VIP The following Communications have been judged by at least two referees to be "very important papers" and will be published online at www.angewandte.org soon:

*T. Lewis, M. Faubel, B. Winter, J. C. Hemminger**
CO_2 Capture in an Aqueous Solution of an Amine: Role of the Solution Interface

*Y. H. Kim, S. Banta**
Complete Oxidation of Methanol in an Enzymatic Biofuel Cell by a Self-Assembling Hydrogel Created from Three Modified Dehydrogenases

*L. Furst, J. M. R. Narayanam, C. R. J. Stephenson**
Total Synthesis of (+)-Gliocladin C Enabled by Visible-Light Photoredox Catalysis

*Y. Kitagawa, H. Segawa, K. Ishii**
Magnetochiral Dichroism of Organic Compounds

P. Höhn, F. Jach, B. Karabiyik, S. Agrestini, F. R. Wagner, M. Ruck, L. H. Tjeng, R. Kniep**
Highly Reduced Cobaltates $Sr_3[Co(CN)_3]$ and $Ba_3[Co(CN)_3]$: Crystal Structure, Chemical Bonding, and Conceptional Considerations

R. M. Culik, A. L. Serrano, M. R. Bunagan, F. Gai**
Achieving Secondary Structural Resolution in Kinetic Measurements of Protein Folding: A Case Study of the Folding Mechanism of Trp-cage

*J. Huber, B. Scheinhardt, T. Geldhauser, J. Boneberg, S. Mecking**
Laser-Interference Patterning of Polymerization Catalysts

*S. Bernhardt, G. Manolikakes, T. Kunz, P. Knochel**
Preparation of Solid Salt-Stabilized Organozinc Reagents: Application to Cross-Couplings and Carbonyl Additions

*L. P. Hansen, Q. M. Ramasse, C. Kisielowski, M. Brorson, E. Johnson, H. Topsøe, S. Helveg**
Atomic-Scale Edge Structures on Industrial MoS_2 Nanocatalysts

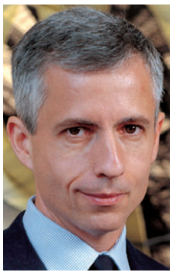
C.-Y. Chang, C.-E. Wu, S.-Y. Chen, C. Cui, Y.-J. Cheng, C.-S. Hsu, Y.-L. Wang,* Y. Li*
Enhanced Performance and Stability of a Polymer Solar Cell by Incorporating Vertically Aligned, Cross-Linked Fullerene Nanorods

Author Profile

"My favorite place on earth is with friends and family. The greatest scientific advance in the next decade will be the union of directed evolution and metal catalysis. …"
This and more about Michael J. Krische can be found on page 8782.

News

P. Bäuerle



E. N. Jacobsen

K. Tanino

G. A. Somorjai

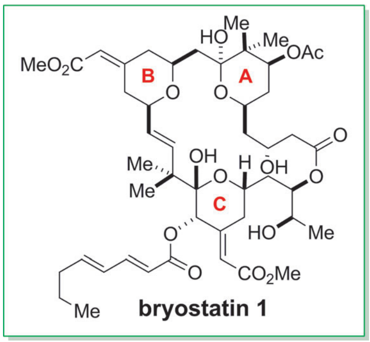
Books

Highlights

Total Synthesis

S. Manaviazar, K. J. Hale* ___ **8786 – 8789**

Total Synthesis of Bryostatin 1: A Short Route



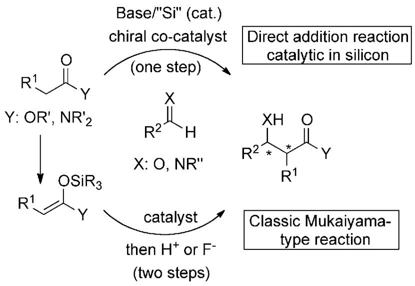
A chemical legacy: Keck and his team have chemically pursued the bryostatin 1 structure with great vigor in recent years and, in late 2010, they finally completed their quest of developing a short and efficient total synthesis of this complex natural product (see structure). The present Highlight provides a brief but nevertheless detailed overview of the Keck synthesis and its chemical legacy in terms of new reactions.

Catalytic Processes

J. M. García, M. Oiarbide, C. Palomo* ___ **8790 – 8792**

Towards Direct Mukaiyama-Type Reactions Catalytic in Silicon

Direct catalytic enolate generation from unactivated carboxylic acid derivatives may provide new routes for asymmetric carbon–carbon bond formation (see scheme). Recent studies demonstrate the potential of silicon catalysts or promoters in this endeavor, and this is best illustrated by a Mannich-type reaction of simple amides.



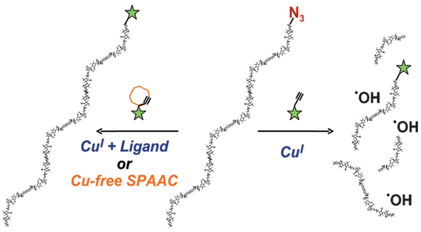
Minireviews

Clicking Biomacromolecules

E. Lallana, R. Riguera, E. Fernandez-Megia* ___ **8794 – 8804**

Reliable and Efficient Procedures for the Conjugation of Biomolecules through Huisgen Azide–Alkyne Cycloadditions

Efficient and benign bioconjugation: Cu^I-catalyzed azide–alkyne cycloaddition (CuAAC) is an established coupling method because of its high reliability and straightforward experimental procedure. However, the Cu catalyst has often proved detrimental to proteins, nucleic acids, and polysaccharides. Cu^I ligands and Cu-free strain-promoted procedures (SPAAC) have been developed that are efficient and avoid degradation of the resulting bioconjugates.



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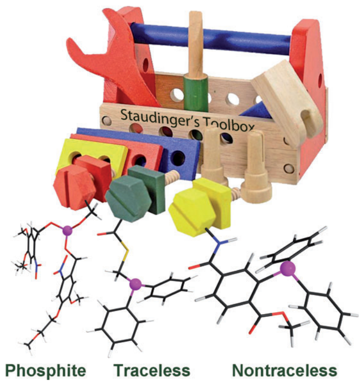
Reviews

Staudinger Ligation

S. S. van Berkel, M. B. van Eldijk,
J. C. M. van Hest* ———— **8806 – 8827**

Staudinger Ligation as a Method for Bioconjugation



Phosphorus and azides have a high affinity for one another. This discovery has led to the development of various phosphorus-containing bioconjugation probes. At present, traceless, nontraceless, and phosphite Staudinger ligation probes are frequently applied. The current status of their utilization in life sciences and materials science is described in this Review.

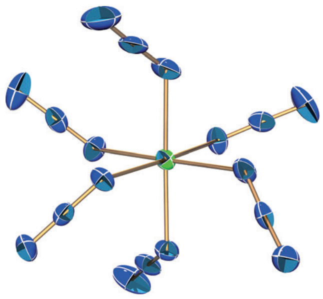
Communications

Polyazides

R. Haiges,* J. A. Boatz, J. M. Williams,
K. O. Christe* ———— **8828 – 8833**

Preparation and Characterization of the Binary Group 13 Azides $M(N_3)_3$ and $M(N_3)_3{\cdot}CH_3CN$ (M = Ga, In, Tl), $[Ga(N_3)_5]^{2-}$, and $[M(N_3)_6]^{3-}$ (M = In, Tl)

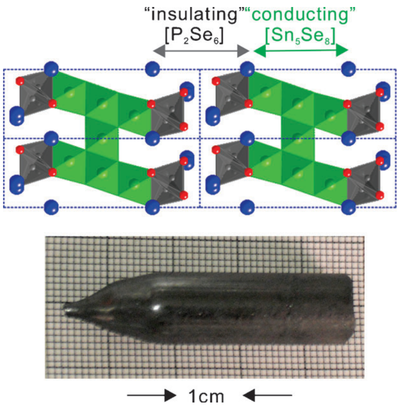
Proceed with caution: The use of fluoride starting materials and SO_2 as a solvent yields neat triazides $M(N_3)_3$ (M = Ga, In, Tl), thus firmly establishing the existence of thallium triazide. In CH_3CN, the new $M(N_3)_3{\cdot}CH_3CN$ donor–acceptor adducts were obtained. Reactions of the triazides with tetraphenylphosphonium azide in CH_3CN yields exclusively the novel $[Ga(N_3)_5]^{2-}$, $[In(N_3)_6]^{3-}$ and $[Tl(N_3)_6]^{3-}$ anions (see picture, M green, N blue).



Conducting Layered Materials

I. Chung, K. Biswas, J.-H. Song,
J. Androulakis, K. Chondroudis,
K. M. Paraskevopoulos, A. J. Freeman,
M. G. Kanatzidis* ———— **8834 – 8838**

$Rb_4Sn_5P_4Se_{20}$: A Semimetallic Selenophosphate



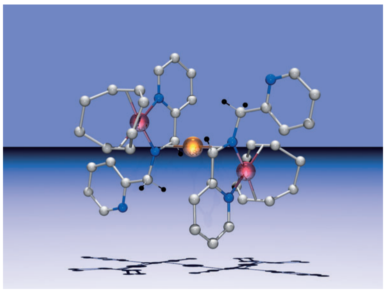
Moonlight metal: The valence-precise compound $Rb_4Sn_5P_4Se_{20}$ (see picture, Rb blue, Sn green, P black, Se red) is the first metallic selenophosphate. It features a new structure hybrid of "conducting" $[Sn_5Se_8]$ layers and "insulating" $[P_2Se_6]$ ligands. It shows the highest electrical conductivity among the chalcophosphates and an extremely low thermal conductivity of 0.44 $W\,m^{-1}\,K^{-1}$ at room temperature.

Non-Innocent Ligands

C. Tejel,* L. Asensio, M. P. del Río,
B. de Bruin, J. A. López,
M. A. Ciriano ———— **8839 – 8843**

Developing Synthetic Approaches with Non-Innocent Metalloligands: Easy Access to Ir^I/Pd^0 and $Ir^I/Pd^0/Ir^I$ Cores

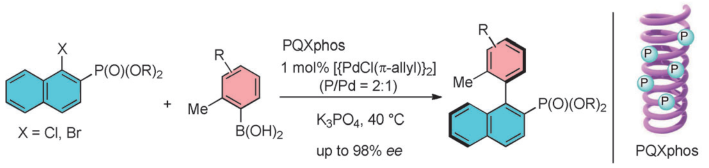
Guilty as charged is the verdict for anionic Ir complex $[Ir(bpa{-}2H)(cod)]^-$ in its reactions with Pd^{II} compounds. The net transfer of two electrons from the Ir complex to Pd allows easy preparation of di- and trinuclear π-imine-coordinated Pd^0 compounds such as $[\{Ir(PyCH_2NCHPy)(cod)\}_2Pd]$ (see picture; C white, Ir red, N blue, Pd yellow). bpa−2H: doubly deprotonated form of *N*,*N*-bis(2-picolyl)amine (bpa); cod: 1,5-cyclooctadiene.



Asymmetric Synthesis

T. Yamamoto, Y. Akai, Y. Nagata,
M. Suginome* ________ 8844 – 8847

Highly Enantioselective Synthesis of Axially Chiral Biarylphosphonates: Asymmetric Suzuki–Miyaura Coupling Using High-Molecular-Weight, Helically Chiral Polyquinoxaline-Based Phosphines

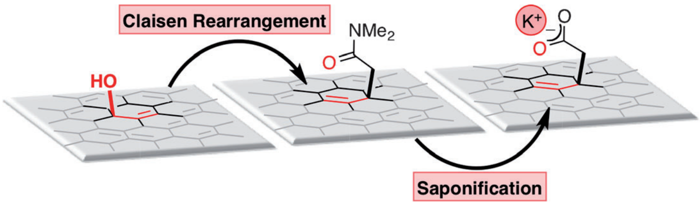


Taking a new turn: An asymmetric Suzuki–Miyaura coupling of 1-bromo-2-naphthalenephosphonic esters with *o*-methyl-substituted phenylboronic acids proceeds with high enantioselectivity in the presence of high-molecular-weight helically chiral polyquinoxaline-based phosphines (PQXphos) bearing pendant diarylphosphino groups.

Graphene

W. R. Collins, W. Lewandowski,
E. Schmois, J. Walish,
T. M. Swager* ________ 8848 – 8852

Claisen Rearrangement of Graphite Oxide: A Route to Covalently Functionalized Graphenes

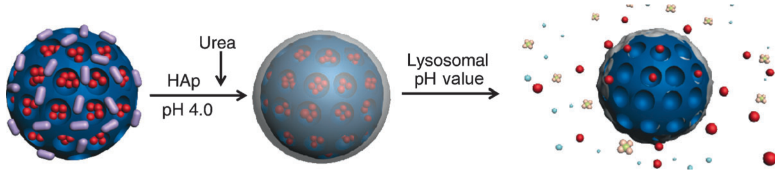


On the GO: The basal plane allylic alcohol functionality of graphite oxide (GO) can be converted into *N*,*N*-dimethylamide groups through an Eschenmoser–Claisen sigmatropic rearrangement by using *N*,*N*-dimethylacetamide dimethyl acetal. Subsequent saponification of these groups affords the carboxylic acids (see picture), which, when deprotonated, electrostatically stabilize the graphene sheets in an aqueous environment.

Drug Delivery

H. P. Rim, K. H. Min, H. J. Lee,
S. Y. Jeong,* S. C. Lee* ________ 8853 – 8857

pH-Tunable Calcium Phosphate Covered Mesoporous Silica Nanocontainers for Intracellular Controlled Release of Guest Drugs

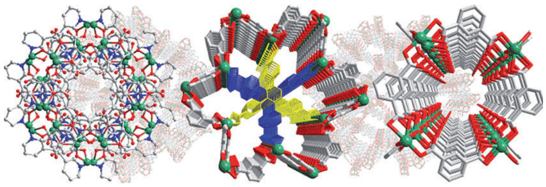


Springing the trap: A pH-responsive mesoporous silica nanoparticle with a calcium phosphate (CaP) pore-blocking coating was developed by enzyme-mediated surface mineralization under mild conditions. Upon exposure to cellular lysosomal pH, guest anticancer drug was released from the pore by dissolution of the CaP pore blocker (see picture; HAp = hydroxyapatite).

Metal–Organic Frameworks

S.-T. Zheng, J. J. Bu, T. Wu, C. Chou,
P. Feng,* X. Bu* ________ 8858 – 8862

Porous Indium–Organic Frameworks and Systematization of Structural Building Blocks

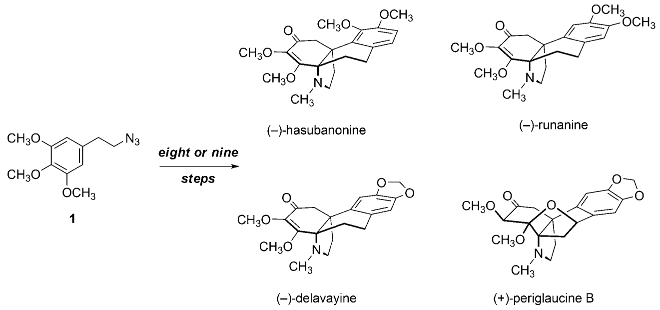


The indium family tree: The discovery of an elusive dimeric indium cluster together with super-trimeric indium clusters in five porous indium–organic frameworks reveals the systematics of indium-based building blocks and their cooperative and competitive roles in the crystallization of chiral and achiral porous frameworks. One of these materials has the smallest possible charge-balancing organic cation and a very high Langmuir surface area.

Natural Products Synthesis

S. B. Herzon,* N. A. Calandra, S. M. King ——— 8863 – 8866

Efficient Entry to the Hasubanan Alkaloids: First Enantioselective Total Syntheses of (−)-Hasubanonine, (−)-Runanine, (−)-Delavayine, and (+)-Periglaucine B

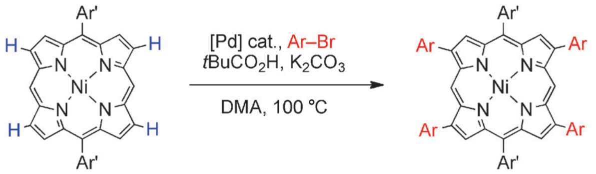


Maximized divergence: The hasubanan alkaloids given in the scheme have been synthesized in eight or nine steps from the aryl azide **1**. The utility of 5-trimethylsilylcyclopentadiene as an easily removed, stabilizing stereocontrol element has been demonstrated.

Porphyrinoids

Y. Kawamata, S. Tokuji, H. Yorimitsu,* A. Osuka* ——— 8867 – 8870

Palladium-Catalyzed β-Selective Direct Arylation of Porphyrins

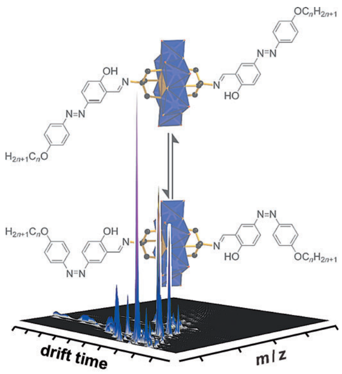


Four birds with one stone: A palladium catalyst/potassium carbonate/pivalic acid system enables direct arylation of porphyrins by aryl bromides (see scheme; Ar′ = 3,5-$t\mathrm{Bu}_2\mathrm{C}_6\mathrm{H}_3$). The C−H arylation shows excellent β selectivity and does not require porphyrin prefunctionalization, hence representing an extremely efficient method for rapidly providing a series of new β-arylated porphyrins.

Mass Spectrometry

J. Thiel, D. Yang, M. H. Rosnes, X. Liu, C. Yvon, S. E. Kelly, Y.-F. Song,* D.-L. Long, L. Cronin* ——— 8871 – 8875

Observing the Hierarchical Self-Assembly and Architectural Bistability of Hybrid Molecular Metal Oxides Using Ion-Mobility Mass Spectrometry

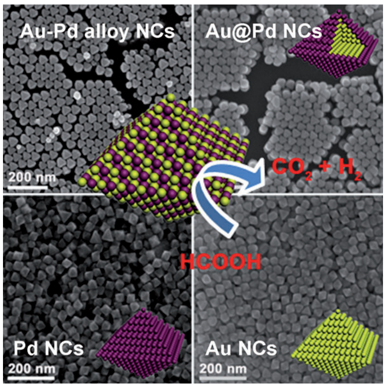


Ion-mobility mass spectrometry has been explored as a new technique in the analysis of polyoxometalates and was utilized for the differentiation between photoswitchable isomers of organic–inorganic hybrid compounds (see picture).

Nanocrystal Catalysts

J. W. Hong, D. Kim, Y. W. Lee, M. Kim, S. W. Kang, S. W. Han* ——— 8876 – 8880

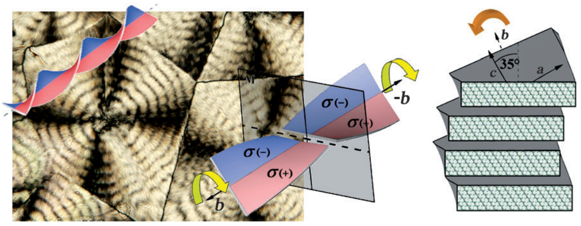
Atomic-Distribution-Dependent Electrocatalytic Activity of Au–Pd Bimetallic Nanocrystals



In the mix: Au–Pd alloy, Au@Pd core–shell, Pd, and Au nanocrystals (NCs) with an identical octahedral shape and with similar NC size were prepared to examine exclusively the effect of atomic distribution on the catalytic performance of NCs (see picture). The catalytic activities and stabilities toward formic acid oxidation highly depend on the atomic distribution in the NCs: Au–Pd alloy > Au@Pd core–shell > Pd ≫ Au NCs.

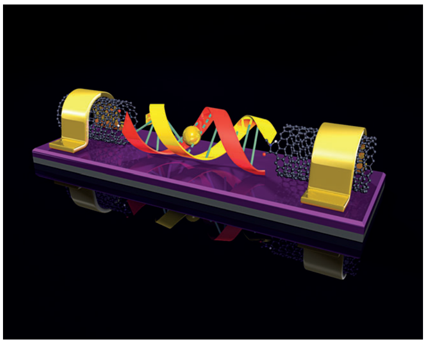
Contents

Crystallization



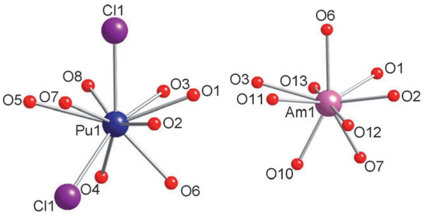
Twisted crystals: Upon crystallization, achiral polymers can form chiral crystalline lamellae, such as right- and left-handed helicoids. The chiral parameter imparted by crystallization is the chain tilt with respect to the lamellar normal. Thus, lamella having crystalline stems tilted to the right from the normal to the basal plane will form right-handed helicoids, and vice versa.

Electrical Conductance



Bridging the gap: The electrical conductance of individual metallo-DNA duplexes that bridge a carbon nanotube gap can be measured and switched by use of Cu^{2+} ions (see picture, yellow sphere: Cu^{2+}). These studies form the basis for new exciting research that interfaces molecular nanodevices with biological systems.

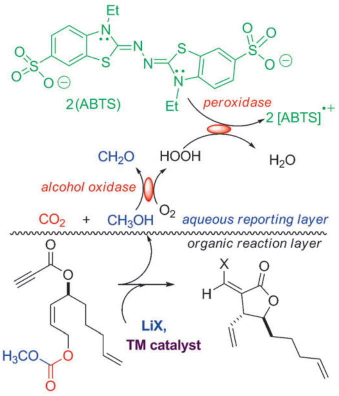
Actinides



A matter of size: A dramatic change occurs between the reactivity of Pu^{III} and Am^{III} centers in molten boric acid. The resulting complexes display different inner-sphere ligands and different coordination environments (see $Pu[B_4O_6(OH)_2Cl]$ and $Am[B_9O_{13}(OH)_4]\cdot H_2O$ in the picture).

Synthetic Methods

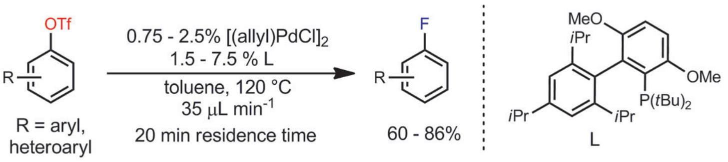
For the big screen: An alcohol oxidase/peroxidase-based screen for combinatorial catalysis produces a signal in the visible region and in real time. A targeted high-throughput screen uncovered a bromometalation/carbocyclization route to bicyclic terpenoid cores and a thiocyano palladation/carbocyclization for the ready installation of vinyl thiocyanates.



Fluorination in Flow

T. Noël, T. J. Maimone,
S. L. Buchwald* ______ 8900 – 8903

Accelerating Palladium-Catalyzed C–F Bond Formation: Use of a Microflow Packed-Bed Reactor

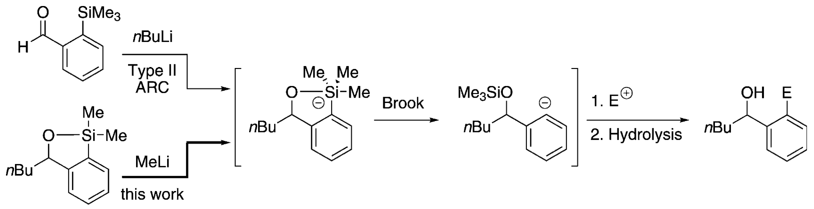


A flow process for Pd-catalyzed C–F bond formation is described. A microreactor with a packed-bed design allows for easy handling of large quantities of insoluble CsF with precise control over reaction times, efficient mixing, and the ability to safely handle elevated temperatures and pressures. A variety of aryl triflates, including heteroaryl ones, were converted into aryl fluorides in short reaction times (see scheme).

Synthetic Methods

A. B. Smith, III,* R. Tong, W.-S. Kim,
W. A. Maio ______ 8904 – 8907

Anion Relay Chemistry: Access to the Type II ARC Reaction Manifold through a Fundamentally Different Reaction Pathway Exploiting 1-Oxa-2-silacyclopentanes and Related Congeners

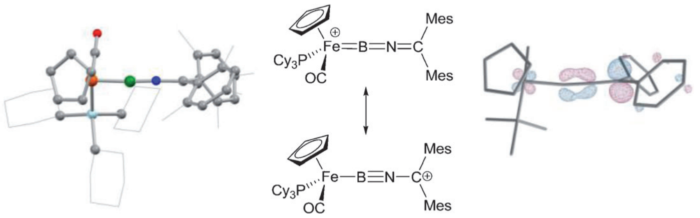


Distinctly different: Two 1-oxa-2-silacyclopentenes and a saturated congener have been synthesized and demonstrated to provide access to type II anion relay chemistry (ARC) through a fundamentally new mechanistic pathway. Similar to previous studies, but contrary to initial hypothesis, Brook rearrangement additives (hexamethylphosphoramide and CuI) are necessary to promote Si migration and anion capture.

Boron Ligands

J. Niemeyer, D. A. Addy, I. Riddlestone,
M. Kelly, A. L. Thompson, D. Vidovic,
S. Aldridge* ______ 8908 – 8911

Extending the Chain: Synthetic, Structural, and Reaction Chemistry of a BN Allenylidene Analogue

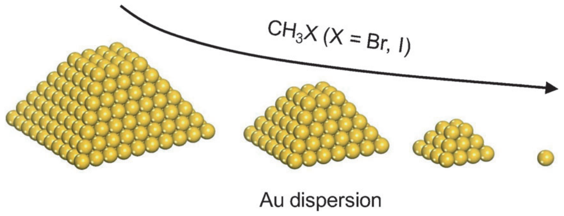


α versus γ: [CpFe(CO)(PCy$_3$)(BNCMes$_2$)]$^+$, synthesized by halide abstraction, represents the first example of a BN allenylidene analogue, and features an unsaturated MBNC π system. Although DFT calculations show significant LUMO amplitude at the γ (carbon) position, primary reactivity towards nucleophiles occurs at the sterically less hindered α (boron) center.

Heterogeneous Catalysis

J. Sá, A. Goguet, S. F. R. Taylor,
R. Tiruvalam, C. J. Kiely, M. Nachtegaal,
G. J. Hutchings,
C. Hardacre* ______ 8912 – 8916

Influence of Methyl Halide Treatment on Gold Nanoparticles Supported on Activated Carbon



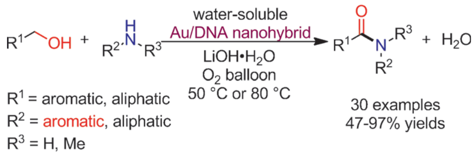
Catalyzing concept: Methyl halides have been used to disperse large (around 20 nm) gold nanoparticles supported on carbon into dispersed gold atoms/dimers at low temperature and atmospheric pressure (see picture). The process occurs through the progressive removal of gold–halogen entities from the metal nanoparticles and a gradual decrease in the size of the gold nanoparticles on the minute timescale.

Contents

Heterogeneous Catalysis

Y. Wang, D. Zhu, L. Tang, S. Wang,*
Z. Wang* ———— **8917 – 8921**

Highly Efficient Amide Synthesis from Alcohols and Amines by Virtue of a Water-Soluble Gold/DNA Catalyst



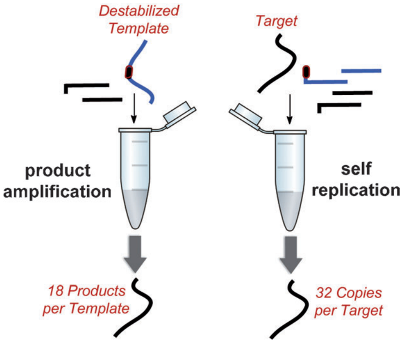
Gold takes to water: The synthesis of amides directly from alcohols and amines was realized by using a water-soluble Au/DNA nanohybrid as the catalyst. The interactions between the gold nanoparticles, DNA, and water lead to high catalytic efficiency under mild reaction conditions. The wide substrate scope includes less-basic aromatic amines, and this catalyst is recyclable.

Engineering DNA Turnover

A. Kausar, R. D. McKay, J. Lam,
R. S. Bhogal, A. Y. Tang,
J. M. Gibbs-Davis* ———— **8922 – 8926**

Tuning DNA Stability To Achieve Turnover in Template for an Enzymatic Ligation Reaction

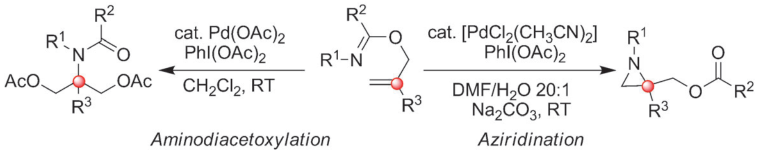
Learning to let go: Introducing destabilizing modifications into a DNA template leads to turnover in a DNA-templated ligation reaction. By incorporating a cross-catalytic cycle, self-replication was also achieved, with one target able to make 32 copies of itself (see picture). This destabilization approach represents a general method for incorporating amplification into DNA ligation processes using T4 DNA ligase.



Palladium Catalysis

S. Cui, L. Wojtas,
J. C. Antilla* ———— **8927 – 8930**

Palladium-Catalyzed Tunable Functionalization of Allylic Imidates: Regioselective Aminodiacetoxylation and Aziridination



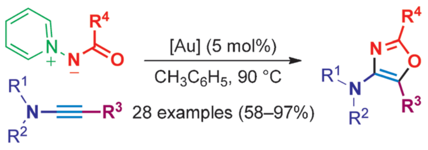
In control: The title reaction has been shown to be highly general and efficient, thus exhibiting valuable potential synthetic utility (see scheme; DMF = *N*,*N*-dimethylformamide). Isotope labeling and two proposed mechanistic pathways, which invoke a Pd^{II}/Pd^{IV} catalytic cycle, show divergent C–N and C–O bond formation.

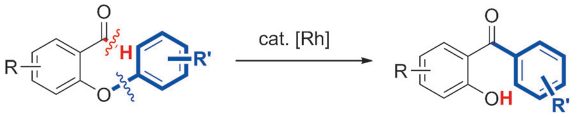
Synthetic Methods

P. W. Davies,* A. Cremonesi,
L. Dumitrescu ———— **8931 – 8935**

Intermolecular and Selective Synthesis of 2,4,5-Trisubstituted Oxazoles by a Gold-Catalyzed Formal [3 + 2] Cycloaddition

Oxazole new world: A gold-catalyzed intermolecular reaction of pyridine-N-aminides with ynamides can be used to prepare trisubstituted 1,3-oxazoles with a variety of functional groups. This formal [3 + 2] cycloaddition employs robust conjugated N-ylides as N-nucleophilic N-acyl nitrene equivalents for a highly chemo-selective and regioselective addition across electron-rich C–C triple bonds.



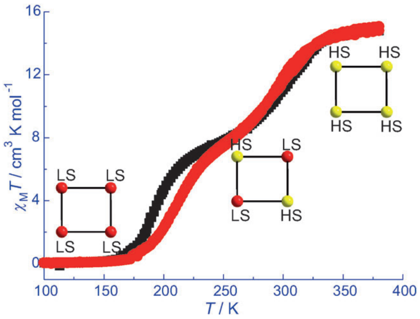


Lost in the shuffle: An unprecedented rearrangement of the title compounds proceeds by the simultaneous rhodium-catalyzed cleavage of aryloxy C—O and aldehyde C—H bonds (see scheme). The reaction tolerates the presence of various catalytically reactive substituents such as aryl halides, nitrile, and esters.

Homogeneous Catalysis

H. Rao, C.-J. Li* ———— **8936 – 8939**

Rearrangement of 2-Aryloxybenzaldehydes to 2-Hydroxybenzophenones by Rhodium-Catalyzed Cleavage of Aryloxy C—O Bonds

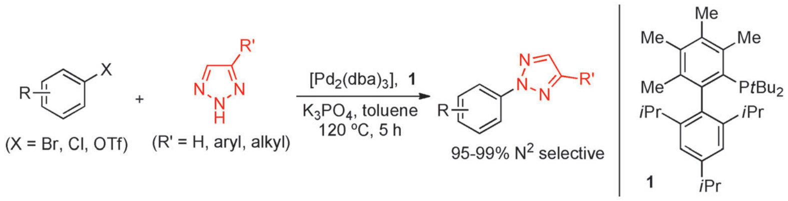


High or low? A square Fe$^{II}_4$ compound exhibits complete thermally and optically activated transition from four low-spin (LS) centers to four high-spin (HS) centers in two steps (see plot of magnetic susceptibility). Reversible desorption and resorption of guest water molecules causes a single-crystal-to-single-crystal transformation.

Spin Crossover

R.-J. Wei, Q. Huo, J. Tao,* R.-B. Huang, L.-S. Zheng ———— **8940 – 8943**

Spin-Crossover Fe$^{II}_4$ Squares: Two-Step Complete Spin Transition and Reversible Single-Crystal-to-Single-Crystal Transformation

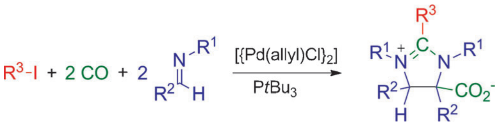


A familiar ring? Highly N^2-selective arylation of 4,5-unsubstituted and 4-substituted 1,2,3-triazoles was achieved for the first time by the Pd/**1** catalyst system. A wide range of N^2-aryl-1,2,3-triazoles were prepared from aryl bromides, chlorides, and triflates with excellent N^2 selectivity (see scheme). Density functional theory calculations suggest that the formation of N^2-arylated 1,2,3-triazoles is favored kinetically. dba = dibenzylideneacetone, Tf = trifluoromethanesulfonyl.

Synthetic Methods

S. Ueda, M. Su, S. L. Buchwald* ———— **8944 – 8947**

Highly N^2-Selective Palladium-Catalyzed Arylation of 1,2,3-Triazoles



Take five: A new method employing aryl halide carbonylation to directly access heterocycles has been described (see scheme). In a single palladium-catalyzed reaction the catalyst mediates two consecutive carbonylation steps, thereby converting five components (aryl iodide, two units imine, and two units CO) into an imidazoline ring.

Multicomponent Reactions

S. Bontemps, J. S. Quesnel, K. Worrall, B. A. Arndtsen* ———— **8948 – 8951**

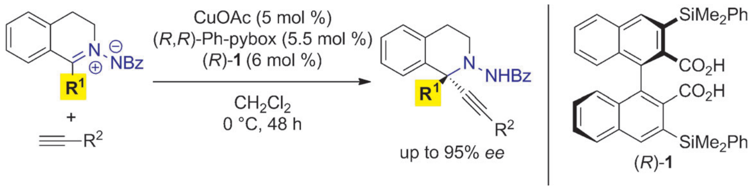
Palladium-Catalyzed Aryl Iodide Carbonylation as a Route to Imidazoline Synthesis: Design of a Five-Component Coupling Reaction

Contents

Asymmetric Catalysis

T. Hashimoto, M. Omote, K. Maruoka* ———— **8952 – 8955**

Catalytic Asymmetric Alkynylation of C1-Substituted C,N-Cyclic Azomethine Imines by Cu^I/Chiral Brønsted Acid Co-Catalyst

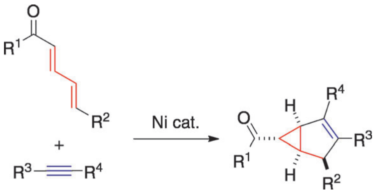


It all adds up: The title reaction was developed for the synthesis of chiral tetrahydroisoquinoline derivatives with a tetrasubstituted carbon center at the C1-position (see scheme, Bz = benzoyl, pybox = 2,6-bis(2-oxazolinyl)pyridine). The reaction was facilitated effectively by the co-catalyst system composed of copper(I)/Ph-pybox and an axially chiral dicarboxylic acid.

Cycloaddition

H. Horie, T. Kurahashi,* S. Matsubara* ———— **8956 – 8959**

Nickel-Catalyzed Cycloaddition of α,β,γ,δ-Unsaturated Ketones with Alkynes

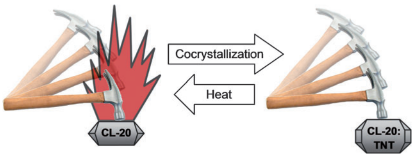


As easy as α, β, γ, δ: The title reaction unexpectedly resulted in the stereoselective synthesis of bicyclo[3.1.0]hexenes (see scheme). The high level of stereoselection is attributed to a mechanistic pathway involving the oxidative cyclization of nickel(0) with α,β,γ,δ-unsaturated ketones and alkynes, and the subsequent intramolecular carbonickelation.

Energetic Materials

O. Bolton, A. J. Matzger* — **8960 – 8963**

Improved Stability and Smart-Material Functionality Realized in an Energetic Cocrystal

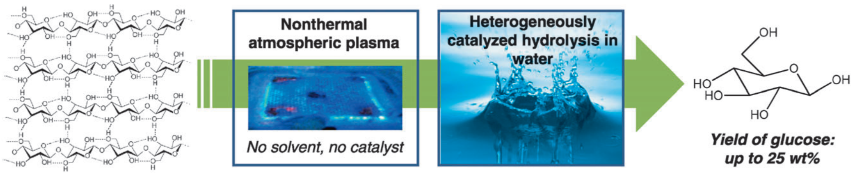


Handle with care: CL-20, a high-power explosive suffering from high sensitivity, has been cocrystallized with TNT to produce a novel high-power, low-sensitivity explosive. This cocrystal can be used directly for explosives applications or stored in this insensitive form then activated by heat to return it to its high-sensitivity form.

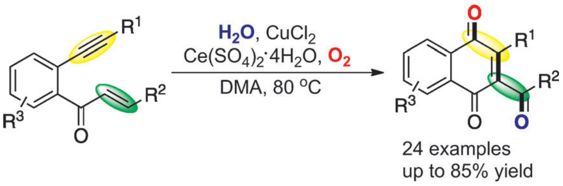
Sustainable Chemistry

M. Benoit, A. Rodrigues, Q. Zhang, E. Fourré, K. De Oliveira Vigier, J.-M. Tatibouët, F. Jérôme* – **8964 – 8967**

Depolymerization of Cellulose Assisted by a Nonthermal Atmospheric Plasma



Biomass breakdown: The reactivity of recalcitrant cellulose towards hydrolysis is enhanced by pretreatment with a nonthermal atmospheric plasma. Glucose was produced in up to 25 wt% yield from microcrystalline cellulose and α-cellulose (see picture). This technology is also applicable to the deconstruction of starch and inulin.

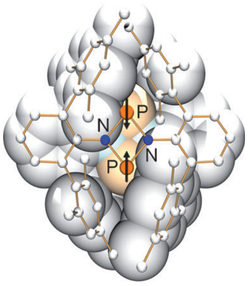


The novel CuCl$_2$-catalyzed title reaction of enynes has been developed for synthesizing substituted naphthoquinones (see scheme; DMA = dimethylacetamide). The method represents the first example of a copper-catalyzed enyne oxidative cyclization for constructing 1,4-naphthoquinones by the incorporation of two oxygen atoms into the organic framework from molecular oxygen and water.

Synthetic Methods

Z.-Q. Wang, W.-W. Zhang, L.-B. Gong, R.-Y. Tang, X.-H. Yang, Y. Liu, J.-H. Li* **8968 – 8973**

Copper-Catalyzed Intramolecular Oxidative 6-*exo*-trig Cyclization of 1,6-Enynes with H$_2$O and O$_2$



Radical protection makes a biradical: High-temperature-stable biradicaloids [P(μ-NR)]$_2$ (R = Ter, Hyp) were isolated from [ClP(μ-NR)]$_2$ when mild reducing agents were employed. The bulky substituents prevent dimerization. Ter = 2,6-Mes$_2$C$_6$H$_3$, with Mes = 2,4,6-Me$_3$C$_6$H$_2$; Hyp = (Me$_3$Si)$_3$Si.

P,N Biradicaloids

T. Beweries, R. Kuzora, U. Rosenthal, A. Schulz,* A. Villinger **8974 – 8978**

[P(μ-NTer)]$_2$: A Biradicaloid That Is Stable at High Temperature

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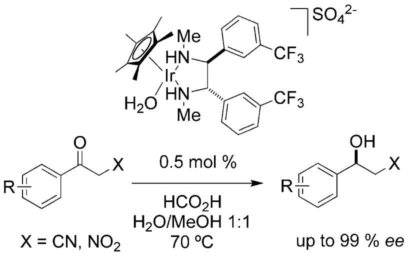

A simple and very efficient chiral aqua iridium(III) diamine complex leads to excellent enantioselectivities in the asymmetric transfer hydrogenation of various α-cyano and α-nitro ketones. The catalyst provides the *ortho*-substituted aromatic alcohols with especially high *ee* values. The diamine ligands can be used directly as chiral ligands; conversion into the corresponding sulfamide is not necessary.

Asymmetric Transfer Hydrogenation

H. Vázquez-Villa, S. Reber, M. A. Ariger, E. M. Carreira* **8979 – 8981**

An Iridium Diamine Catalyst for the Asymmetric Transfer Hydrogenation of Ketones

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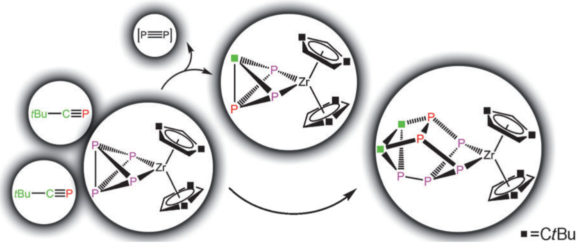


The missing member [Cp′′$_2$Zr(η^2-P$_3$C*t*Bu)] (Cp′′ = η^5-C$_5$H$_3$*t*Bu$_2$) of the phosphorus-containing bicyclobutane zirconium complex family was synthesized by reaction between tetraphosphazirconocene derivative [Cp′′$_2$Zr(η^2-P$_4$)] and a phosphaalkyne with the release of a formal P$_2$ unit. Synthetic evidence of another unknown isomer [Cp′′$_2$Zr(η^2-P$_2$(C*t*Bu)$_2$)] was found; according to DFT calculations, it is the stable form if a Cp′′$_2$Zr moiety is used.

Phosphorus Ligands

U. Vogel, M. Eberl, M. Eckhardt, A. Seitz, E.-M Rummel, A. Y. Timoshkin, E. V. Peresypkina, M. Scheer* **8982 – 8985**

Access to Phosphorus-Rich Zirconium Complexes

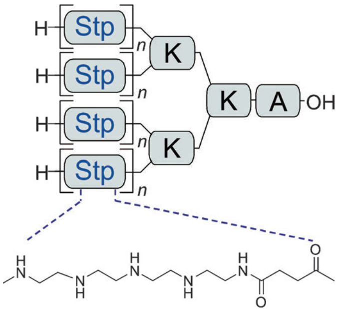
Contents

Transfection Polymers

D. Schaffert, C. Troiber, E. E. Salcher, T. Fröhlich, I. Martin, N. Badgujar, C. Dohmen, D. Edinger, R. Kläger, G. Maiwald, K. Farkasova, S. Seeber, K. Jahn-Hofmann, P. Hadwiger, E. Wagner* ______ **8986–8989**

🖥 Solid-Phase Synthesis of Sequence-Defined T-, i-, and U-Shape Polymers for pDNA and siRNA Delivery

Artificial oligo(ethylene amino) acids, together with selected natural amino acids and fatty acid modifications, have been used for the solid-phase-assisted synthesis of polymers with precise sequence, topology, and modifications (see picture). First proof-of-concept studies demonstrate the high potential of such polymers in pDNA and siRNA delivery. K = lysine, A = alanine.



🖥 Supporting information is available on www.angewandte.org (see article for access details).

A video clip is available as Supporting Information on www.angewandte.org (see article for access details).

This article is available online free of charge (Open Access)

Service

Corrigendum

Primary and Secondary Aminophosphines as Novel P-Stereogenic Building Blocks for Ligand Synthesis

M. Revés, C. Ferrer, T. León, S. Doran, P. Etayo, A. Vidal-Ferran, A. Riera,* X. Verdaguer* ______ **9452–9455**

Angew. Chem. Int. Ed. **2010**, *49*

DOI 10.1002/anie.201004041

In this Communication, the enantiomeric excess reported for the hydrogenation of *N*-(3,4-dihydronaphthalen-2-yl)acetamide was incorrect. An unnoticed impurity contained in the racemic sample led to the use of an inappropriate HPLC method for the determination of the optical purity. Reanalyzing the sample with a correct HPLC method (Chiralcel OD-H, hexanes/isopropyl alcohol (95:5), 1.0 mL min^{-1}, 210 nm, $t(-) = 23.5$ min, $t(+) = 27.5$ min)[1] showed that the reduction product was obtained in only 9% *ee*. The authors apologize for this error.

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[1] J. L. Renaud, P. Dupau, A.-E. Hay, M. Guingouain, P. H. Dixneuf, C. Bruneau, *Adv. Synth. Catal.* **2003**, *345*, 230–238.