl group. Notably, the phenolic ring was found to be tilted with respect to the surface. Competitive adsorption of various other alcohols was also investigated at the catalytic solid–liquid interface. The presence of methanol inhibited the adsorption of 2-PrOH to a significantly greater degree than phenol. Therefore, it is proposed that hydrogen transfer hydrogenation of the phenolic ring is inhibited in the presence of additional alcohols mainly due to the competitive adsorption with 2-PrOH. Several polyols were found to interact through a bidentate interaction with the catalyst surface, which explains their stronger inhibition compared to primary alcohols. In a broader context, this study proposes the effect of hemicellulose sugars and sugar alcohols, formed in the CUB process, upon the product selectivity of CUB catalyzed by Raney Ni and using 2-PrOH as an H-donor.

A Heterogeneous Catalyst for the Transformation of Fatty Acids to α -Olefins

Anamitra Chatterjee, Vidar R. Jensen

[ACS Catal. 2017, 7, 2543.](#)



Heterogeneous catalysts have so far not been very efficient [turnover frequency (TOF) < 19 h⁻¹] or very selective ($\leq 60\%$) for α -olefin formation in deoxygenation of fatty acids. Here we report more than 20-fold higher activity (TOF = 420 h⁻¹) and high selectivity (>95%) for one such deoxygenation, decarbonylative dehydration, by using a heterogeneous Pd/C catalyst in the presence of phosphine ligands. The process is solvent free, allows for catalyst recycling, and does not require in situ distillation of the product to maintain high selectivity.

Promoted Synergic Catalysis between Metal Ni and Acid–Base Sites toward Oxidant-Free Dehydrogenation of Alcohols

Hao Chen, Shan He*, Ming Xu, Min Wei*, David G. Evans, and Xue Duan

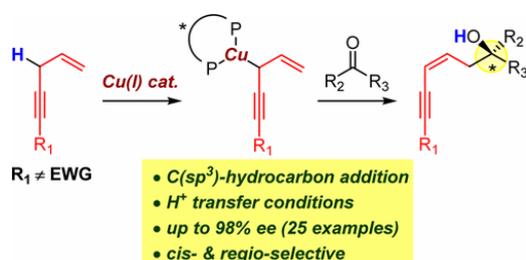
[ACS Catal. 2017, 7, 2735.](#)



In a number of heterogeneous catalysis processes, synergic catalysis of metal and acid–base sites of supports is of vital importance and remains a challenge to obtain largely improved catalytic performance. Herein, an acid–base-promoted Ni nanocatalyst supported on Ni/Al mixed metal oxide (denoted as Ni/NiAl-MMO) was prepared on the basis of the in situ structural topotactic transformation of NiAl-layered double hydroxide (NiAl-LDH) precursor. In situ studies including XRD, Raman, and EXAFS verify that the cubic NiO-like phase (Al³⁺-doped NiO species), with medium-strong acid–base sites (Ni δ^+ –O δ^- pair), are well-distributed in the amorphous Al₂O₃ to form NiAl-MMO support. The concentration of Ni active site and acid–base sites can be simultaneously enhanced by precisely tuning the in situ structural topotactic transformation parameters of LDH precursor as revealed by CO pulse chemisorption, CO₂-TPD, and NH₃-TPD, so as to achieve a promoted synergic catalysis between metal Ni and acid–base sites. The resulting Ni/NiAl-MMO(400) shows largely enhanced catalytic performance (formation rate of 2-octanone: 78.5 mmol g⁻¹ h⁻¹) toward oxidant-free dehydrogenation of 2-octanol to 2-octanone, which is 3.9 times larger than the conventional Ni/Al₂O₃ catalyst (formation rate of 2-octanone: 20.1 mmol g⁻¹ h⁻¹). Studies on the structure–property correlation based on operando time-resolved EXAFS spectra and kinetic isotope effect (KIE) measurements reveal that such an excellent catalytic performance is attributed to the optimized synergic catalysis between NiO and medium-strong acid–base sites of support, which accelerates the bond cleavage of kinetically key steps: α -C–H and O–H, respectively.

Copper(I)-Catalyzed Enantioselective Addition of Enynes to Ketones

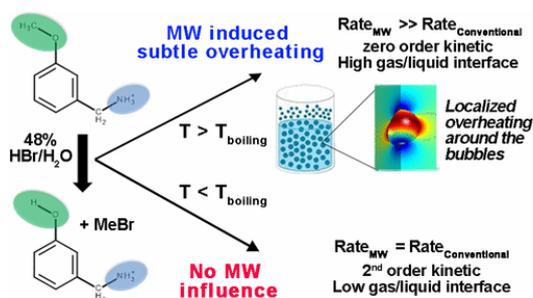
Xiao-Feng Wei†, Xiao-Wei Xie†, Yohei Shimizu*†, and Motomu Kanai*††

[J. Am. Chem. Soc. 2017, 139, 4647.](#)

A copper(I)-catalyzed enantioselective addition of enynes to ketones was developed. The method allows facile construction of enantiomerically enriched tertiary alcohols using skipped enynes as stable hydrocarbon pronucleophiles. The combination of a soft copper(I)-conjugated Brønsted base catalyst with a chiral diphosphine ligand, (S,S)-Ph-BPE, enabled chemoselective deprotonation of the skipped enynes in the presence of ketones bearing intrinsically more acidic α -protons. The catalytically generated chiral allylcopper species enantio-, diastereo-, regio-, and chemoselectively reacted with ketones, thereby demonstrating excellent substrate generality with functional group tolerance. The skipped enyne moieties of the pronucleophiles were exclusively converted to cis-conjugated enynes, which will eventually allow for further versatile transformations.

Subtle Microwave-Induced Overheating Effects in an Industrial Demethylation Reaction and Their Direct Use in the Development of an Innovative Microwave Reactor

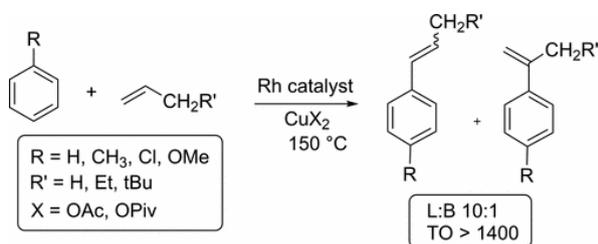
Mario De bruyn, Vitaliy L. Budarin, Guido S. J. Sturm // , Georgios D. Stefanidis, Marilena Radoiu, Andrzej Stankiewicz, Duncan J. Macquarrie

[J. Am. Chem. Soc. 2017, 139, 5431.](#)

A systematic study of the conventional and microwave (MW) kinetics of an industrially relevant demethylation reaction is presented. In using industrially relevant reaction conditions the dominant influence of the solvent on the MW energy dissipation is avoided. Below the boiling point, the effect of MWs on the activation energy E_a and k_0 is found nonexistent. Interestingly, under reflux conditions, the microwave-heated (MWH) reaction displays very pronounced zero-order kinetics, displaying a much higher reaction rate than observed for the conventionally thermal-heated (CTH) reaction. This is related to a different gas product (methyl bromide, MeBr) removal mechanism, changing from classic nucleation into gaseous bubbles to a facilitated removal through escaping gases/vapors. Additionally, the use of MWs compensates better for the strong heat losses in this reaction, associated with the boiling of HBr/water and the loss of MeBr, than under CTH. Through modeling, MWH was shown to occur inhomogeneously around gas/liquid interfaces, resulting in localized overheating in the very near vicinity of the bubbles, overall increasing the average heating rate in the bubble vicinity vis-à-vis the bulk of the liquid. Based on these observations and findings, a novel continuous reactor concept is proposed in which the escaping MeBr and the generated HBr/water vapors are the main driving forces for circulation. This reactor concept is generic in that it offers a viable and low cost option for the use of very strong acids and the managed removal/quenching of gaseous byproducts.

Catalytic Synthesis of “Super” Linear Alkenyl Arenes Using an Easily Prepared Rh(I) Catalyst

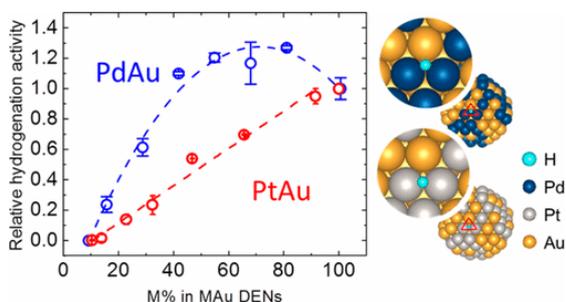
Michael S. Webster-Gardiner, Junqi Chen, Benjamin A. Vaughan, Bradley A. McKeown, William Schinski, T. Brent Gunnoe

[J. Am. Chem. Soc. 2017, 139, 5474.](#)

Linear alkyl benzenes (LAB) are global chemicals that are produced by acid-catalyzed reactions that involve the formation of carbocationic intermediates. One outcome of the acid-based catalysis is that 1-phenylalkanes cannot be produced. Herein, it is reported that $[\text{Rh}(\mu\text{-OAc})(\eta^2\text{-C}_2\text{H}_4)_2]_2$ catalyzes production of 1-phenyl substituted alkene products via oxidative arene vinylation. Since C=C bonds can be used for many chemical transformations, the formation of unsaturated products provides a potential advantage over current processes that produce saturated alkyl arenes. Conditions that provide up to a 10:1 linear:branched ratio have been achieved, and catalytic turnovers >1470 have been demonstrated. In addition, electron-deficient and electron-rich substituted benzenes are successfully alkylated. The Rh catalysis provides ortho:meta:para selectivity that is opposite to traditional acid-based catalysis.

Tunability of the Adsorbate Binding on Bimetallic Alloy Nanoparticles for the Optimization of Catalytic Hydrogenation

Long Luo, Zhiyao Duan, Hao Li, Joohoon Kim, Graeme Henkelman, Richard M. Crooks

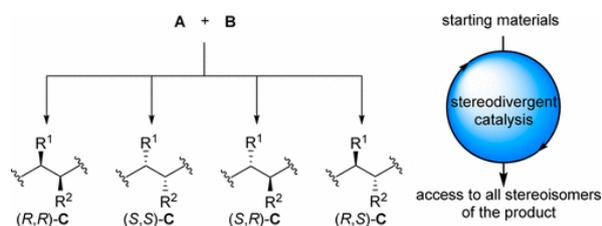
[J. Am. Chem. Soc. 2017, 139, 5538.](#)

In this paper, we show that PtAu and PdAu random alloy dendrimer-encapsulated nanoparticles with an average size of ~1.6 nm have different catalytic activity trends for allyl alcohol hydrogenation. Specifically, PtAu nanoparticles exhibit a linear increase in activity with increasing Pt content, whereas PdAu dendrimer-encapsulated nanoparticles show a maximum activity at a Pd content of ~60%. Both experimental and theoretical results suggest that this contrasting behavior is caused by differences in the strength of H binding on the PtAu and PdAu alloy surfaces. The results have significant implications for predicting the catalytic performance of bimetallic nanoparticles on the basis of density functional theory calculations.

Stereodivergence in Asymmetric Catalysis

Simon Krautwald, Erick M. Carreira

[J. Am. Chem. Soc. 2017, 139, 5627.](#)

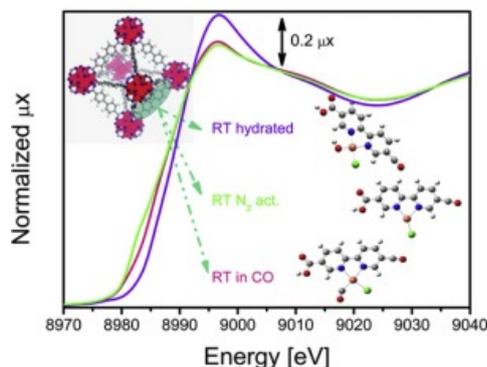


This Perspective presents an overview of catalytic enantioselective transformations that allow convenient access to all stereoisomers of a given product with multiple stereogenic centers. Particular focus is placed on discussion of the concept of stereodivergent dual catalysis and its application in target-oriented synthesis. The potential of this concept in the development of new transformations as well as implications for achieving stereochemical diversity in library design and diversity-oriented synthesis are also discussed.

Exploring structure and reactivity of Cu sites in functionalized UiO-67 MOFs

Luca Braglia, Elisa Borfecchia, Lorenza Maddalena, Sigurd Øien, Kirill A. Lomachenko, Aram L. Bugaev, Silvia Bordiga, Alexander V. Soldatov, Karl Petter Lillerud, Carlo Lamberti

[Catalysis Today, 283, 2017, 89–103](#)



The exceptional thermal stability of the UiO-67/68-family MOFs makes them ideal candidates to explore post-synthetic functionalization routes aiming to the heterogenization of homogeneous catalysts. We previously demonstrated that a small fraction of the linkers in the UiO-67 MOF can be replaced by bipyridine-dicarboxylate (bpydc) moieties exhibiting metal-chelating ability and enabling the grafting of Pt(II) and Pt(IV) ions in the MOF framework [Chem. Mater., 27 (2015) 1042]. Herein, we investigate a novel Cu-functionalized UiO-67 MOF obtained by a simple synthesis method, consisting in contacting the bpydc-containing UiO-67-bpy MOF with a CuCl_2 dihydrate precursor. By combining *in situ* and *operando* XAS and FTIR spectroscopies, we assessed the successful incorporation of well-defined Cu complexes in the UiO-67 framework and explored local coordination geometry, redox properties and reactivity of the dominant Cu species formed in different conditions relevant to potential future applications in catalysis. EXAFS fits and XANES simulations, based on DFT-optimized geometries, yielded detailed structural and electronic information on the major Cu-species formed. Data analysis revealed three-coordinated Cu(I) complexes with the bpydc linker of the Cu-UiO-67 MOFs and a Cl^- ligand, formed after thermal treatment at 523 K in inert gas flow able to efficiently and reversibly form Cu(I)-mono-carbonyl adducts with CO adsorbate.

ATR-IR spectroscopic cell for in situ studies at solid-liquid interface at elevated temperatures and pressures

Kamila Koichumanova, Aura Visan, Bert Geerdink, Rob G.H. Lammertink, Barbara L. Mojet, K. Seshan, Leon Lefferts

[Catalysis Today, 283, 2017, 185-194](#)

An in situ ATR-IR spectroscopic cell suitable for studies at solid-liquid interface is described including the design and experimental details in continuous flow mode at elevated temperatures (230 °C) and pressures (30 bar). The design parameters considered include the cell geometry, the procedure to immobilize the catalyst on a cylindrical internal reflection element (IRE), as well as shape and material of choice for the IRE, optics configuration and temperature/pressure control. The hydrodynamics and concentration profiles in the cell were assessed via numerical simulations using incompressible Navier-Stokes equation and convection-diffusion model showing significant deviation from ideal plug flow. Experimental response times at ambient and elevated temperatures derived from ATR-IR spectra agree well with the simulations, demonstrating that the hydrodynamics of the reactor is accurately described. Homogeneous Pt/ZrO₂ and AlO(OH) layers were obtained by spray-coating which are stable for at least 12 h during testing in 2 mL/min water flow. Preliminary spectra collected during aqueous phase reforming of hydroxyacetone demonstrated that the cell can be operated at 230 °C and 30 bar with simultaneous detection of IR-active species both in the liquid as well as adsorbed on the surface of the catalyst.

Naked d -orbital in a centrochiral Ni(II) complex as a catalyst for asymmetric [3+2] cycloaddition

Yoshihiro Sohtome, Genta Nakamura, Atsuya Muranaka, Daisuke Hashizume, Sylvain Lectard, Teruhisa Tsuchimoto, Masanobu Uchiyama & Mikiko Sodeoka

[Nature Communications 8, 2017, 14875](#)

Chiral metal catalysts have been widely applied to asymmetric transformations. However, the electronic structure of the catalyst and how it contributes to the activation of the substrate is seldom investigated. Here, we report an empirical approach for providing insights into the catalytic activation process in the distorted Ni(II)-catalysed asymmetric [3+2] cycloaddition of α -ketoesters. We quantitatively characterize the bonding nature of the catalyst by means of electron density distribution analysis, showing that the distortion around the Ni(II) centre makes the dz^2 orbital partially 'naked', wherein the labile acetate ligand is coordinated with electrostatic interaction. The electron-deficient dz^2 orbital and the acetate act together to deprotonate the α -ketoester, generating the (Λ)-Ni(II)-enolate. The solid and solution state analyses, together with theoretical calculations, strongly link the electronic structure of the centrochiral octahedral Ni(II) complex and its catalytic activity, depicting a cooperative mechanism of enolate binding and outer sphere hydrogen-bonding activation.

Easy access to nucleophilic boron through diborane to magnesium boryl metathesis

Anne-Frédérique Pécharman, Annie L. Colebatch, Michael S. Hill, Claire L. McMullin, Mary F. Mahon & Catherine Weetman

[Nature Communications 8, 2017, 15022](#)

Organoboranes are some of the most synthetically valuable and widely used intermediates in organic and pharmaceutical chemistry. Their synthesis, however, is limited by the behaviour of common boron starting materials as archetypal Lewis acids such that common routes to organoboranes rely on the reactivity of boron as an electrophile. While the realization of convenient sources of nucleophilic boryl anions would open up a wealth of opportunity for the development of new routes to organoboranes, the synthesis of current candidates is generally limited by a need for highly reducing reaction conditions. Here, we report a simple synthesis of a magnesium boryl through the heterolytic activation of the B–B bond of bis(pinacolato)diboron, which is achieved by treatment of an easily generated magnesium diboranate complex with 4-dimethylaminopyridine. The magnesium boryl is shown to act as an unambiguous nucleophile through its reactions with iodomethane, benzophenone and N,N' -di-isopropyl carbodiimide and by density functional theory.

Pd-catalysed ligand-enabled carboxylate-directed highly regioselective arylation of aliphatic acids

Yan Zhu, Xiaolan Chen, Chunchen Yuan, Guobao Li, Jingyu Zhang & Yingsheng Zhao

[Nature Communications 8, 2017, 14904](#)

α -amino acids bearing aromatic side chains are important synthetic units in the synthesis of peptides and natural products. Although various β -C-H arylation methodologies for amino acid derivatives involving the assistance of directing groups have been extensively developed, syntheses that directly employ N -protected amino acids as starting materials remain rare. Herein, we report an N -acetyl-glycine-enabled Pd-catalysed carboxylate-directed β -C(sp^3)-H arylation of aliphatic acids. In this way, various non-natural amino acids can be directly prepared from phthaloylalanine in one step in good to excellent yields. Furthermore, a series of aliphatic acids have been shown to be amenable to this transformation, affording β -arylated propionic acid derivatives in moderate to good yields. More importantly, this ligand-enabled direct β -C(sp^3)-H arylation could be easily scaled-up to 10 g under reflux conditions, highlighting the potential utility of this synthetic method.

Homogeneously catalysed conversion of aqueous formaldehyde to H₂ and carbonate

M. Trincado, Vivek Sinha, Rafael E. Rodríguez-Lugo, Bruno Pribanic, Bas de Bruin & Hansjörg Grützmacher

[Nature Communications 8, 2017, 14990](#)

Small organic molecules provide a promising solution for the requirement to store large amounts of hydrogen in a future hydrogen-based energy system. Herein, we report that diolefin–ruthenium complexes containing the chemically and redox non-innocent ligand trop₂dad catalyse the production of H₂ from formaldehyde and water in the presence of a base. The process involves the catalytic conversion to carbonate salt using aqueous solutions and is the fastest reported for acceptorless formalin dehydrogenation to date. A mechanism supported by density functional theory calculations postulates protonation of a ruthenium hydride to form a low-valent active species, the reversible uptake of dihydrogen by the ligand and active participation of both the ligand and the metal in substrate activation and dihydrogen bond formation.

Solid-state synthesis of ordered mesoporous carbon catalysts via a mechanochemical assembly through coordination cross-linking

Pengfei Zhang, Li Wang, Shize Yang, Jennifer A. Schott, Xiaofei Liu, Shannon M. Mahurin, Caili Huang, Yu Zhang, Pasquale F. Fulvio, Matthew F. Chisholm & Sheng Dai

[Nature Communications 8, 2017, 15020](#)

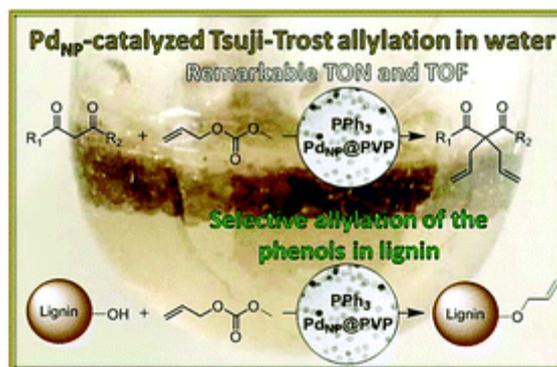
Ordered mesoporous carbons (OMCs) have demonstrated great potential in catalysis, and as supercapacitors and adsorbents. Since the introduction of the organic–organic self-assembly approach in 2004/2005 until now, the direct synthesis of OMCs is still limited to the wet processing of phenol-formaldehyde polycondensation, which involves soluble toxic precursors, and acid or alkali catalysts, and requires multiple synthesis steps, thus restricting the widespread application of OMCs. Herein, we report a simple, general, scalable and sustainable solid-state synthesis of OMCs and nickel OMCs with uniform and tunable mesopores (~4–10 nm), large pore volumes (up to 0.96 cm³ g⁻¹) and high-surface areas exceeding 1,000 m² g⁻¹, based on a mechanochemical assembly between polyphenol-metal complexes and triblock co-polymers. Nickel nanoparticles (~5.40 nm) confined in the cylindrical nanochannels show great thermal stability at 600 °C. Moreover, the nickel OMCs offer exceptional activity in the hydrogenation of bulky molecules (~2 nm).

A. Llevot, B. Monney, A. Sehlinger, S. Behrens and M. A. R. Meier. **Highly efficient Tsuji–Trost allylation in water catalyzed by Pd-nanoparticles.**

Chem. Commun., 2017

DOI: [10.1039/C7CC02380D](https://doi.org/10.1039/C7CC02380D)

Palladium nanoparticles stabilized by poly(vinylpyrrolidone) catalyze Tsuji–Trost allylations in water with very high turnover numbers. The di-allylation of methylene active compounds and the allylation of bio-based phenols was performed in high yield. **The allylation of lignin** showed a high selectivity towards the phenolic OH groups.

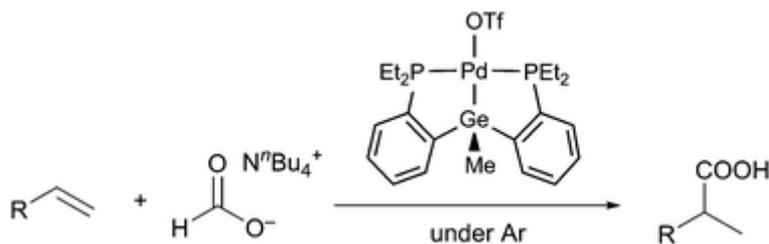


Jun Takaya, Ko Miyama, Chuan Zhu and Nobuharu Iwasawa. **Metallic reductant-free synthesis of α -substituted propionic acid derivatives through hydrocarboxylation of alkenes with a formate salt.**

Chem. Commun., 2017, **53**, 3982-3985

DOI: [10.1039/C7CC01377A](https://doi.org/10.1039/C7CC01377A)

A PGeP–pincer palladium-catalyzed hydrocarboxylation of styrenes to obtain pharmaceutically important α -arylpropionic acid derivatives was achieved using a formate salt as both a reductant and a CO₂ source. The reaction was also applicable to vinylsulfone and acrylates. Isotope labeling experiments demonstrated that a CO₂-recycling mechanism is operative through generation and reaction of a benzylpalladium complex as a carbon nucleophile. This protocol has realized a mild and atom economical CO₂-fixation reaction without the necessity of using strong metallic reductants.

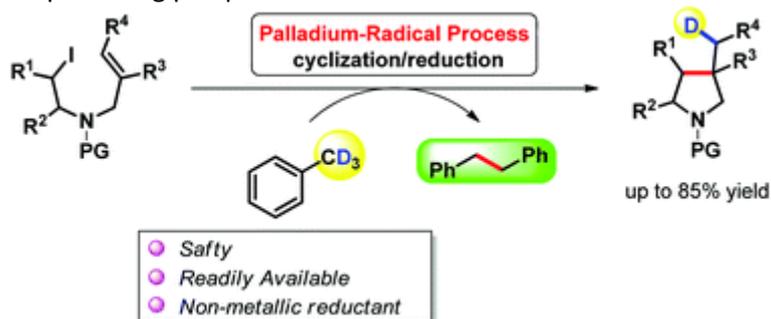


Xu Dong, Jie Cui, Jian Song, Ying Han, Qing Liu, Yunhui Dong and Hui Liu. **Palladium-catalyzed intramolecular reductive olefin hydrocarbonation: benzylic hydrogen serving as a new hydrogen donor.**

Chem. Commun., 2017

DOI: [10.1039/C7CC01423F](https://doi.org/10.1039/C7CC01423F)

A palladium-catalyzed intramolecular hydrocarbonation of unactivated alkenes was achieved, in which toluene is used as a hydrogen donor for the first time. The radical transfer hydrogenation is designed and realized based on the Bond Dissociation Energy (BDE) value. A toluene derivative, which is cheap, readily available and easy to handle, serves as a new hydrogen donor in radical involved reactions, providing a novel and promising perspective for future reductive reactions.

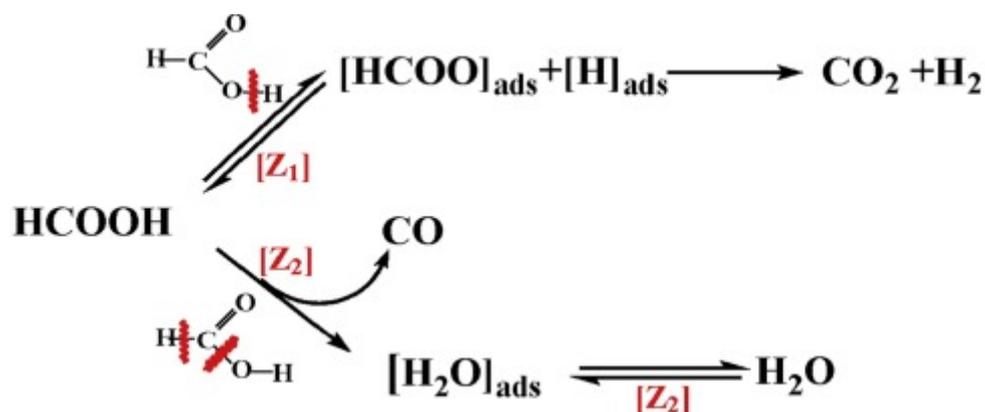


E.M. Sadovskaya, Yu. A. Chesalov, V.B. Goncharov, V.I. Sobolev, T.V. Andrushkevich. **Formic acid decomposition over V-Ti oxide catalyst: Mechanism and kinetics.**

Journal of Molecular Catalysis A: Chemical, 2017, **430**, 54–62

DOI: [10.1016/j.molcata.2016.12.010](https://doi.org/10.1016/j.molcata.2016.12.010)

- HCOOH decomposition to CO₂ and CO on V-Ti catalyst proceeds via distinct routes.
- Dehydrogenation to CO₂ proceeds via the conventional “formate” mechanism.
- Dehydration proceeds via molecular adsorbed HCOOH decomposing to CO and hydroxyls.
- Rate constants and activation energies of the limiting stages are calculated.

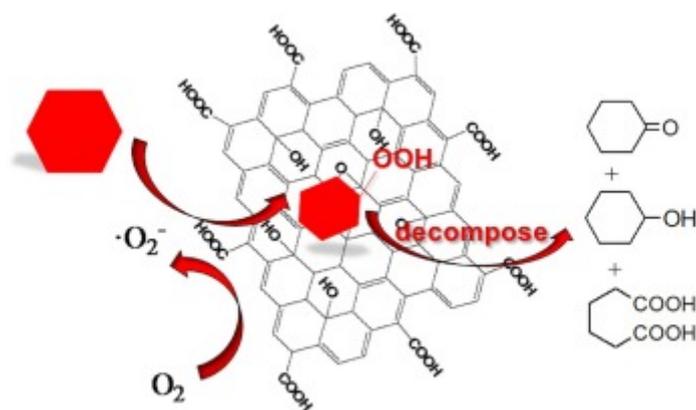


Yepeng Xiao, Jincheng Liu, Kaihong Xie, Weibin Wang, Yanxiong Fang. **Aerobic oxidation of cyclohexane catalyzed by graphene oxide: Effects of surface structure and functionalization.**

Journal of Molecular Catalysis A: Chemical, 2017, **431**, 1–8

DOI: [10.1016/j.mcat.2017.01.020](https://doi.org/10.1016/j.mcat.2017.01.020)

- Highest conversion of 17.7% was obtained by using NGO as a metal-free catalyst.
- The catalytic activity and stability were improved by decreasing the size of GO sheets.
- The increased content of –COOH in the GO was in favour of the catalytic activity.
- Superoxide radical ($\cdot\text{O}_2^-$) was the active oxygen species in this catalytic oxidation process.
- The peroxide decomposition was accelerated by the intact sp² system within GO sheets.

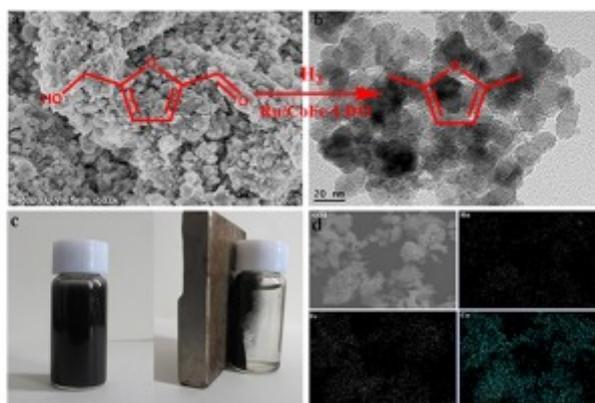


Qingyang Li, Ping Man, Liqian Yuan, Pilan Zhang, Yan Li, Shiyun Ai. **Ruthenium supported on CoFe layered double oxide for selective hydrogenation of 5-hydroxymethylfurfural.**

Journal of Molecular Catalysis A: Chemical, 2017, **431**, 32–38

DOI: [10.1016/j.mcat.2017.01.011](https://doi.org/10.1016/j.mcat.2017.01.011)

- LDH and derived LDO were prepared as support.
- The supported Ru catalyst was employed used in HMF hydrogenation reaction.
- Ru/CoFe-LDO exhibited good stability and catalytic activity.
- The calcination temperature influences the activity and selectivity greatly.
- The cooperation between metallic Ru and CoFe-LDO facilitates the process of HMF hydrogenation.

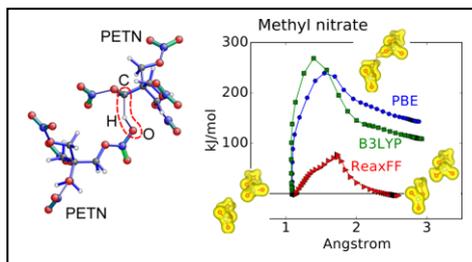


Hydrogen Transfer in Energetic Materials from ReaxFF and DFT Calculations

Oleg V. Sergeev, and Alexey V. Yanilkin.

[J. Phys. Chem. A 2017, 121, 3019.](#)

(TOC)



Abstract

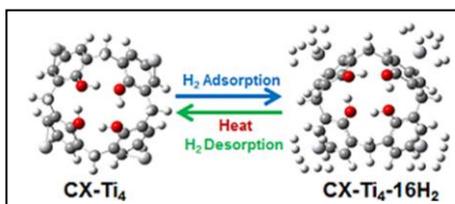
Energetic materials are characterized by fast and complex chemical reactions. It makes them hardly available for kinetic experiments in relevant conditions and a good target for reactive molecular dynamics simulations. In this work, unimolecular and condensed-phase thermal decomposition of pentaerythritol tetranitrate (PETN) are investigated by ReaxFF molecular dynamics. It is shown that the decomposition kinetics in condensed phase may be described with the activation barrier lower by a factor of 2 than that for isolated molecules. The effect of the intermolecular hydrogen transfer is revealed in condensed phase. Energetic barriers for hydrogen transfer in two energetic materials (methyl nitrate, which is a nitroester as well as PETN, and o-nitrotoluene) are studied with ReaxFF and DFT using nudged elastic band technique. The results indicate that ReaxFF gives significantly lower activation energy for intermolecular hydrogen transfer in nitroesters than different DFT approximations, which explains the molecular dynamics results for PETN.

Fundamental Study of Reversible Hydrogen Storage in Titanium- and Lithium-Functionalized Calix[4]arene

Sandeep Kumar and T. J. Dhillip Kumar

[J. Phys. Chem. C 2017, 121, 8703–8710.](#)

(TOC)



Abstract

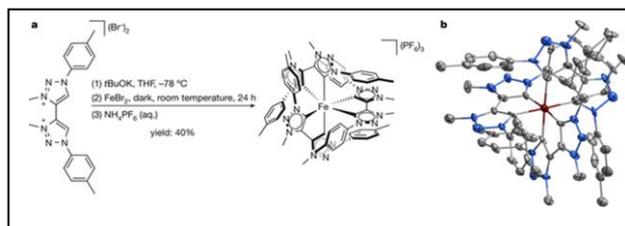
Hydrogen is the most promising candidate for a sustainable energy source in the transport sector. However, the storage of hydrogen is a major problem. Calix[4]arene (CX) is functionalized with Ti and Li metals on the delocalized π electrons of benzene rings, and the metal-functionalized system is studied for hydrogen storage efficiency by applying density functional theory using the M06 hybrid functional and 6-311G(d,p) basis set. The calculated binding energy indicates Ti coordinates with CX strongly while Li coordinates weakly and the binding of CX and metal is through Dewar mechanism. On saturation with hydrogen, each Ti atom traps four H₂ molecules while each Li atom traps three H₂ molecules on CX. Hydrogen molecules are adsorbed on the metal atoms by Kubas–Niu–Rao–Jena interaction. The global reactivity index obtained for the system obeys the maximum hardness and minimum electrophilicity principle. Molecular dynamics simulations are performed using spin-polarized generalized gradient approximation with the Perdew–Burke–Ernzerhof functional including Grimme diffusion parameter on H₂ saturated systems. The dissociation of H₂ molecules in the Ti-functionalized CX system begins from 273 K, while all the H₂ molecules are desorbed by 473 K. The storage capacity is found to be 8.7 wt % for Ti and 10.1 wt % for Li-functionalized CX. When the Ti atom is intercalated between the two CX moieties, the storage capacity does not reduce significantly. This study reveals that the Tifunctionalized CX is a potential reversible hydrogen storage material.

A low-spin Fe(III) complex with 100-ps ligand-to-metal charge transfer photoluminescence

Pavel Chábera, Yizhu Liu, Om Prakash, Erling Thyrhaug, Amal El Nahhas, Alireza Honarfar, Sofia Essén, Lisa A. Fredin, Tobias C. B. Harlang, Kasper S. Kjær, Karsten Handrup, Fredric Ericson, Hideyuki Tatsuno, Kelsey Morgan, Joachim Schnadt, Lennart Häggström, Tore Ericsson, Adam Sobkowiak, Sven Lidin, Ping Huang, Stenbjörn Styring, Jens Uhlig, Jesper Bendix, Reiner Lomoth, Villy Sundström, Petter Persson³ & Kenneth Wärnmark.

[Nature 2017, 543, 695.](#)

(TOC)



Abstract

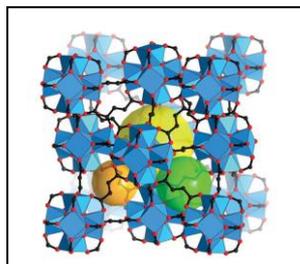
Transition-metal complexes are used as photosensitizers¹, in light-emitting diodes, for biosensing and in photocatalysis². A key feature in these applications is excitation from the ground state to a charge-transfer state^{3,4}; the long charge-transfer-state lifetimes typical for complexes of ruthenium⁵ and other precious metals are often essential to ensure high performance. There is much interest in replacing these scarce elements with Earth-abundant metals, with iron⁶ and copper⁷ being particularly attractive owing to their low cost and non-toxicity. But despite the exploration of innovative molecular designs^{6,8–10}, it remains a formidable scientific challenge¹¹ to access Earth-abundant transition-metal complexes with long-lived charge-transfer excited states. No known iron complexes are considered¹² photoluminescent at room temperature, and their rapid excited-state deactivation precludes their use as photosensitizers^{13–15}. Here we present the iron complex $[\text{Fe}(\text{btz})_3]^{3+}$ (where btz is 3,3'-dimethyl-1,1'-bis(p-tolyl)-4,4'-bis(1,2,3-triazol-5-ylidene)), and show that the superior σ -donor and π -acceptor electron properties of the ligand stabilize the excited state sufficiently to realize a long charge-transfer lifetime of 100 picoseconds (ps) and room-temperature photoluminescence. This species is a low-spin Fe(III) d^5 complex, and emission occurs from a long-lived doublet ligand-to-metal charge-transfer (2LMCT) state that is rarely seen for transition metal complexes^{4,16,17}. The absence of intersystem crossing, which often gives rise to large excited-state energy losses in transition metal complexes, enables the observation of spin-allowed emission directly to the ground state and could be exploited as an increased driving force in photochemical reactions on surfaces. These findings suggest that appropriate design strategies can deliver new iron-based materials for use as light emitters and photosensitizers.

Water harvesting from air with metal-organic framework powered by natural sunlight

Hyunho Kim, Sungwoo Yang, Sameer R. Rao, Shankar Narayanan, Eugene A. Kapustin, Hiroyasu Furukawa, Ari S. Umans, Omar M. Yaghi, Evelyn N. Wang

[Science 2017, 356, 430.](#)

(TOC)



Abstract

Atmospheric water is a resource equivalent to ~10% of all fresh water in lakes on Earth. However, an efficient process for capturing and delivering water from air, especially at low humidity levels (down to 20%), has not been developed. We report the design and demonstration of a device based on a porous metal-organic framework {MOF-801, [Zr₆O₄(OH)₄(fumarate)₆]}. This device captures water from the atmosphere at ambient conditions by using low-grade heat from natural sunlight at a flux of less than 1 sun (1 kilowatt per square meter). This device is capable of harvesting 2.8 liters of water per kilogram of MOF daily at relative humidity levels as low as 20% and requires no additional input of energy.