

Contents

Special Issue: Chirality in Organometallic Chemistry: New Ligands, New Complexes and New Applications

Foreword 2071

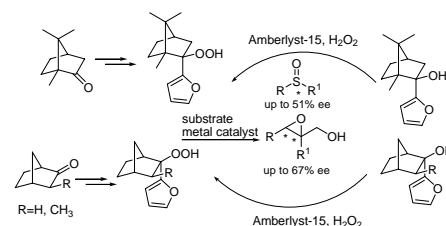
Reviews

Alessandra Lattanzi, Arrigo Scettri

J. Organomet. Chem. 691 (2006) 2072

Metal-catalyzed asymmetric oxidations mediated by optically pure furyl hydroperoxides

Metal-catalyzed asymmetric oxidations using optically pure furyl hydroperoxides as oxygen and chirality source are reviewed. The synthetic sequence to enantiopure furyl hydroperoxides, easily accessible from ketones of the chiral pool is firstly described. Examples of metal-catalyzed asymmetric oxidations using these compounds for the production of enantiomerically enriched sulfoxides and epoxy alcohols are shown.

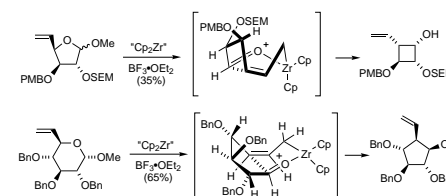


Leo A. Paquette

J. Organomet. Chem. 691 (2006) 2083

Zirconocene-mediated deoxygenative ring contractions of vinyl-substituted carbohydrates: An expedient route to enantiomerically pure, densely functionalized 4-to-8-membered carbocycles

The zirconocene reagent reacts with vinyl furanosides and pyranosides, readily available via established carbohydrate transformations, to furnish enantiopure cyclobutanols and cyclopentanols. These transformations proceed with predictable regioselectivity via chelated transition states, such that the hydroxyl and neighboring vinyl substituents are ultimately *cis* related. Some synthetic uses to which these products have been applied are briefly described.

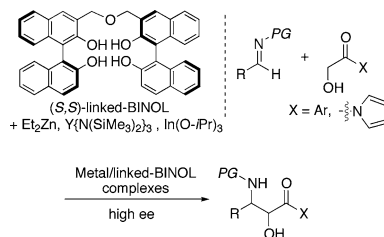


Masakatsu Shibasaki, Shigeki Matsunaga

J. Organomet. Chem. 691 (2006) 2089

Metal/linked-BINOL complexes: Applications in direct catalytic asymmetric Mannich-type reactions

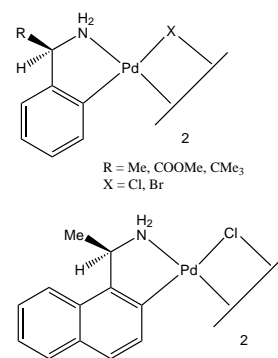
Development of metal/linked-BINOL complexes and their applications in direct catalytic asymmetric Mannich-type reactions of hydroxyketones are reviewed. Et_2Zn , $\text{Y}\{\text{N}(\text{Si-Me}_3)_2\}_3$, and $\text{In}(\text{O-}i\text{Pr})_3$ /linked-BINOL complexes gave β -amino- α -hydroxy carbonyl compounds in good diastereoselectivity and high ee.



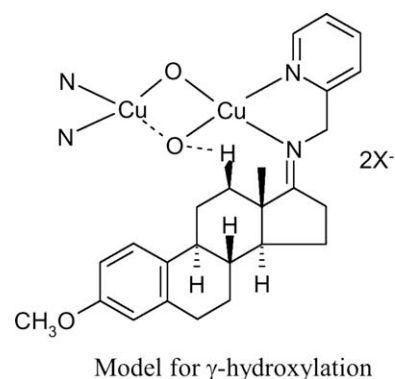
Joan Albert, Jaume Granell, Guillermo Muller*J. Organomet. Chem.* 691 (2006) 2101

Synthesis and applications of optically active metallacycles derived from primary amines

The synthesis of optically active cyclopalladated derivatives containing primary amines and their application as resolving agents of Lewis bases is reviewed.

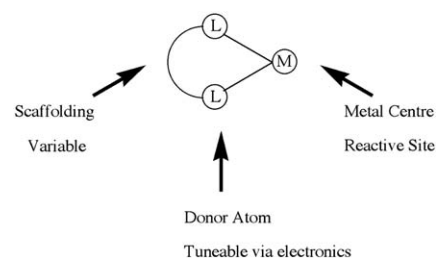
**B. Schönecker, C. Lange***J. Organomet. Chem.* 691 (2006) 2107

Steroids as chiral model compounds for selective reactions with metals

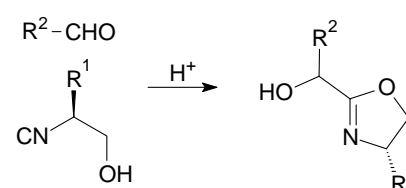
Our work on reactions with nickelacycles, (π -allyl) zircon-oxy-carbene complexes, iron tricarbonyl complexes, the Ru-catalyzed synthesis of 1,3-dihydropyrrol-2-ones, the Pd-catalyzed cyclopropanation of α,β -unsaturated imines, syntheses with cuprio steroids, copper complexes of amino alcohol derivatives and the copper-mediated hydroxylation of non-activated C-H bonds with molecular oxygen is reviewed.**Susan P. Flanagan, Patrick J. Guiry***J. Organomet. Chem.* 691 (2006) 2125

Substituent electronic effects in chiral ligands for asymmetric catalysis

The importance of electronic variations within a selection of chiral ligands for asymmetric catalysis will be reviewed.

**Communications****Michael Bauer, Uli Kazmaier***J. Organomet. Chem.* 691 (2006) 2155

A new, modular approach towards 2-(1-hydroxyalkyl)oxazolines, effective bidentate chiral ligands

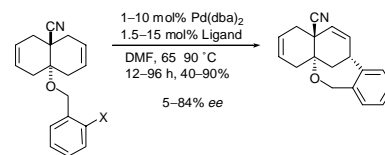
Addition of β -hydroxyisocyanides towards aldehydes gives rise to hydroxyalkyl oxazolines, an interesting class of bidentate chiral ligands. This concept allows a very easy ligand tuning and optimization of the ligand structure as illustrated in a first example.

Matthias E.P. Lormann, Martin Nieger, Stefan Bräse

J. Organomet. Chem. 691 (2006) 2159

Desymmetrisation of bicyclo[4.4.0]decadienes: A planar-chiral complex proved to be most effective in an asymmetric Heck reaction

The synthesis and desymmetrisation of bicyclo[4.4.0]decadienes is described; the enantioselective Heck reaction using JOSIPHOS as a planar-chiral complex produces a tetracyclic system with three stereogenic centers in up to 84% enantiomeric purity.



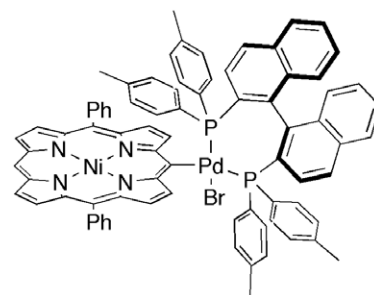
Regular papers

Margaret J. Hodgson, Victor V. Borovkov, Yoshihisa Inoue, Dennis P. Arnold

J. Organomet. Chem. 691 (2006) 2162

A new type of chiral porphyrin: Organo-palladium porphyrins with chiral chelating diphosphine ligands

Peripherally palladated Ni(II) porphyrins with chiral ligands, [PdBr(NiDPP)(CHIRAPHOS)], [CHIRAPHOS = 2,3-bis(diphenylphosphino)butane], [PdBr(NiDPP)(Tol-BINAP)] [Tol-BINAP = 2,2'-bis(di-*p*-tolylphosphino)-1,1'-binaphthyl] and [PdBr(NiDPP)(diphos)] [diphos = 1,2-bis(methylphenylphosphino)benzene] have been prepared. The induced asymmetry in the porphyrin was readily detected by ¹H NMR and CD spectroscopy. The three types of chiral ligand influence the CD spectral profiles in individual ways.

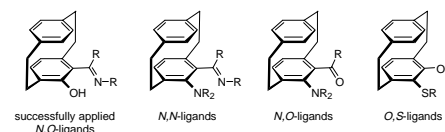


Michael Kreis, Martin Nieger, Stefan Bräse

J. Organomet. Chem. 691 (2006) 2171

Synthesis of novel planar-chiral [2.2]paracyclophane derivatives as potential ligands for asymmetric catalysis

The synthesis of a variety of new 4,5-disubstituted [2.2]paracyclophane derivatives has been achieved employing different cross-coupling reactions. By this methodology, a heteroatom-variation of successful catalyst ligands was achieved, giving rise to a modular ligand system. The X-ray structure of 4-hydroxy-5-(1'-hydroxy-1'-phenylethyl)-[2.2]paracyclophane was determined to elucidate the configuration.

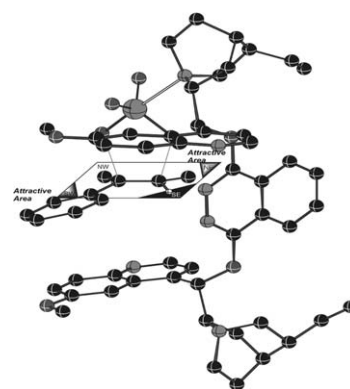


Peter Fristrup, Gitte Holm Jensen, Marie Louise Nygaard Andersen, David Tanner, Per-Ola Norrby

J. Organomet. Chem. 691 (2006) 2182

Combining Q2MM modeling and kinetic studies for refinement of the osmium-catalyzed asymmetric dihydroxylation (AD) mnemonic

The role of each moiety of one of the most popular ligands in the Sharpless AD reaction has been elucidated in detail using a combination of kinetic and computational studies.

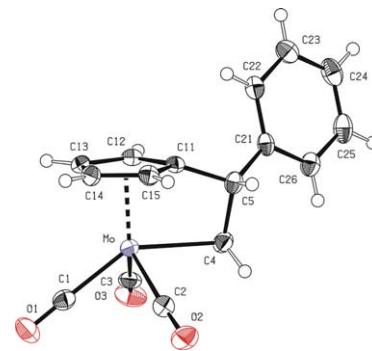


Jin Zhao, Eberhardt Herdtweck, Fritz E. Kühn

J. Organomet. Chem. 691 (2006) 2199

Chiral *ansa*-bridged η^5 -cyclopentadienyl molybdenum complexes: Synthesis, structure and application in asymmetric olefin epoxidation

Ansa-bridged η^5 -cyclopentadienyl carbonyl molybdenum complexes were synthesized with stereogenic centers located in the side chain. The compounds show a good catalytic activity, comparable to activities observed for the related non-chiral complexes of composition $\text{CpMo}(\text{CO})_3\text{X}$ ($\text{X} = \text{Cl}, \text{CH}_3$). The high ring strain of the *ansa*-bridged system hampers, unfortunately, its stability under oxidative condition.

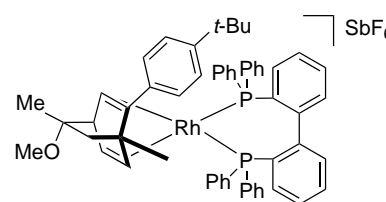


J.W. Faller, Jeremy C. Wilt

J. Organomet. Chem. 691 (2006) 2207

Resolution of BIPHEP on Rh with a chiral diene auxiliary

Resolution of the atropisomerically chiral BIPHEP ligand on Rh has been achieved with the aid of a chiral diene ligand. The diene complex containing an (*S*)-BIPHEP ligand was found to be configurationally stable in CDCl_3 solution at RT. Conversion of the diene complex to a dicarbonyl Rh complex that had a barrier of 25.0 kcal/mol for atropisomerization of the BIPHEP ligand.

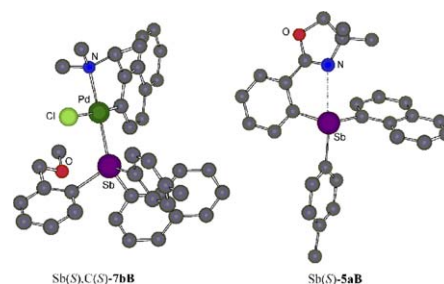


**Shuji Yasuike, Yoshihito Kishi,
Shin-ichiro Kawara, Kentaro Yamaguchi,
Jyoji Kurita**

J. Organomet. Chem. 691 (2006) 2213

Synthesis of enantiomerically pure Sb-chirogenic organoantimony compounds and their crystal structures

Sb-chirogenic organoantimony compounds bearing heteroatom groups on the *o*-position of an aryl group have been prepared by nucleophilic displacement of the ethynyl moiety on (1-naphthyl)(phenylethynyl)(*p*-tolyl)stibane with aryllithium reagents. Optical resolution of the racemic compounds thus synthesized was achieved via separation of a diastereomeric mixture of their palladium complexes.

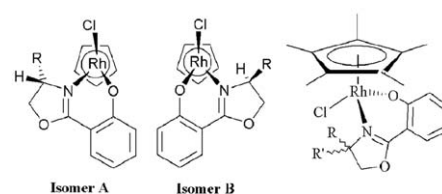


**Adam J. Davenport, David L. Davies,
John Fawcett, David R. Russell**

J. Organomet. Chem. 691 (2006) 2221

Cp^* rhodium complexes with salicyloxazolines: Diastereoselective synthesis, configurational stability and use as asymmetric catalysts for a Diels–Alder reaction

Complexes $[\text{RhCl}(\text{R-saloxaz})\text{Cp}^*]$ have been synthesised, the nature of R determines which diastereomer (A or B) is favoured. The absolute configuration at the metal is unstable, epimerisation occurring at a rate comparable with the NMR timescale.

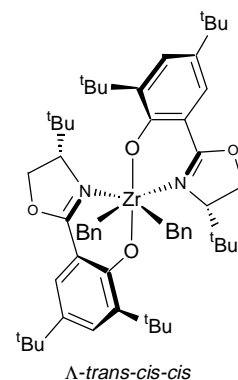


**Ian Westmoreland, Ian J. Munslow,
Adam J. Clarke, Guy Clarkson,
Robert J. Deeth, Peter Scott**

J. Organomet. Chem. 691 (2006) 2228

Expression of chirality in salicyloxazolinato complexes of zirconium

DFT calculations and dynamic NMR spectra indicate that $[L_2ZrX_2]$ (L = salicyloxazolinato) exhibits excellent thermodynamic diastereoselection for metal-centred chirality, although it is argued that the chirality of the system is not well expressed in the environment of the co-ligands.

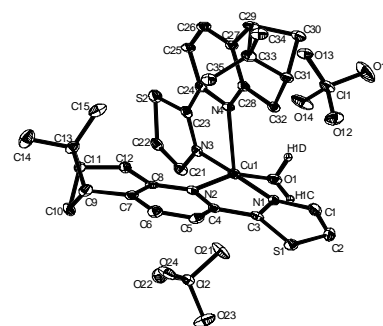


**Pang-Fei Teng, Chui-Shan Tsang,
Ho-Lun Yeung, Wing-Leung Wong,
Hoi-Lun Kwong, Ian D. Williams**

J. Organomet. Chem. 691 (2006) 2237

New chiral bidentate ligands containing thiazolyl and pyridyl donors for copper-catalyzed asymmetric allylic oxidation of cyclohexene

Chiral bidentate pyridyl–thiazole ligands were prepared. The structure of a copper(II) perchlorate ligand complex was characterized with X-ray crystallography. The copper(I) thiazolyl–pyridine complexes prepared in situ are active catalysts in the enantioselective allylic oxidation of cyclohexene.

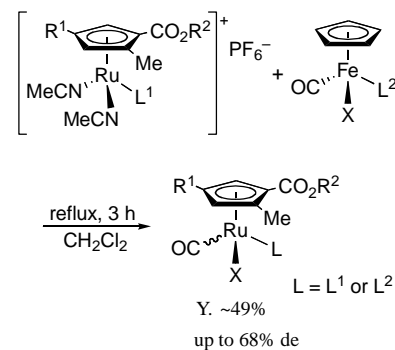


**Taku Katayama, Kiyotaka Onitsuka,
Shigetoshi Takahashi**

J. Organomet. Chem. 691 (2006) 2245

Diastereoselectivity at chiral metal center of half-sandwich-type ruthenium complexes with planar-chiral cyclopentadienyl ligands in multiple ligand transfer reaction

The multiple ligand transfer reaction between planar-chiral cyclopentadienyl–ruthenium complexes $[Cp^*Ru(NCMe)_2(L^1)]PF_6$ and iron complexes $Cp^*Fe(CO)(L^2)X$ resulted in the formation of metal-centered chiral ruthenium complexes $Cp^*Ru(CO)(L^1)X$ or $Cp^*Ru(CO)(L^2)X$ in moderate yields with diastereoselectivities of up to 68% de.

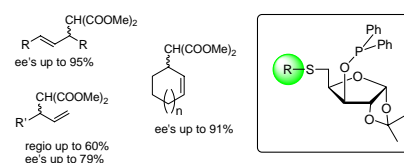


**Montserrat Diéguez, Oscar Pàmies,
Carmen Claver**

J. Organomet. Chem. 691 (2006) 2257

Furanoside thioether–phosphinite ligands for Pd-catalyzed asymmetric allylic substitution reactions: Scope and limitations

A series of readily available thioether–phosphinite ligands with different electronic and steric properties has been tested in the Pd-catalyzed allylic substitution reactions of several acyclic and cyclic allylic substrates.

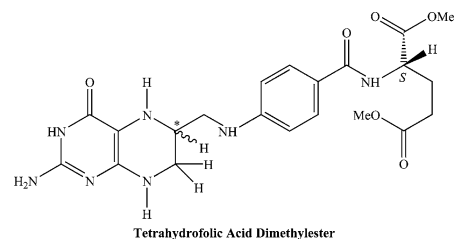


Wolfgang Braun, Beatrice Calmuschi-Cula, Albrecht Salzer, Viola Groehn

J. Organomet. Chem. 691 (2006) 2263

Diastereoselective hydrogenation of folic acid esters with the Daniphos ligand

The “Daniphos” ligand was employed in the hydrogenation of folic acid dimethyl ester benzenesulfonate. Tetrahydrofolic acid dimethylester has been obtained with selectivities of up to 42% *de*, matching “the state of the art”. An X-ray structure of the most successful ligand is presented and discussed.

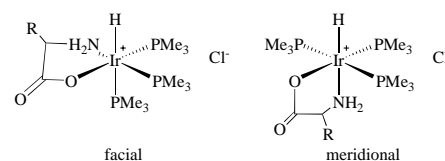


Christopher P. Roy, Lisa A. Huff, Nick A. Barker, Michael A.G. Berg, Joseph S. Merola

J. Organomet. Chem. 691 (2006) 2270

Iridium(III) hydrido amino acid compounds: Chiral complexes and a helical extended lattice

$[\text{Ir}(\text{COD})(\text{PMe}_3)_3]\text{Cl}$, **1**, reacts with amino acids in water to yield cationic hydride amino acid complexes, $[\text{Ir}(\text{aa})(\text{H})(\text{PMe}_3)_3]\text{Cl}$, **2**. In general, complexes **2** display octahedral geometry with a meridional arrangement of the PMe_3 ligands, with the amino acid chelating through O and N and with hydride *trans* to N. Disubstituted amino acids on the other hand favor the formation of octahedral complexes with a facial arrangement of PMe_3 ligands. The crystal structure of the valine complex, **2c**, was obtained and, in addition to confirming the structure of the complex, showed a helical extended lattice structure due to intermolecular N–H–O bonding.

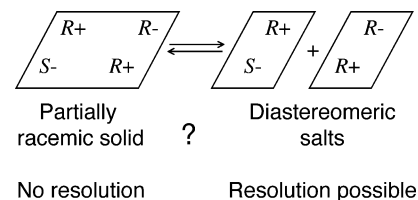


Irmgard Kalf, Ruimin Wang, Ulli Englert

J. Organomet. Chem. 691 (2006) 2277

Unexpected solids from enantiopure cationic palladium complexes and racemic anions: A structural study of chiral non-discrimination

Enantiomerically pure organopalladium cations form partially racemic salts with racemic mandelate and hydratropate anions. The resulting solids and their more popular crystallization alternatives have been characterized and compared in terms of crystal packing and lattice energy.

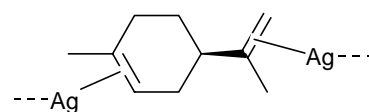


Justine R.A. Cottam, Peter J. Steel

J. Organomet. Chem. 691 (2006) 2286

X-ray crystal structures of discrete and polymeric chiral silver complexes of monoterpenoid alkenes

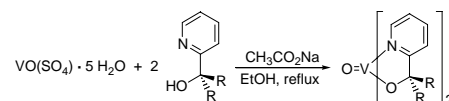
X-ray crystal structures are reported for five silver(I) complexes of four naturally occurring monoterpenes, including discrete mononuclear species and coordination polymers.



**Gerhard M. Lobmaier, Harald Trauthwein,
Guido D. Frey, Bernd Scharbert,
Eberhardt Herdtweck, Wolfgang A. Herrmann**
J. Organomet. Chem. 691 (2006) 2291

Oxovanadium(IV) complexes as molecular catalysts in epoxidation: Simple access to pyridylalkoxide derivatives

Reaction of bis(aryl)-2-pyridylmethanols with $\text{VO}(\text{SO}_4) \cdot 5\text{H}_2\text{O}$ results in the formation of vanadium-oxo complexes $[\text{VO}(\text{N}-\text{O})_2]$. The metal-oxo complexes demonstrated the ability to catalyse epoxidation reactions of alkenes with molecular oxygen.

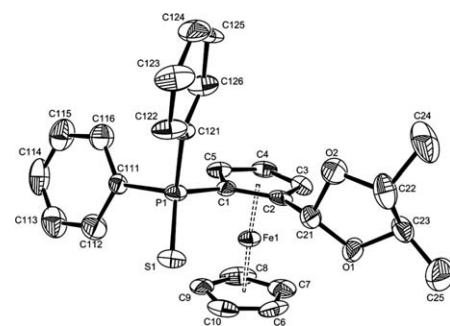


**Nuno Mateus, Lucie Routaboul,
Jean-Claude Daran, Eric Manoury**

J. Organomet. Chem. 691 (2006) 2297

Synthesis and catalytic applications of new chiral ferrocenyl P,O ligands

New chiral ferrocenyl phosphine-acetals ligands have been synthesized in an enantiomerically pure form from chiral 1,2 or 1,3-diols and the two isomers of 2-diphenylphosphino-ferrocenecarboxaldehyde. These new P,O ligands were successfully used in the palladium-catalyzed asymmetric allylic substitution of 1,3-diphenylprop-2-enylacetate with good enantioselectivities (up to 77%).

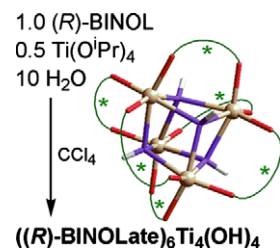


**Gennaro Pescitelli, Lorenzo Di Bari,
Piero Salvadori**

J. Organomet. Chem. 691 (2006) 2311

Effect of water on BINOL/Ti(OⁱPr)₄ solution mixtures: The nature of a catalytic precursor of enantioselective sulfoxidation

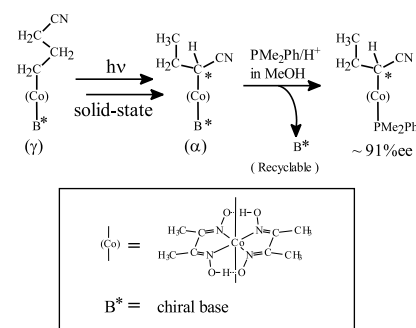
1:0.5:10 (*R*)-BINOL/Ti(OⁱPr)₄/H₂O mixtures in CCl₄ (conditions employed for catalyzing enantioselective sulfoxidation) contain a single titanium BINOLate species, which is identified (by NMR, CD and MS) as the *T*-symmetric (BINOLate)₆Ti₄(μ₃-OH)₄ compound. Sample preparation conditions were varied to rationalize some aspects of the catalytic behavior, e.g., non-linear effects.



**Yoshiaki Ohgo, Kanako Ishida,
Yoshito Hiraga, Yoshifusa Arai, Seiji Takeuchi**
J. Organomet. Chem. 691 (2006) 2319

Solid state-specific and chiral lattice-controlled asymmetric photoisomerization of 3-substituted propyl cobalt complexes, and direct observation of the intermediate complex

Solid state-specific and chiral lattice-controlled asymmetric photoisomerization of 3-cyano-propyl cobaloxime complexes coordinated with chiral axial ligand occurred with relatively high enantioselectivities (~91%ee). The structure (including absolute configuration) of the intermediate 2-cyanopropyl complex was directly observed by X-ray analyses of a single-crystal-to-single-crystal reaction of (*S*)-1-cyclohexylethylamine-coordinated 3-cyano-propyl cobaloxime.



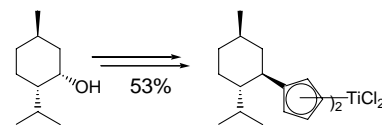
Notes

**Andreas Gansäuer, Sanjay Narayan,
Noëlle Schiffer-Ndene, Harald Bluhm,
J. Enrique Oltra, Juan Manuel Cuerva,
Antonio Rosales, Martin Nieger**

J. Organomet. Chem. 691 (2006) 2327

An improved synthesis of Kagan's menthyl substituted titanocene and zirconocene dichloride, comparison of their crystal structures, and preliminary catalyst evaluation

An improved synthesis of **1** and **2** is described that allows access to these complexes in multigram quantities necessary for catalytic applications. The crystal structures of **1** and **2** are compared and the conformational preferences of the ligands, that are important for catalytic applications, are discussed. Complex **2** was evaluated as a catalyst for carbomagnesation reactions.



**Gabriela A. Grasa, Antonio Zanotti-Gerosa,
William P. Hems**

J. Organomet. Chem. 691 (2006) 2332

A chiral [(dipyridylphosphine)RuCl₂(1,3-diphenylpropanediamine)] catalyst for the hydrogenation of aromatic ketones

The use of chiral 1,3-diphenylpropanediamine in combination with Ru-Xyl-P-Phos, gave up to 95% ee in the hydrogenation of acetophenone.

