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:

*J. H. Ahn, B. Temel, E. Iglesia**
Selective Homologation Routes to 2,2,3-Trimethylbutane on Solid Acids

J. England, M. Martinho, E. R. Farquhar, J. R. Frisch, E. L. Bominaar, E. Münck,* L. Que, Jr.**
A Synthetic High-Spin Oxoiron(IV) Complex: Generation, Spectroscopic Characterization, and Reactivity

*C. R. Hess, T. Weyhermüller, E. Bill, K. Wieghardt**
[{Fe(tim)}$_2$]: An Fe–Fe Dimer Containing an Unsupported Metal–Metal Bond and Redox-Active N$_4$-Macrocyclic Ligands

*J. Tolosa, C. Kub, U. H. F. Bunz**
Hyperbranched: A Universal Conjugated Polymer Platform?

D. Xu, Z. Liu, H. Yang, Q. Liu, J. Zhang, J. Fang, S. Zou,* K. Sun*
Solution-Based Evolution of Monodisperse Pt–Cu Nanocubes and Their Enhanced Methanol Oxidation Activity

*H. Moroder, J. Steger, D. Graber, K. Fauster, K. Trappl, V. Marquez, N. Polacek, D. N. Wilson, R. Micura**
Nonhydrolyzable RNA–Peptide Conjugates: A Powerful Advance in the Synthesis of Mimics for 3'-Peptidyl tRNA Termini

*J. L. Alonso-Gómez, P. Rivera-Fuentes, N. Harada, N. Berova, F. Diederich**
An Enantiomerically Pure Alleno-Acetylenic Macrocycle: Synthesis and Rationalization of Its Outstanding Chiroptical Response

News


H.-U. Blaser


D. Scheschkewitz

Author Profile

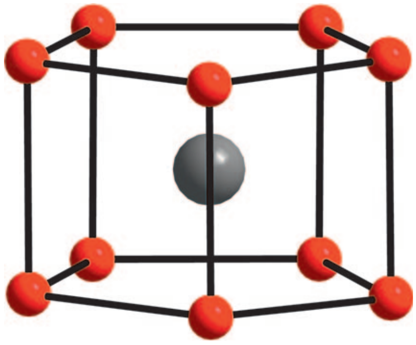
"My biggest motivation is to see my students' progress. When I was eighteen I wanted to be unexcitingly, a chemist…!"
This and more about Stefan Mecking can be found on page 3213.

Books

Highlights

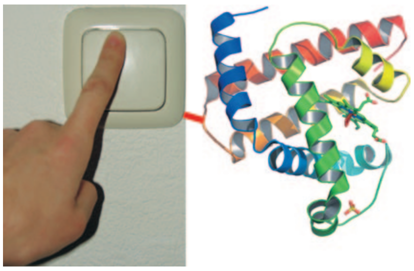
Endohedral Germanium Clusters

A different drummer: The existence of endohedral germanium clusters was predicted earlier by gas-phase experiments. The $[Co@Ge_{10}]^{3-}$ anion now synthesized is surprising, as it breaks with a long line of exclusively deltahedral structures found in the past. Instead, it has a regular pentagonal-prismatic structure (see picture; Co gray, Ge red).

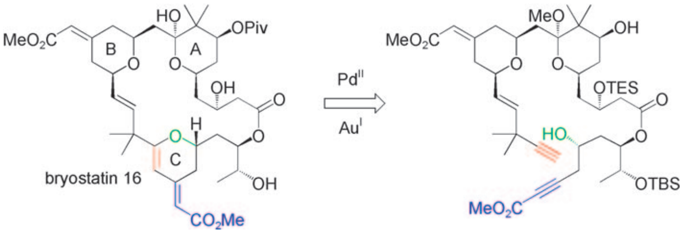


Protein Design

Long-distance service: Finding a selective small-molecule modulator for every domain of every human protein is a Herculean task. Wouldn't it be much easier to control the activity of any protein of choice by simply fusing it with a generally adaptable switch protein and controlling protein activity indirectly?



Bryostatins



Adding up: A recent total synthesis of bryostatin 16 is highlighted by two transition-metal-catalyzed addition reactions. The first forges the B ring while establishing its relative stereochemistry. The second closes the macrocycle with a rare isomerization. These reactions neither require substrate activation nor do they generate byproducts. The powerful macrocyclization should be considered alongside more traditional methods.

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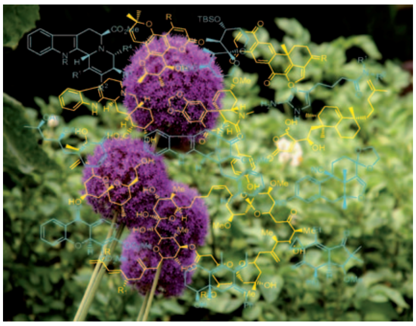
Minireviews

Medicinal Chemistry

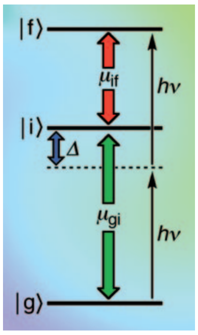
Mimicking nature synthetically: The successful development of multistep stereoselective syntheses gives access to natural product inspired compound collections having carbo-, oxa-,and azacyclic scaffold structures which promise to provide sources for new reagents in medicinal chemistry and chemical biology research.



Reviews

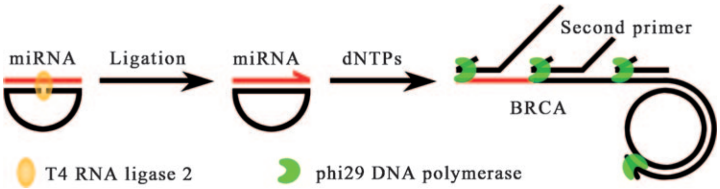
Chromophores and π Systems

Two photons are better than one: This principle applies to a wide range of applications, ranging from engineering to physiology. Recent advances in our understanding of the phenomenon of two-photon absorption (see picture) and in the design of two-photon dyes are rapidly increasing the scope of this field.



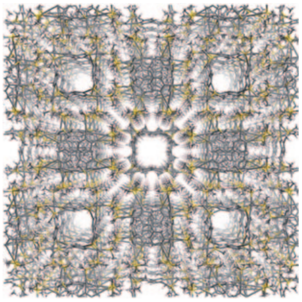
Communications

MicroRNA Detection



One-nucleotide differences in microRNAs (miRNAs) can be discriminated in an assay based on a branched rolling-circle amplification (BRCA) reaction and fluorescence quantification. With the proposed method miRNA can be detected at concentrations as low as 10 fM, and the miRNA in a total RNA sample of a few nanograms can be determined.

Organic Zeolites

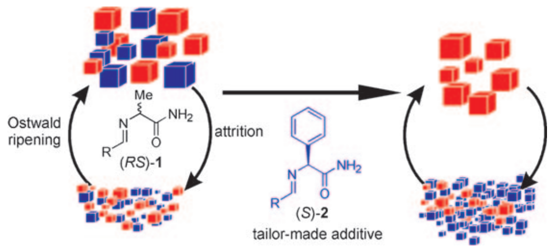


Quick on the uptake: Following its identification during a targeted search, the intriguing crystal structure of 3,3′,4,4′-tetra(trimethylsilylethynyl)biphenyl was investigated. Simple removal of the included solvent provides an organic crystal with an open microporous structure that has a striking similarity to that of zeolite A (see picture). Reversible adsorption of nitrogen and hydrogen gases at 77 K confirms that the microporosity is permanent.

Chiral Resolution

W. L. Noorduin, P. van der Asdonk,
H. Meekes, W. J. P. van Enckevort,
B. Kaptein, M. Leeman, R. M. Kellogg,
E. Vlieg* ——— 3278 – 3280

Complete Chiral Resolution Using Additive-Induced Crystal Size Bifurcation During Grinding

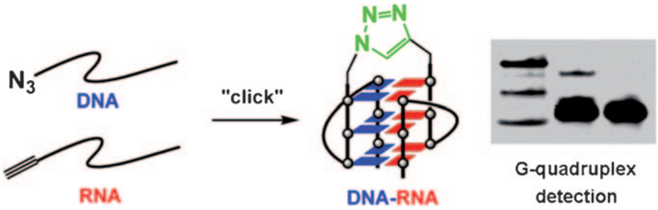


Grinding them down: By using a tailor-made additive, even in the absence of racemization in solution, abrasive grinding can yield an enantiopure solid state. This novel chiral resolution technique is based on an asymmetric bifurcation in the crystal size distribution as a result of stereoselective hampered crystal growth. R = *o*-tolyl.

Biological Structures

Y. Xu,* Y. Suzuki,
M. Komiyama* ——— 3281 – 3284

Click Chemistry for the Identification of G-Quadruplex Structures: Discovery of a DNA–RNA G-Quadruplex



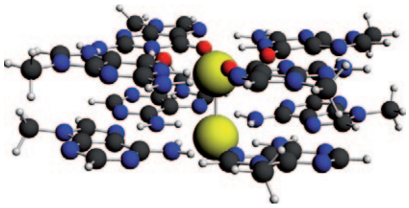
A trap that closes with a "click": The copper-catalyzed azide–alkyne cycloaddition can occur in different G-quadruplex structures (see scheme). The species trapped by the click reaction can then be separated and analyzed. By using this approach, a DNA–RNA hybrid-type G-quadruplex structure formed by human telomeric DNA and RNA sequences was detected.

Ion-Pair Receptors

T. van der Wijst, C. Fonseca Guerra,
M. Swart, F. M. Bickelhaupt,*
B. Lippert* ——— 3285 – 3287

A Ditopic Ion-Pair Receptor Based on Stacked Nucleobase Quartets

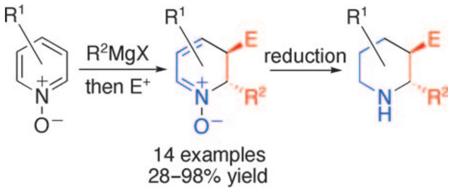
Pass the salt, please! State-of-the-art computations indicate that the stacking complex of a guanine quartet and an adenine quartet (G_4A_4) can function as a potent ditopic receptor for NaCl in aqueous solution (see picture; Na^+, Cl^- yellow, O red, N blue, C black, H white).



Heterocycles

H. Andersson, M. Gustafsson,
D. Boström, R. Olsson,*
F. Almqvist* ——— 3288 – 3291

The Regio- and Stereoselective Synthesis of *trans*-2,3-Dihydropyridine *N*-oxides and Piperidines

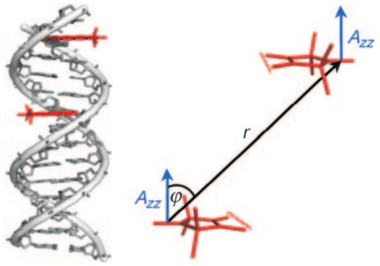


Reactivity N–Own: Pyridine *N*-oxides can be used for the complete regio- and stereoselective synthesis of *trans*-substituted piperidines. The sequential addition of Grignard reagents and aldehydes or ketones to pyridine *N*-oxides yields a complete regio- and stereoselective *trans* 2,3-addition reaction in high yields, and the substituted 2,3-dihydropyridine *N*-oxide can be reduced to form 2,3-*trans*-substituted piperidines (see scheme).

PELDOR Spectroscopy

O. Schiemann,* P. Cekan, D. Margraf,
T. F. Prisner,
S. Th. Sigurdsson* ——— **3292 – 3295**

Relative Orientation of Rigid Nitroxides by PELDOR: Beyond Distance Measurements in Nucleic Acids

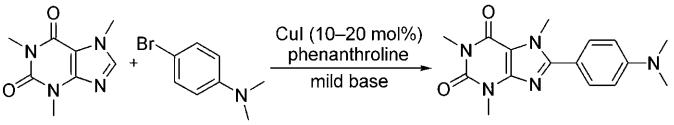


Show me your angle: Incorporation of the rigid spin label **Ç** allows determination of both distance and orientation of two nitroxide spin labels in DNA by PELDOR experiments at common X-band frequencies. The orientational information is obtained by varying the position of the detection pulses over the nitroxide spectrum. Simulation of the set of time traces yields very precise distances and angles.

Heterocycles

D. Zhao, W. Wang, F. Yang, J. Lan, L. Yang,
G. Gao, J. You* ——— **3296 – 3300**

Copper-Catalyzed Direct C Arylation of Heterocycles with Aryl Bromides: Discovery of Fluorescent Core Frameworks



A window of opportunity: A general copper-catalyzed C−H bond-activation path allows arylation of heterocycles with a wide range of aryl bromides (see scheme). The reaction shows excellent regioselectivity and exhibits good functional group tolerance. The 8-aryl xanthines exhibit fluorescence in a variety of solvents and show promise as reagents for biological imaging.

Protein Design

H. Liang, H. Chen, K. Fan, P. Wei, X. Guo,
C. Jin, C. Zeng, C. Tang,
L. Lai* ——— **3301 – 3303**

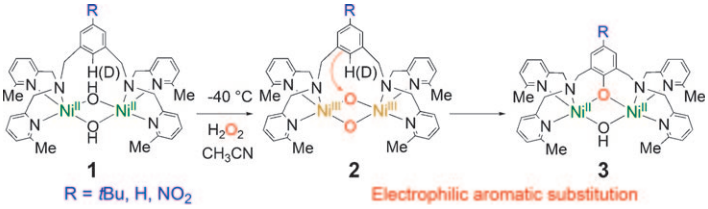
De Novo Design of a βαβ Motif

A designer monomeric protein with a βαβ fold—two parallel β strands connected by an α helix (see structure)—was constructed solely from coded amino acids. The high thermal stability of the structure is due to a large extent to tryptophan–tryptophan interactions between the two β strands.

Nickel(III) Complexes

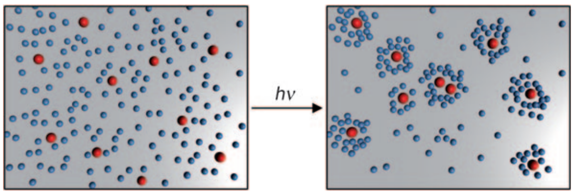
K. Honda, J. Cho, T. Matsumoto, J. Roh,
H. Furutachi, T. Tosha, M. Kubo,
S. Fujinami, T. Ogura, T. Kitagawa,
M. Suzuki* ——— **3304 – 3307**

Oxidation Reactivity of Bis(μ-oxo) Dinickel(III) Complexes: Arene Hydroxylation of the Supporting Ligand



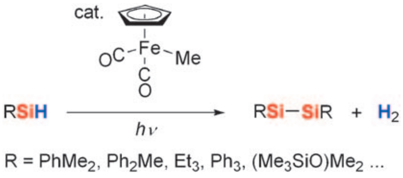
In the nick(el) of time: Bis(μ-oxo) dinickel(III) complexes **2** (see scheme), generated in the reaction of **1** with H_2O_2, are capable of hydroxylating the xylyl linker of the supporting ligand to give **3**. Kinetic studies reveal that hydroxylation proceeds by electrophilic aromatic substitution. The lower reactivity than the corresponding μ-η^2:η^2-peroxo dicopper(II) complexes can be attributed to unfavorable entropy effects.

Colloids



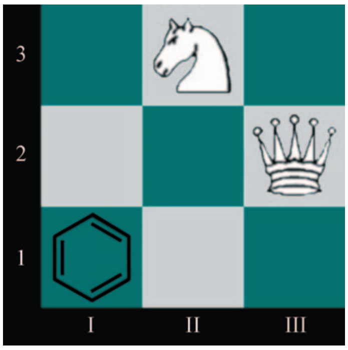
A new school of thought: Micrometer-sized silver chloride (AgCl) particles (red) in deionized water move under UV illumination by self-diffusiophoresis (see picture). Each AgCl particle secretes ions to which the other particles respond, and they are observed to “school” into regions with higher concentrations of particles. Photo-inactive silica particles (blue) also respond to the chemical secretion by swimming towards and surrounding individual AgCl particles.

Si–Si Coupling



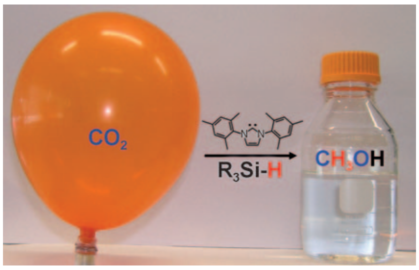
A variety of tertiary silanes, even those with functional substituents, undergo an unprecedented iron-catalyzed dehydrogenative coupling (see scheme) in a convenient approach to disilanes, including unsymmetrical disilanes and polymers with Si–Si bonds in the backbone. Consideration of the catalytic reaction pathway revealed the intermediacy of a hydrido(disilyl)iron(IV) complex.

Inverse Crown Compounds



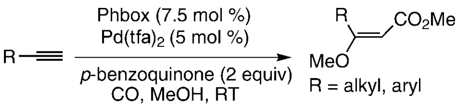
Check M(etal)ate: The chessboard and the figures represent a special reaction in which different low-polarity metals can metalate arenes directly when they are brought into the right position. In a combination of queen (sodium) and knight (chromium or iron), it is possible for the knight (usually the weaker piece) to make a direct deadly hit on the king (benzene) in this game of elemental chess.

CO_2 Reduction



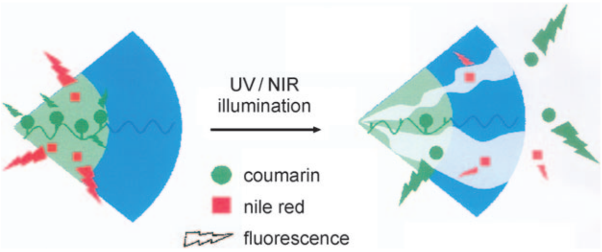
Activate and reduce: Carbon dioxide was reduced with silane using a stable N-heterocyclic carbene organocatalyst to provide methanol under very mild conditions. Dry air can serve as the feedstock, and the organocatalyst is much more efficient than transition-metal catalysts for this reaction. This approach offers a very promising protocol for chemical CO_2 activation and fixation.

Synthetic Methods



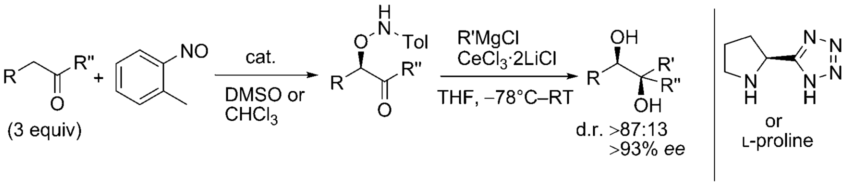
Boxing clever: Direct conversion of a terminal alkyne group into a β-methoxyacrylate is realized with the aid of the bis(oxazoline) ligand (box). Acetyl and ketal protecting groups, free hydroxy groups, and acid-sensitive glycosidic bonds are not affected under the reaction conditions. The one-pot synthesis of (±)-dihydrokawain from the homopropargyl alcohol is also achieved. tfa = trifluoroacetate

Micelles



Easily disrupted: Micelles of a new amphiphilic block copolymer that bear coumarin groups are sensitive to near infrared light by two-photon absorption of the chromophore. Disruption of the micelles under irradiation at 794 nm results in release of both photocleaved coumarin and encapsulated nile red from the hydrophobic core of micelle into aqueous solution, which results in opposing changes in fluorescence emission intensity.

Synthetic Methods



Chiral 1,2-diols have been prepared from α-aminoxylated aldehydes or cyclohexanone and Grignard reagents with L-proline or its tetrazole derivative as the catalyst. The presence of the ate complex of $CeCl_3$·2 LiCl is essential for the high overall yields and good selectivities (see scheme; DMSO = dimethyl sulfoxide, THF = tetrahydrofuran, Tol = tolyl).

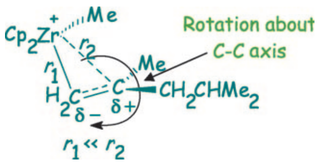
Porphyrin Analogues

At the crossroads: A unique carbon-bridged annulene motif—dehydroquatyrin—is imprinted into the molecular structure of the tetraazuliporphyrin tetracation (see picture). The macrocycle, which lies at the intersection of annulene, carbocation, and porphyrin chemistry, is obtained by the standard condensation of azulene and arylaldehyde followed by oxidation. The meso positions of the tetracation are susceptible to anionic or weak nucleophilic attack.

Reactive Intermediates

F. Sauriol, E. Wong, A. M. H. Leung,
I. E. Donaghue, M. C. Baird,*
T. Wondimagegn,
T. Ziegler* ——— 3342 – 3345

Structures and Properties of Nonchelated, d^0 Alkyl Alkene Complexes of the Type $[Cp_2ZrMe(alkene)]^+$: Elusive Intermediates during Ziegler–Natta Polymerizations of Alkenes

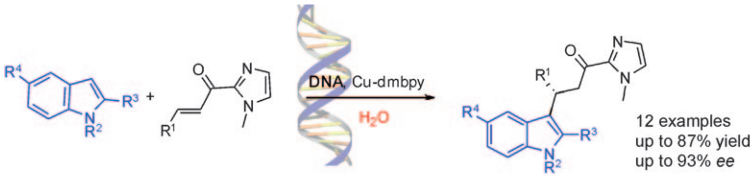


Caught in the act: An alkyl alkene Zr^{IV} complex (see picture; $Cp = C_5H_5$) has been synthesized and characterized for the first time. The alkene bonding mode is highly asymmetric, and C2 is quite carbocationic. There is also evidence for rotation about the C1–C2 bond. This extremely unusual complex provides an exemplar of previously unknown intermediates in Ziegler–Natta and carbocationic polymerization reactions of alkenes.

Asymmetric Catalysis

A. J. Boersma, B. L. Feringa,*
G. Roelfes* ——— 3346 – 3348

Enantioselective Friedel–Crafts Reactions in Water Using a DNA-Based Catalyst

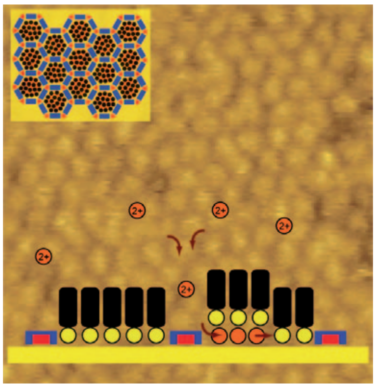


Taking the plunge: The first example of a Lewis acid catalyzed asymmetric Friedel–Crafts alkylation with olefins in water is described. By using loadings of a DNA-based copper catalyst as low as 0.15 mol %, good yields and excellent enantioselectivities were obtained in the reaction of α,β-unsaturated 2-acyl imidazoles with heteroaromatic π nucleophiles. dmbpy = 4,4′-dimethyl-2,2′-bipyridine.

Self-Assembled Structures

C. Silien, M. T. Räisänen,
M. Buck* ——— 3349 – 3352

A Supramolecular Hydrogen-Bonded Network as a Diffusion Barrier for Metal Adatoms

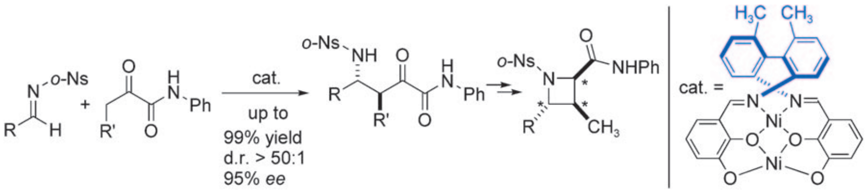


Confined in a molecular corral: A supramolecular network changes the mechanism by which underpotential deposition (UPD) of copper proceeds on a gold electrode modified by a self-assembled monolayer (SAM). Lateral diffusion of Cu adatoms is suppressed between adjacent cells of a network/SAM hybrid structure. Instead, UPD occurs by direct deposition into the SAM filled pores of the network, where the Cu adatoms are confined.

Asymmetric Catalysis

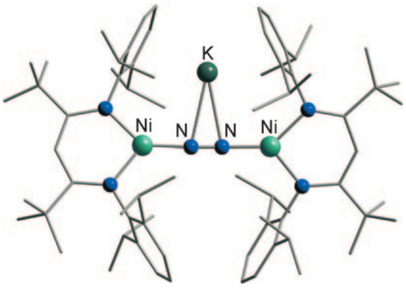
Y. Xu, G. Lu, S. Matsunaga,*
M. Shibasaki* ——— 3353 – 3356

Direct *anti*-Selective Catalytic Asymmetric Mannich-Type Reactions of α-Ketoanilides for the Synthesis of γ-Amino Amides and Azetidine-2-amides



Breaking with convention: A homodinuclear nickel complex derived from a biphenyldiamine-based Schiff base catalyzed an *anti*-selective Mannich-type reaction of α-ketoanilides (see scheme) to afford unique building blocks for the synthesis of azetidine-2-amides and α-hydroxy γ-amino amides. This approach stands in contrast to conventional Mannich-type reactions for the synthesis of β-amino carbonyl compounds. *o*-Ns = *o*-nitrobenzenesulfonyl.

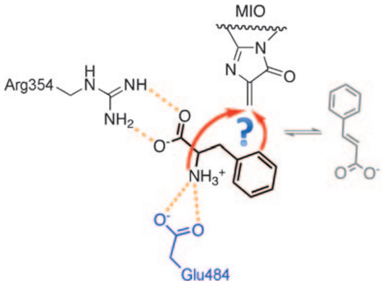
N_2 Activation



Electron by electron: β-Diketiminato nickel(I) complex fragments are capable of activating N_2 through coordination. The resulting complex can be reduced in two single-electron steps, which further activates the N–N bond. The picture shows the structure of the singly reduced complex with μ-η^1:η^1-bound N_2.

Enzyme Mechanism

All ways lead to Rome? Computer modeling and kinetic measurements identified a distinct residue in Phe/Tyr ammonia lyases (PAL/TAL) which controls whether the Friedel–Crafts or an E_1cB reaction mechanism takes place. Hence, Glu484 in *pc*PAL favors the Friedel–Crafts reaction (see picture, MIO = 4-methylidene imidazol-5-one) whereas an Asn in TAL gives an elimination reaction. These mechanistic investigations also reveal activity of a PAL mutant and a TAL towards an amino alcohol.



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).

Service

Corrigendum

The complete acknowledgment for this communication should read as follows: "This work was supported by Precursory Research for Embryonic Science and Technology (PRESTO),the Japan Science and Technology Agency (JST), and Creative Research Initiatives (Center for Time-Resolved Diffraction) of MOST/KOSEF (H.I.). D.J. thanks the JSPS Asian core program. J.G. was supported by a JSPS Fellowship for Young Scientists."

A Belt-Shaped, Blue Luminescent, and Semiconducting Covalent Organic Framework

S. Wan, J. Guo, J. Kim, H. Ihee, D. Jiang* ______ **8826–8830**

Angew. Chem. Int. Ed. **2008**, *47*

DOI 10.1002/anie.200803826