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Volume 690, issue 20, 10 October 2005



www.elsevier.com/locate/jorganchem

Contents

Special Issue: 14th International Symposium on Homogeneous Catalysis

Reviews

Yasunori Yoshida, Shigekazu Matsui, Terunori Fujita

J. Organomet. Chem. 690 (2005) 4382

Bis(pyrrolide-imine) Ti complexes with MAO: A new family of high performance catalysts for olefin polymerization

PI Catalysts, which were discovered based on a "ligand-oriented catalyst design concept", copolymerize ethylene with norbornene in a highly controlled living fashion at room temperature, displaying excellent incorporation capability for norbornene. The unique catalytic performance stems from the highly electrophilic and sterically open nature of the active species.



Rieko Furuyama, Junji Saito, Seiichi Ishii, Haruyuki Makio, Makoto Mitani, Hidetsugu Tanaka, Terunori Fujita

J. Organomet. Chem. 690 (2005) 4398

Fluorinated bis(phenoxy-imine) Ti complexes with MAO: Remarkable catalysts for living ethylene and syndioselective living propylene polymerization Ti–FI Catalysts can carry out highly controlled, thermally robust living ethylene and highly syndioselective living propylene polymerizations, stemming from the attractive interaction between the ligand and a growing polymer chain and the fluxionality of an octahedral framework coupled with 2,1regiochemistry.



High performance living ethylene and syndioselective living propylene polymerization catalysts

Ti-FI Catalysts

Kazushi Mashima, Hayato Tsurugi

J. Organomet. Chem. 690 (2005) 4414

Uniqueness and versatility of iminopyrrolyl ligands for transition metal complexes

In this review, synthesis and structural features of transition metal and main metal complexes with multidentate iminopyrrole ligands are reported. Some of these complexes are acting as precatalysts for polymerization of ethylene and α -olefins.



Regular papers

F. Estevan, P. Lahuerta, J. Lloret, D. Penno, M. Sanaú, M.A. Úbeda

J. Organomet. Chem. 690 (2005) 4424

Rhodium (II) compounds with functionalized metalated phosphines as bridging ligands Two biscyclometalated compounds of formula $Rh_2(O_2CCH_3)_2[PC] \cdot [PC'] \cdot 2CH_3CO_2H$ containing a mixed set of orthometalated phosphimes, $P(4\text{-}BrC_6H_4)_2(C_6H_5)$ and $P(C_6H_5)_3$ have been obtained. The compounds contain a backbone configuration and a stereogenic centre. They have been resolved in the corresponding *M* and *P* enantiomers that show good enantioselectivities in catalytic transformation of α -diazocarbonyl compounds.



Nicolas Imlinger, Klaus Wurst, Michael R. Buchmeiser

J. Organomet. Chem. 690 (2005) 4433

Rh(1,3-bis(2,4,6-trimethylphenyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD) tetrafluoroborate, an unsymmetrical Rh-homoazallylcarbene: synthesis, X-ray structure and reactivity in carbonyl arylation and hydrosilylation reactions Novel Rh(1,3-bis(2,4,6-trimethylphenyl)-3,4, 5,6-tetrahydropyrimidin-2-ylidene) (η^4 -1,5cyclooctadiene) tetrafluoroborate was prepared and used in carbonyl arylation and hydrosilylation reactions allowing turn-over numbers up to 2000.



Kai C. Hultzsch, Denis V. Gribkov, Frank Hampel

J. Organomet. Chem. 690 (2005) 4441

Non-metallocene rare earth metal catalysts for the diastereoselective and enantioselective hydroamination of aminoalkenes The hydroamination is a highly atom economical process for the synthesis of amines via addition of N–H bonds to alkenes. New rare earth metal catalysts based on diamidoamine, biphenolate and binaphtholate ligand sets have emerged as efficient catalysts for stereoselective hydroamination/cyclization reactions. Enantioselectivities of up to 83% ee have been achieved.



András Nagy, Zoltán Novák, András Kotschy

J. Organomet. Chem. 690 (2005) 4453

Sequential and domino Sonogashira coupling: Efficient tools for the synthesis of diarylalkynes

The Sonogashira coupling reaction of aryl halides with a masked acetylene, leading to the formation of diarylethynes is reviewed. The process is either run in a sequential coupling-deprotection-coupling manner, or sometimes it is carried out in one-pot, a reaction we coined domino coupling. The procedures were also extended to the synthesis of compound libraries.



Ian J.S. Fairlamb, Stephanie Grant, Adrian C. Whitwood, John Whitthall, Andrei S. Batsanov, Jonathan C. Collings

J. Organomet. Chem. 690 (2005) 4462

Synthesis of Pd(II) and Pt(II) complexes possessing bicyclo[3.2.0]heptanyl phosphinite ligands: Identification of a novel Pd(II) precatalyst for 1,6-diene cycloisomerisation The synthesis of monodentate and bidentate phosphinite ligands, possessing the unusual bicyclo[3.2.0]heptane framework, are reported. A convenient, tin-free synthesis of a key intermediate, namely 3-*endo*-6-*endo*-di-hydroxybicyclo[3.2.0]heptane, is described.



Marcin Jankowiak, Hieronim Maciejewski, Jacek Gulinski

J. Organomet. Chem. 690 (2005) 4478

Catalytic reactions of hydrosiloxanes with allyl chloride

Catalytic reactivity of Si–H bond of di-, trisiloxanes with allyl chloride in the presence of platinum catalyst has been examined. Hydrosilylation process competes with hydrogen substitution by chlorine and/or propenyl group. The effect of the reaction conditions on the yield and selectivity of the number of products has been discussed.



Christophe M. Thomas, Christophe Letondor, Nicolas Humbert, Thomas R. Ward

J. Organomet. Chem. 690 (2005) 4488

Aqueous oxidation of alcohols catalyzed by artificial metalloenzymes based on the biotin-avidin technology Based on the incorporation of biotinylated organometallic catalyst precursors within (strept)avidin, we have developed artificial metalloenzymes for the oxidation of secondary alcohols using *tert*-butylhydroperoxide as oxidizing agent. In the presence of avidin as host protein, the biotinylated aminosulfonamide ruthenium piano stool complex **1** (0.4 mol%) catalyzes the oxidation of *sec*-phenethyl alcohol at room temperature within 90 h in over 90% yield. Gel electrophoretic analysis of the reaction mixture suggests that the host protein is not oxidatively degraded during catalysis.



Magdalena Jankowska, Olga Shuvalova, Natalia Bespalova, Mariusz Majchrzak, Bogdan Marciniec

J. Organomet. Chem. 690 (2005) 4492

Cross-coupling of vinyldisilacyclobutane with olefins catalyzed by [RuH(Cl)(CO)-(PCy₃)₂]

Silylative *cross*-coupling reaction of vinyldisilacyclobutane with a variety of olefins in the presence of $[RuH(CI)(CO)(PCy_3)_2]$ leads to highly stereoselective formation of functionalized organosilicon compounds – attractive monomers for ROP. However, the *homo*-coupling reaction of vinyldisilacyclobutane gives a mixture of *E*- and *gem*-bis(silyl) ethenes.



Georgiy B. Shul'pin, Galina V. Nizova, Yuriy N. Kozlov, Vladimir S. Arutyunov, Ana Cláudia M. dos Santos, Ana Carolina T. Ferreira, Dalmo Mandelli

J. Organomet. Chem. 690 (2005) 4498

Joost N.H. Reek, Marc Röder,

prepare bidentate ligands

P. Elsbeth Goudriaan, Paul C.J. Kamer,

J. Organomet. Chem. 690 (2005) 4505

Piet W.N.M. van Leeuwen, Vincent F. Slagt

Supraphos: A supramolecular strategy to

Oxidations by the system "hydrogen peroxide- $[Mn_2L_2O_3][PF_6]_2$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane)-oxalic acid". Part 6. Oxidation of methane and other alkanes and olefins in water

Oxidation of alkanes and olefins with hydrogen peroxide in water solution at 10-50 °C is efficiently catalyzed by [1][PF6]2 if oxalic acid is present as a co-catalyst.



We report a new strategy for the preparation of chelating bidentate ligands, which involves just mixing of two monodentate ligands functionalized with complementary binding sites. Phosphite zinc(II) porphyrins 1-6 and the nitrogen donor ligands b-i form a library of 60 palladium catalysts based on 48 bidentate ligands assemblies. The relatively small catalysts library gave a large variety in the selectivity of the alkylation of rac-1,3- diphenyl-2-propenyl acetate. Importantly, small variations in the building blocks lead to large differences in the enantioselectivity imposed by the catalyst (upto 97% ee).



Michela Gasperini, Fabio Ragaini, Chiara Remondini, Alessandro Caselli, Sergio Cenini

J. Organomet. Chem. 690 (2005) 4517

The palladium-phenanthroline catalyzed carbonylation of nitroarenes to diarylureas: Effect of chloride and diphenylphosphinic acid

Chloride and diphenylphosphinic acid promote the carbonylation of nitrobenzene and aniline to diphenylurea, catalyzed by palladium trimethylbenzoate/phenanthroline. Kinetic and mechanistic information is provided and discussed.



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