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:

*K. Tedsree, A. T. Kong, S. C. Tsang**
Formate as a Surface Probe for Ru Nanoparticles in Liquid ^{13}C NMR Spectroscopy

*A. Asati, S. Santra, C. Kaittanis, S. Nath, J. M. Perez**
Oxidase Activity of Polymer-Coated Cerium Oxide Nanoparticles

*K. M. Gericke, D. I. Chai, N. Bieler, M. Lautens**
The Norbornene Shuttle: Multicomponent Domino Synthesis of Tetrasubstituted Helical Alkenes through Multiple C–H Functionalization

*J.-Q. Wang, S. Stegmaier, T. F. Fässler**
$[Co@Ge_{10}]^{3-}$: An Intermetalloid Cluster with an Archimedean Pentagonal Prismatic Structure

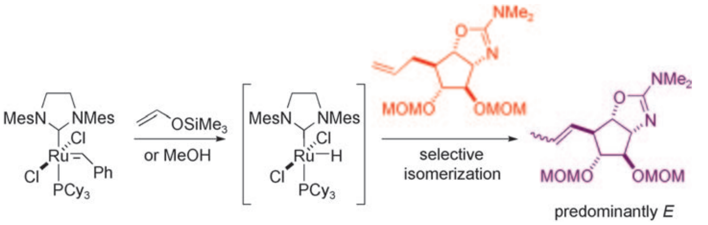
A. Mukherjee, M. Martinho, E. L. Bominaar, E. Münck, L. Que Jr.**
Shape-Selective Interception by Hydrocarbons of the O_2-Derived Oxidant of a Biomimetic Nonheme Iron Complex

A. Katranidis, D. Atta, R. Schlesinger, K. H. Nierhaus, T. Choli-Papadopoulou, I. Gregor, M. Gerrits, G. Büldt, J. Fitter**
Fast Biosynthesis of Green Fluorescent Protein Molecules—A Single-Molecule Fluorescence Study

Author Profile

Highlights

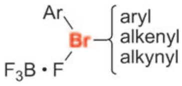
Olefin Isomerization



In, out, olefin about: A ruthenium hydride complex derived from the Grubbs second-generation metathesis catalyst has proven to be an efficient catalyst for the selective isomerization of terminal olefins to the corresponding propenyl derivatives (see scheme). This methodology has been applied in a number of syntheses to enable access to complex natural products. Cy = cyclohexyl, Mes = mesityl, MOM = methoxymethyl.

Bromine Reagents

Moving up a row in the Periodic Table leads from hypervalent iodine compounds to hypervalent bromine compounds, which are now readily available (see scheme). These compounds are more reactive than the well-known heavier analogues and undergo new reactions.

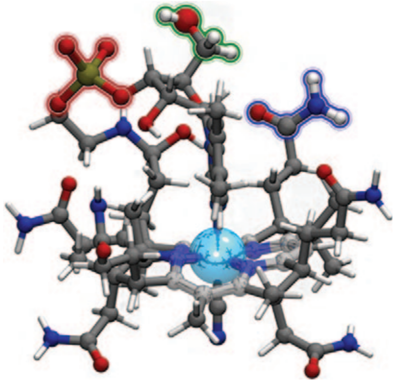


Contents

Minireviews

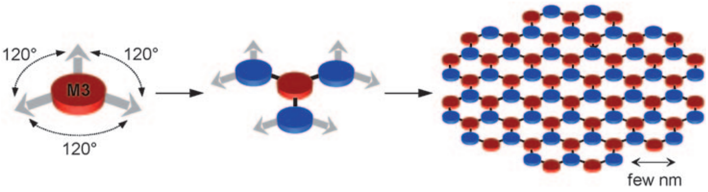
Medicinal Chemistry

Two major obstacles hinder the oral administration of therapeutic peptides and proteins: proteolytic degradation in the stomach and an inadequate mechanism for the absorption of polypeptides within the intestinal lumen. This Minireview focuses on the efficacy of oral peptide/protein delivery by the existing pathway for the dietary uptake of vitamin B_{12} (see picture; common sites of conjugation are highlighted at the top).



Reviews

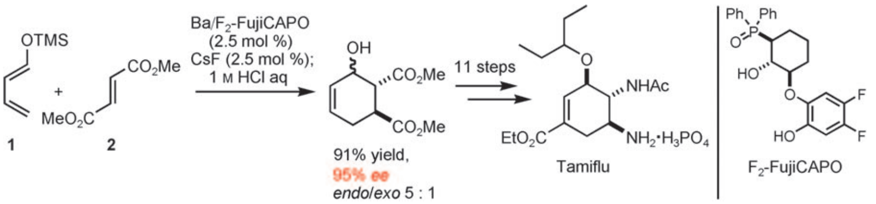
2D Polymers



A "molecular carpet" is a good description for a two-dimensional polymer. True 2D polymers have a thickness of one monomer unit and a regular structure. This Review describes attempts to synthesize such polymers (see scheme, M3: monomer with three functional groups). The focus of this Review is on the factors that must be considered if a truly 2D polymer is to be prepared.

Communications

Asymmetric Synthesis



In pursuit of a better route: A new catalytic asymmetric synthesis of Tamiflu was developed. The key transformation was an asymmetric Diels–Alder-type reaction of **1** and **2** catalyzed by a barium/F_2-FujiCAPO complex in the presence of a CsF cocatalyst to construct the core of Tamiflu (see scheme; TMS = trimethylsilyl). The product was converted into Tamiflu in 11 steps on a gram scale.

For the USA and Canada:
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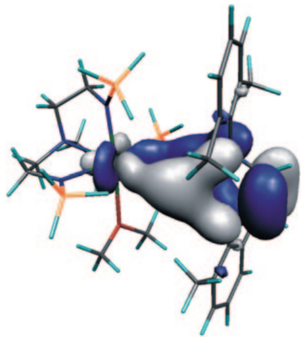
Uranium–Metal Bonds

S. T. Liddle,* J. McMaster, D. P. Mills,
A. J. Blake, C. Jones,*
W. D. Woodul ______ **1077–1080**

σ and π Donation in an Unsupported Uranium–Gallium Bond

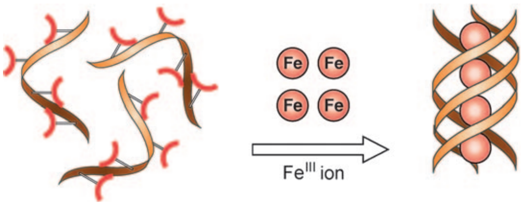
A charitable donation: The gallium center contributes to both π donation and σ donation in a uranium–gallium bond (see picture for results from calculations). The gallium center is isolobal to CO and N-heterocyclic carbenes (NHCs) and indicates that NHC π-donor behavior might be more widespread than previously recognized. The uranium–gallium bond may be regarded as a model for the as yet unreported U^{IV}—$CO^{-\bullet}$ unit.



DNA Structures

Y. Takezawa, W. Maeda, K. Tanaka,
M. Shionoya* ______ **1081–1084**

Discrete Self-Assembly of Iron(III) Ions inside Triple-Stranded Artificial DNA



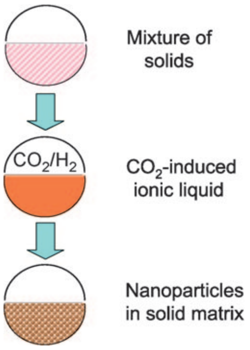
Triplex-rated: Discrete self-assembly of Fe^{III} ions with octahedral coordination geometry occurs within triple-stranded artificial DNA with hydroxypyridone nucleobases as metal ligands through the formation of nonplanar base triplets. Such a novel structural motif in DNA could lead to programmable alignment of six-coordinate transition metals.

Nanoparticle Catalysts

V. Cimpeanu, M. Kočevar,
V. I. Parvulescu,*
W. Leitner* ______ **1085–1088**

Preparation of Rhodium Nanoparticles in Carbon Dioxide Induced Ionic Liquids and their Application to Selective Hydrogenation

In the trap: Catalytically active nanoparticles can be generated and stabilized in solid ionic matrices with the aid of supercritical CO_2. The method allows the use of simple ammonium salts that would not be classified as ionic liquids, and results in solid and easily handled catalyst materials. These materials can selectively catalyze the hydrogenation of highly sterically encumbered aromatic olefins.

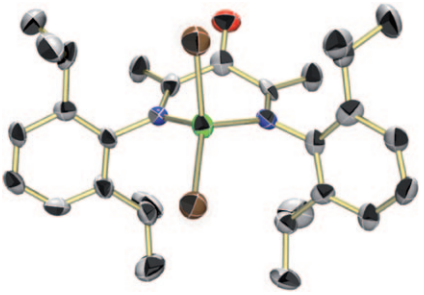


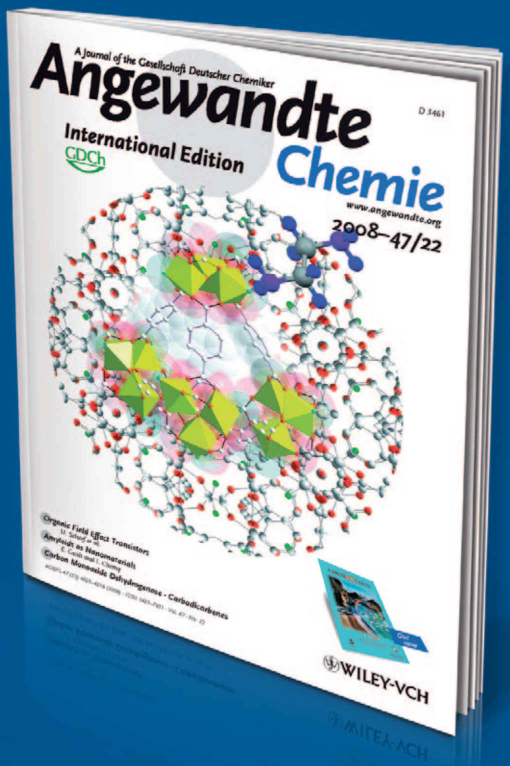
Homogeneous Catalysis

J. D. Azoulay, R. S. Rojas, A. V. Serrano,
H. Ohtaki, G. B. Galland, G. Wu,
G. C. Bazan* ______ **1089–1092**

Nickel α-Keto-β-Diimine Initiators for Olefin Polymerization

A new ligand–metal combination (see picture, Ni green, Br brown, N blue, O red, C gray) was designed to be cationic and to benefit from removal of electron density by the action of a Lewis acid on the ligand framework. In the presence of various activators, the resulting catalytic site is highly active for ethylene polymerization and capable of polymerizing α-olefins to high molecular weights.

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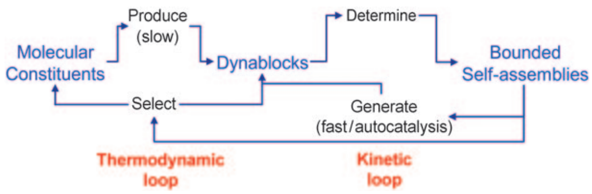
Combinatorial Chemistry

R. Nguyen, L. Allouche, E. Buhler,
N. Giuseppone* ________ 1093 – 1096

Dynamic Combinatorial Evolution within Self-Replicating Supramolecular Assemblies

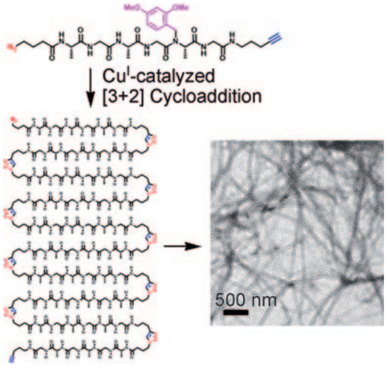


Survival of the fittest: Self-assemblies made of dynamic block copolymers (dynablocks) can self-replicate by catalyzing the formation of their own building blocks. Moreover, in competition experiments, the differential thermodynamic stabilities and autocatalytic efficiencies of these self-assemblies lead to sigmoid growth of the most efficient self-replicator and to depletion of its competitors.

Cycloaddition Polymerization

T. Yu, J. Z. Bai, Z. Guan* ___ 1097 – 1101

Cycloaddition-Promoted Self-Assembly of a Polymer into Well-Defined β Sheets and Hierarchical Nanofibrils

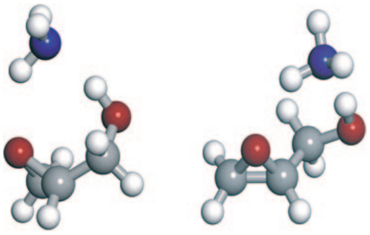


“Click” to fold: Cu^I-catalyzed azide–alkyne cycloaddition polymerization of a peptide monomer induced folding of the resultant polymer into well-defined β sheets, which further self-assemble into hierarchical nanofibrils. The antiparallel β-sheet structure was confirmed by several techniques. Scanning probe micrographs confirm the formation of hierarchical amyloid-like nanofibrils.

Adducts of Ammonia

B. M. Giuliano, S. Melandri, A. Maris,
L. B. Favero, W. Caminati* _ 1102 – 1105

Adducts of NH_3 with the Conformers of Glycidol: A Rotational Spectroscopy Study

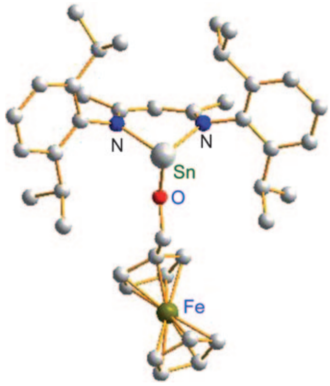


Two locks accept the same master key: Two different complexes of ammonia with two different conformers of glycidol have been characterized by Fourier transform microwave spectroscopy (see picture; gray C, blue N, red O, white H). In both complexes NH_3 is linked to the alcohol molecule through an O–H···N (stronger) and an N–H···O (weaker) hydrogen bond. Structural and energetic features of the hydrogen bonds are given.

Hydrostannylation

A. Jana, H. W. Roesky,* C. Schulzke,
A. Döring ____________ 1106 – 1109

Reactions of Tin(II) Hydride Species with Unsaturated Molecules

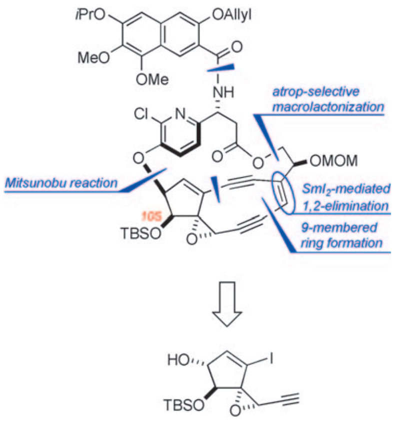


If anything can, tin can: The tin(II) hydride species [LSnH] (L = HC{CMeN(2,6-$i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3$)}$_2$) reacts with various compounds containing unsaturated C–O, C–C, or C–N bonds, which results in simultaneous transfer of hydrogen and {LSn} to the organic substrates and elegantly generates new tin(II) compounds. These unique stannylene compounds incorporate a lone pair of electrons that is suitable for complexation with transition-metal species.

Natural Products

K. Ogawa, Y. Koyama, I. Ohashi, I. Sato, M. Hirama* ________ 1110–1113

Total Synthesis of a Protected Aglycon of the Kedarcidin Chromophore

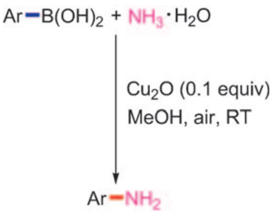


Strong support for the recently proposed structure of the kedarcidin chromophore has been obtained through the convergent synthesis of the aglycon. The key features of the synthesis are an efficient assembly of the four fragments, a novel strategy involving an alkynyl epoxide, a cerium amide promoted nine-membered diyne ring cyclization, and a SmI_2-mediated reductive 1,2-elimination. TBS = *tert*-butyldimethylsilyl, MOM = methoxymethyl.

Heterogeneous Catalysis

H. Rao, H. Fu,* Y. Jiang, Y. Zhao ________ 1114–1116

Easy Copper-Catalyzed Synthesis of Primary Aromatic Amines by Coupling Aromatic Boronic Acids with Aqueous Ammonia at Room Temperature

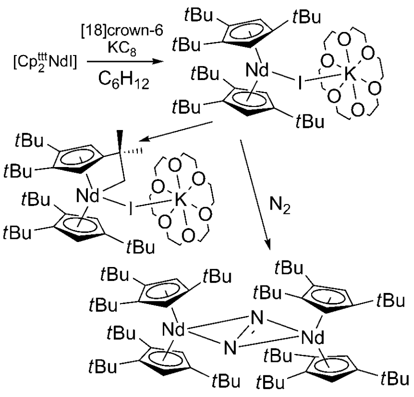


A reaction without the added extras: Aromatic boronic acids have been coupled using inexpensive aqueous ammonia to give primary aromatic amines under copper catalysis. This simple and highly efficient approach can be carried out in air at room temperature and, importantly, no base, ligand, or additive are required (see scheme).

Lanthanide Complexes

F. Jaroschik, A. Momin, F. Nief,* X.-F. Le Goff, G. B. Deacon, P. C. Junk* ________ 1117–1121

Dinitrogen Reduction and C–H Activation by the Divalent Organoneodymium Complex $[(C_5H_2tBu_3)_2Nd(\mu\text{-}I)K([18]\text{-}crown\text{-}6)]$



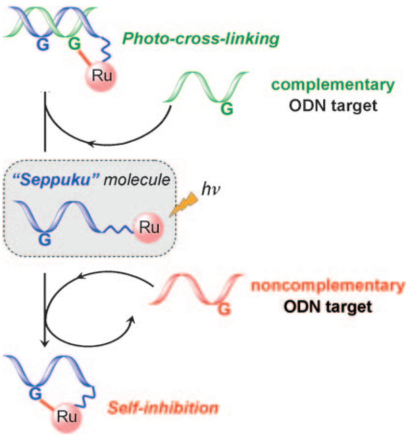
Highly reactive: The first divalent organoneodymium complex has been isolated and characterized by X-ray crystallography. It reacts immediately with all common aromatic and ethereal solvents, reduces dinitrogen to form an isolable dinitrogen complex, and undergoes C–H activation of a ligand *tert*-butyl group to form a crystallizable "tuck-in" complex (see scheme).

Oligonucleotide Labels

S. Le Gac, S. Rickling, P. Gerbaux, E. Defrancq, C. Moucheron, A. Kirsch-De Mesmaeker* __ 1122–1125

A Photoreactive Ruthenium(II) Complex Tethered to a Guanine-Containing Oligonucleotide: A Biomolecular Tool that Behaves as a "Seppuku Molecule"

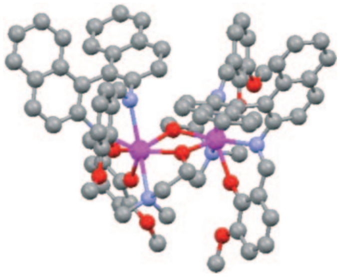
Self-destruction: Attachment of a photoreactive Ru^{II} complex to a guanine-containing oligonucleotide has led to an innovative biomolecular tool for gene silencing studies. This conjugate can be selectively photo-cross-linked with its complementary strand but undergoes a self-inhibition (or "seppuku") process in the presence of a noncomplementary target (see picture), which is an attractive strategy to avoid undesired secondary photoeffects.



Enantioselective Ring-Opening

B. Wu, J. C. Gallucci, J. R. Parquette,* T. V. RajanBabu* ——— **1126 – 1129**

Enantioselective Desymmetrization of *meso*-Aziridines with $TMSN_3$ or TMSCN Catalyzed by Discrete Yttrium Complexes

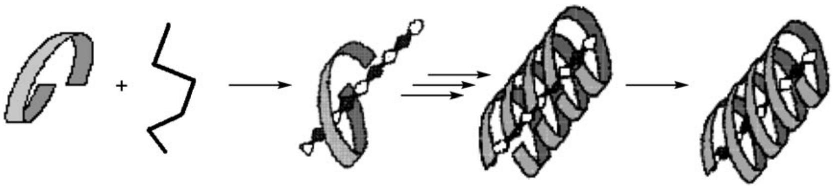


Y is it so? Dimeric yttrium–salen complexes (see structure; N blue, O red, Y magenta) catalyze the highly enantioselective ring-opening of *meso*-aziridines by TMSCN and $TMSN_3$. To explain the dramatic differences in the selectivity between mono- and dimeric catalysts, a dimetallic mechanism based on the solid-state structure of the dimer is proposed.

Self-Assembly

T. Sanji,* N. Kato, M. Tanaka* ——— **1130 – 1132**

Size-Selective Helical Stacking and Template Polymerization of Oligosaccharides around a Linear Polymeric Guest Molecule

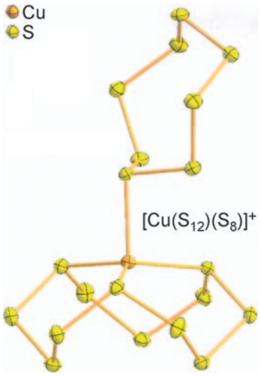


Clip and lock: Linear oligosaccharide host molecules are stacked in a helical manner around a polymeric guest molecule that acts as an axis (see picture). Molecular information such as substrate size and chirality is exchanged between the host and the guest to build up a supramolecular architecture, in which the template polymerization of the stacked oligosaccharide proceeds efficiently.

Cyclosulfur Ligands

G. Santiso-Quiñones, R. Brückner, C. Knapp, I. Dionne, J. Passmore, I. Krossing* ——— **1133 – 1137**

Cyclododecasulfur as a Ligand: From Gas-Phase Experiments to the Crystal Structures of $[Cu(S_{12})(S_8)]^+$ and $[Cu(S_{12})(CH_2Cl_2)]^+$

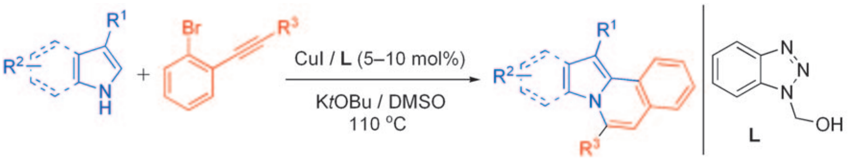


Just say S: Although gas-phase mass spectrometry experiments suggested the existence of Cu^I complexes with cyclosulfur ligands, such complexes had never been detected in the condensed phase. The use of "naked" Cu^I sources with weakly coordinating anions enables the preparation of the first cyclododecasulfur complexes of any metal.

Heterocycles

A. K. Verma,* T. Kesharwani, J. Singh, V. Tandon, R. C. Larock* ——— **1138 – 1143**

A Copper-Catalyzed Tandem Synthesis of Indolo- and Pyrrolo[2,1-*a*]isoquinolines



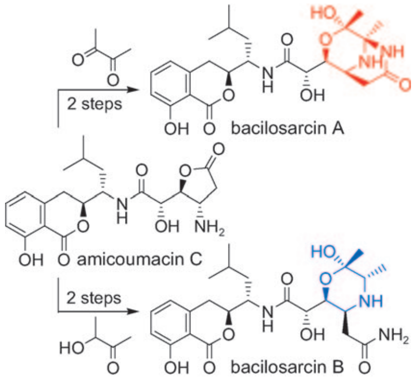
Isoquinoline ring the changes: A novel strategy for the title reaction involves *ortho*-haloarylalkynes which undergo sequential intermolecular addition of N heterocycles onto alkynes and subsequent intramolecular ring closure by arylation. The process involves the use of hydroxymethyl benzotriazole as an efficient and inexpensive ligand for the C—N and C—C coupling reactions.

Contents

Natural Product Synthesis

M. Enomoto, S. Kuwahara* **1144 – 1148**

Total Synthesis of Bacilosarcins A and B

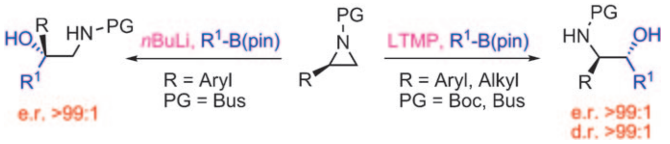


I want to ride my bicycle: The thermodynamic stability of nitrogen-containing heterocyclic ring systems is exploited in the first enantioselective total synthesis of bacilosarcins A and B, which has been achieved in simple two-step sequences from amicoumacin C. Bacilosarcin A incorporates a totally unprecedented heterobicyclic ring system and exhibits a remarkably potent herbicidal activity.

Amino Alcohols

F. Schmidt, F. Keller, E. Vedrenne, V. K. Aggarwal* **1149 – 1152**

Stereocontrolled Synthesis of β-Amino Alcohols from Lithiated Aziridines and Boronic Esters

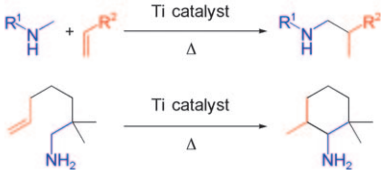


β-Amino alcohols have been prepared with high selectivity by the addition of lithiated aziridines to boronic esters. The regioselectivity of lithiation for aryl aziridines is sensitive to the reaction conditions and to the base employed. This response was exploited to give either class of β-amino alcohols (see scheme; Boc = *tert*-butoxycarbonyl, Bus = *tert*-butylsulfonyl, LTMP = lithium 2,2,6,6-tetramethylpiperidide, pin = pinacolato).

C–H Activation

R. Kubiak, I. Prochnow, S. Doye* **1153 – 1156**

Titanium-Catalyzed Hydroaminoalkylation of Alkenes by C–H Bond Activation at sp^3 Centers in the α-Position to a Nitrogen Atom

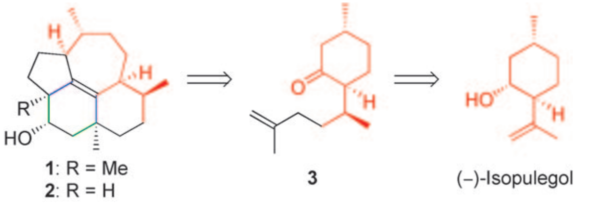


Good for primary and secondary amines: Hydroaminoalkylations of alkenes, which take place by C–H bond activation in the α-position to nitrogen atoms, are catalyzed by various neutral titanium complexes (see scheme). Primary as well as secondary amines can be used as substrates, and the reactions can be achieved intra- and intermolecularly.

Diterpenes

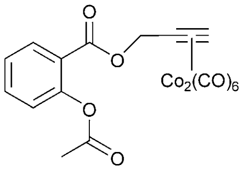
R. Hennig, P. Metz* **1157 – 1159**

Enantioselective Synthesis of 4-Desmethyl-3α-hydroxy-15-rippertene



Let it rip: An intramolecular Diels–Alder reaction and two intramolecular aldol condensations allow the efficient preparation of the title compound **2**, a close analogue of the diterpene **1** which was isolated from the defense secretion of termite soldiers. The synthesis commenced with cyclohexanone **3**, which is rapidly available from (–)-isopulegol.

Beyond treating headaches: The derivatization of biologically active compounds by organometallic units modulates their pharmacological properties. In studies of antitumor-related biochemical properties, the $Co_2(CO)_6$ derivative of aspirin **1** shows significantly modified influence on several relevant pathways, which might be based on an altered interaction with the target enzyme COX-2.



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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).

The issues for December 2008 appeared online on the following dates
Issue 48: November 12. · Issue 49: November 21. · Issue 50: November 26. · Issue 51: December 4. · Issue 52: December 12

Service

Corrigendum

Inadvertently references to structurally related iridates by the research group of Professor Ebbinghaus were omitted in this Communication. The authors apologize for the omission.

---

[55] a) Y. Wang, J. Lin, Y. Du, R. Qin, B. Han, C. Loong, *Angew. Chem.* **2000**, *112*, 2842; *Angew. Chem. Int. Ed.* **2000**, *39*, 2730; b) T. Gotzfried, A. Reller, S. G. Ebbinghaus, *Inorg. Chem.* **2005**, *44*, 6550; c) P. Lunkenheimer, T. Goetzfried, R. Fichtl, S. Weber, T. Rudolf, A. Loidl, A. Reller, S. G. Ebbinghaus, *J. Solid State Chem.* **2006**, *179*, 3965.

$Nd_2K_2IrO_7$ and $Sm_2K_2IrO_7$: Iridium(VI) Oxides Prepared under Ambient Pressure

S. J. Mugavero III, M. D. Smith, W.-S. Yoon, H.-C. zur Loye* ___ **215–218**

Angew. Chem. Int. Ed. **2009**, *48*

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