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Contents

Special Issue: Selective Reactions of Metal-Activated Molecules

Regular papers

Waldemar Adam, Wolfgang Malisch, Konrad J. Roschmann, Chantu R. Saha-Möller, Wolfdieter A. Schenk

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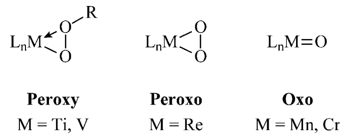
Catalytic oxidations by peroxy, peroxo and oxo metal complexes: an interdisciplinary account with a personal view

An overview of our results on the catalytic selective oxyfunctionalization of organic substrates by peroxy-, peroxo-, and oxo-type metal oxidants is presented. Also reported are the selective oxyfunctionalization of ligands by DMD in appropriately designed transition-metal complexes.



Waldemar Adam, Frank Heckel, Chantu R. Saha-Möller, Peter Schreier

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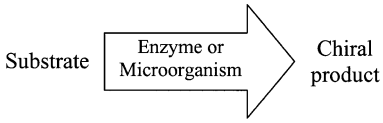
Biocatalytic synthesis of optically active oxyfunctionalized building blocks with enzymes, chemoenzymes and microorganisms

Summarized are our results on the biocatalytic preparation of optically active, oxyfunctionalized compounds (hydroperoxides, alcohols, α-hydroxy carboxylic acids, β-lactones and β-lactams) by enzymes or microorganisms through kinetic resolution and CH oxidation. Also the asymmetric sulfoxidation by *Coprinus* peroxidase (CiP) and microorganisms is reported.



Gerhard Bringmann, Matthias Breuning, Robert-M. Pfeifer, Wolfdieter A. Schenk, Ken Kamikawa, Motokazu Uemura

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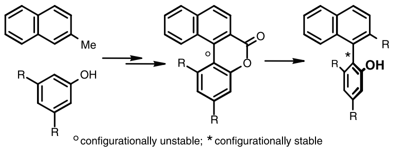
The lactone concept—a novel approach to the metal-assisted atroposelective construction of axially chiral biaryl systems

The atroposelective synthesis of axially chiral biaryls via configurationally unstable, lactone-bridged biaryls is reviewed. The resulting ring-opened configurationally stable biaryls are obtained in mostly excellent chemical and optical yields.



° configurationally unstable; * configurationally stable

Gerhard Bringmann, Stefan Tasler,
Robert-M. Pfeifer, Matthias Breuning

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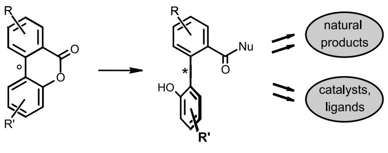
The directed synthesis of axially chiral ligands, reagents, catalysts, and natural products through the 'lactone methodology'

This microreview deals with recent applications of the lactone concept (see preceeding paper) in the atropo-selective syntheses of complex biarylic natural products and axially chiral ligands and auxiliaries.



° configurationally unstable; * configurationally stable

Jens Hartung, Marco Greb

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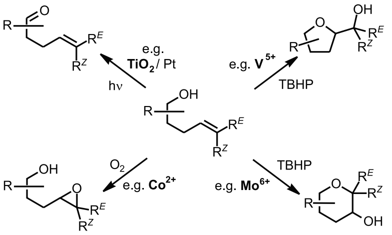
Transition metal-catalyzed oxidations of bishomoallylic alcohols

In recent years, new transition metal-catalyzed reactions for chemo- and stereoselective oxidations of bishomoallylic alcohols have been developed. In view of the diversity of this chemistry, it is the aim of this review to organize the principles of transition metal-catalyzed oxidations of bishomoallylic alcohols and to present its state of the art in modern organic synthesis. An emphasis has been laid on the diastereoselective formation of functionalized cyclic ethers.



Lutz H. Gade

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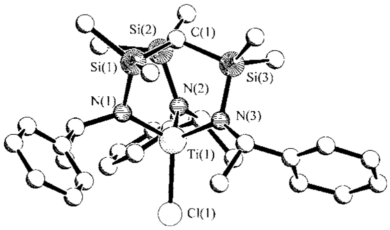
Transition metal complexes with polydentate amido ligands: novel structural building blocks and chemical reagents

Polydentate amido ligands have recently been widely employed in the coordination chemistry of the early transition metals and the heavy p-block elements. Formally, trianionic tripodal amides have provided the key to a systematic program of complex synthesis aimed at the construction of di- or trinuclear compounds through direct metal–metal bonding. These include unsupported, metal–metal bonded early–late heterodimetallic complexes as well as a wide range of transition-metal-Group 14 complexes. These developments as well as the application of C_3-chiral complexes in stereoselective alkylations of organic carbonyl compounds will be reviewed in this article. An extension of the underlying principles of ligand design to a new class of diamidopyridine ligands will also be highlighted.



Wolfgang Malisch, Bernd Klüpfel,
Dirk Schumacher, Martin Nieger

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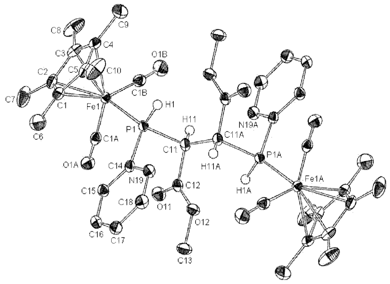
Hydrophosphination with cationic primary phosphine iron complexes: synthesis of P-chiral functionalized phosphines

Novel stereoselective syntheses of P-chiral secondary and tertiary phosphines are described, starting from primary phosphine iron complexes of the type $\{C_5R_5(L)\text{-}Fe[P(R')H_2]\}BF_4$ ($R = H$, Me; $R' =$ alkyl, aryl; $L = 2CO$, diphosphine) by base catalyzed hydrophosphination processes of various organic multibonded systems. Some remarkable products are represented by the compounds **9**, **11d** and **30**.



Frank Baier, Zhaofu Fei, Heinz Gornitzka, Alexander Murso, Stefan Neufeld, Matthias Pfeiffer, Ina Rüdenauer, Alexander Steiner, Thomas Stey, Dietmar Stalke

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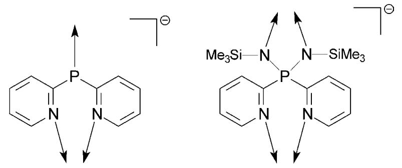
Phosphane- and phosphorane *Janus Head* ligands in metal coordination

2-Pyridyl substituted phosphanides and phosphoranates supply an additional coordination site in the organic substituent periphery. By their σ/π coordination site selectivity these *Janus Head* ligands serve as anionic staples in mixed Group 13/d-block metal complexes. The pyridyl substitution has also considerable impact on the reactivity. It facilitates double P–C bond cleavage and reduction of iminophosphoranes to phosphanamines.



Wolfdieter A. Schenk

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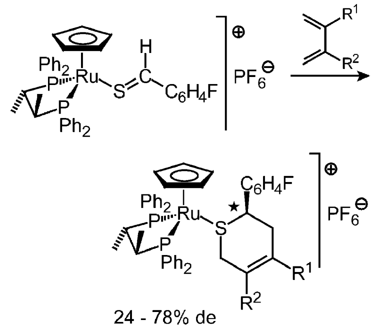
Stereoselective addition reactions of ruthenium thioaldehyde complexes

Halfsandwich-ruthenium complexes of thiobenzaldehydes and thiocinnamaldehydes add a variety of anionic carbon nucleophiles to give complexes of secondary thiolates. Furthermore, they undergo [4+2]-cycloadditions with 1,3-dienes or dienophiles and [4+1]-cycloadditions with diazomethane. Diastereoselective addition reactions are achieved using the enantiomerically pure complex fragment [CpRu{(*S*,*S*)-CHIRAPHOS}]$^+$ as a chiral auxiliary.



Helmut Werner, Kerstin Ilg, Raimund Lass, Justin Wolf

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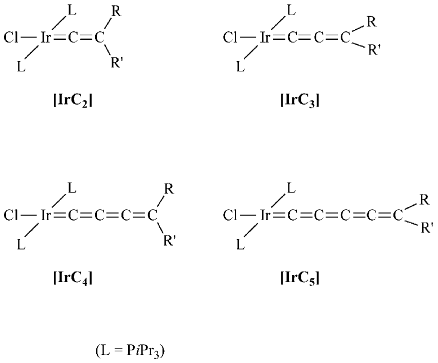
Iridium-containing cumulenes: how to prepare and how to use

This microreview summarizes the work on iridium-containing cumulenes of the general compositions *trans*-[IrX{=C(=C)$_n$RR′}(P*i*Pr$_3$)$_2$] with $n = 1$, 2, 3 and 4, which recently has been carried out in our laboratory. It is shown that all the parent compounds with X = Cl and an Ir=C=C, Ir=C=C=C, Ir=C=C=C=C or Ir=C=C=C=C=C chain can be prepared using [IrH$_2$Cl(P*i*Pr$_3$)$_2$] as the starting material.



Carsten Strohmann, Bors C. Abele, Klaus Lehmen, Fernando Villafañe, Luisa Sierra, Susana Martín-Barrios, Daniel Schildbach

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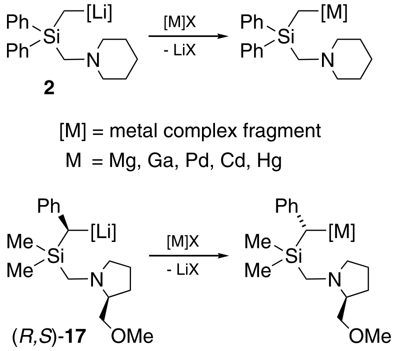
Enantiomerically enriched ‘carbanions’: Studies on the stereochemical course of selective transformations of metal alkyls

Two (aminomethyl)(lithiomethyl)silanes Ph$_2$Si(CH$_2$Li)(CH$_2$NC$_5$H$_{10}$) (NC$_5$H$_{10}$ = 1-piperidinyl) (**2**) and Me$_2$Si{[*R*]-[CHLiPh]}(CH$_2$SMP) {SMP = 1-[(*S*)-2-(methoxymethyl)pyrrolidinyl]} [(*R*,*S*)-**17**] are presented including their solid state structures, the first one non-chiral, the latter highly diastereomerically enriched. By metathesis reactions with metal(II) halides (metal = Mg, Ga, Pd, Cd and Hg), the corresponding bis{[(aminomethyl)silyl]methyl}metal(II) compounds or the [(aminomethyl)silyl]methylmetal(II) halides were obtained.



Torsten Linker

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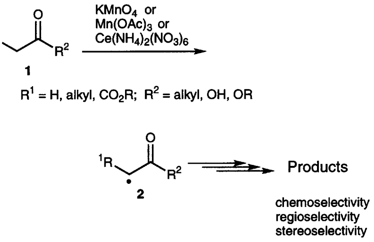
Selective reactions of transition-metal-generated radicals

Radicals **2** are generated from easily available CH-acidic precursors **1** in the presence of potassium permanganate, $Mn(OAc)_3$, or cerium(IV) ammonium nitrate. Addition of the radicals **2** to various alkenes affords products with high chemo-, regio- and stereoselectivities. Applications range from simple tetra-acceptor-substituted alkenes to the synthesis of 2-*C*-branched carbohydrates in high yield.



Michael Schmittel, Andreas Haeuseler

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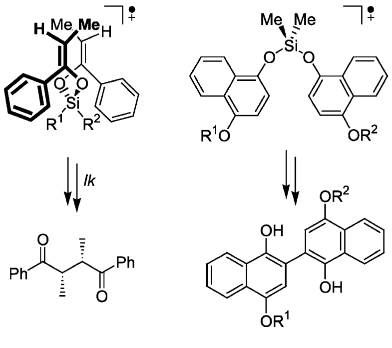
One-electron oxidation of metal enolates and metal phenolates

The design of intramolecular oxidative couplings of metal bisenolates or bisphenolates is being described. Special attention is given to M–O bond cleavage and C–C coupling on the stage of the radical cations.



D. Moigno, B. Callejas-Gaspar,
J. Gil-Rubio, H. Werner, W. Kiefer

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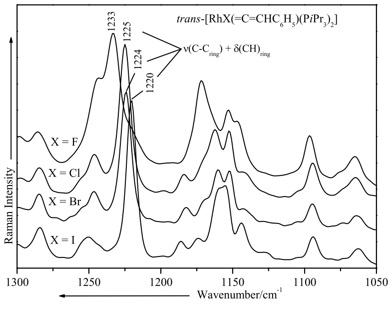
The metal–carbon bond in vinylidene, carbonyl, isocyanide and ethylene complexes

Density functional theory (DFT) calculations were carried out for *trans*-$[RhX(L)(PMe_3)_2]$ ($L = C{=}CH_2$, $C{=}CHC_6H_5$, CO, 2,6-$Me_2C_6H_3NC$, C_2H_4) which served as model compounds for the analysis of the vibrational spectra of related complexes. The characterization of the metal–carbon stretching mode allowed to study the *trans* influence of a series of ligands on the metal–carbon bond in vinylidene, carbonyl and isocyanide complexes. Furthermore, the comparison of the FT-Raman spectra of the complexes *trans*-$[RhF(CO)(PiPr_3)_2]$ and *trans*-$[RhF(^{13}C{=}^{13}CH_2)(PiPr_3)_2]$ which possess the same reduced mass ($^{13}C{=}^{13}CH_2$ vs. CO) allowed for an evaluation of the Rh–C bond strength free of any mass effects and therefore only showing effects of electronic nature.



M. Erdmann, O. Rubner, Z. Shen, V. Engel

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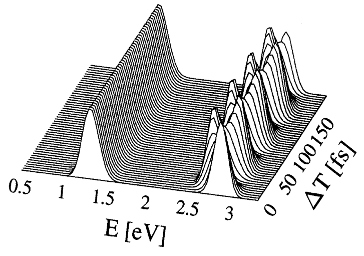
Time-resolved photoelectron spectroscopy: A unique tool to monitor the vibrational and fragmentation dynamics of metal carbonyls

Femtosecond time-resolved photoelectron spectroscopy can be used to characterize the dynamics of metal–carbon vibrations and bond cleavage. Calculations are presented for pulse induced FeCO bound-state motion and photodissociation of $Fe(CO)_5$.



M. Bergt, T. Brixner, C. Dietl, B. Kiefer, G. Gerber

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Time-resolved organometallic photochemistry
Femtosecond fragmentation and adaptive control of $CpFe(CO)_2X$ (X = Cl, Br, I)

We report a systematic experimental study of the influence of metal–ligand bonding properties on the ultrafast photofragmentation dynamics and on quantum control of organometallic molecules in the gas phase, employing the techniques of femtosecond pump–probe time-of-flight mass spectrometry as well as adaptive femtosecond laser pulse shaping.