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Contents

Special Issue: Insertion Chemistry of the Metal—Carbon Bond

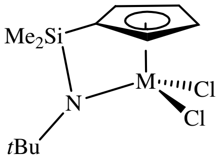
Research Papers

Jesus Cano, Klaus Kunz

J. Organomet. Chem. 692 (2007) 4411

How to synthesize a constrained geometry catalyst (CGC) – A survey

Since the early 1990s constrained geometry complexes of group 4 metals have been studied as catalysts in olefin polymerizations and are now of major industrial importance. This article describes the development of this structurally highly diverse catalyst family providing a concise overview on synthetic entries to these organometallic complexes.

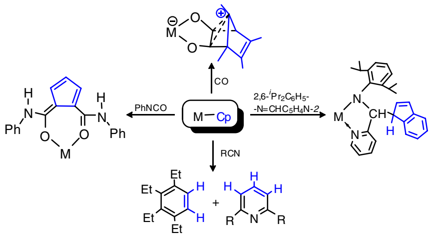


Ruiting Liu, Xigeng Zhou

J. Organomet. Chem. 692 (2007) 4424

Reactivity of the metal–cyclopentadienyl (indenyl, fluorenyl and cycloheptatrienyl) bonds

The focus of this review concerns the reactivity patterns of metal–cyclopentadienyl (indenyl, fluorenyl and cycloheptatrienyl) bonds. The advances in metal–carbon(η^5) insertion chemistry have demonstrated that the π-bonding character provides additional reaction opportunities which are not shown by metal–alkyl compounds and these differences are highlighted.

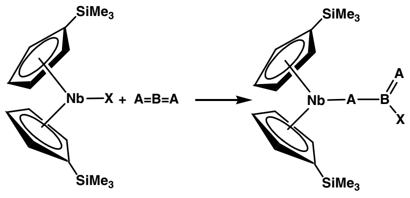


Antonio Antiñolo, Santiago García-Yuste, Antonio Otero, Elena Villaseñor

J. Organomet. Chem. 692 (2007) 4436

On the insertion processes of unsaturated molecules into the Nb–X σ-bond of "Cp'_2NbX" moieties ($Cp' = \eta^5\text{-}C_5H_4SiMe_3$; X = H, C, P)

The Nb–X σ-bond of the formally 16-electron moieties "Cp'_2NbX" ($Cp' = \eta^5\text{-}C_5H_4SiMe_3$; X = H, C, P) undergoes insertion processes of different types of unsaturated molecules, namely CO, CO_2, isocyanates, isothiocyanates, isonitriles, olefins and activated alkynes.



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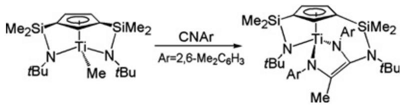
doi:10.1016/S0022-328X(07)00643-2

Jesús Cano, María Sudupe, Pascual Royo

J. Organomet. Chem. 692 (2007) 4448

Synthesis and reactivity of di(silylamido)-cyclopentadienyl titanium and zirconium complexes

A short account of our recent contributions to the synthesis and reactivity of doubly silylamido-bridged cyclopentadienyl titanium and zirconium chelates is presented with particular emphasis on the insertion reactions of isocyanides into their M–N and M–C bonds and the efficiency of their alkyl-free cationic species as ethene polymerization catalysts and their deactivation pathways.

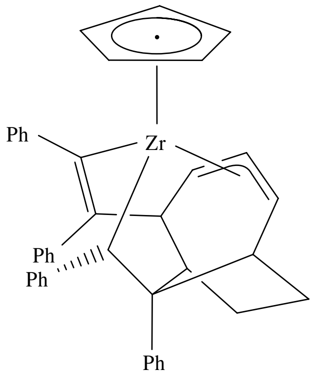


Benjamin G. Harvey, Vichien Kulsomphob, Atta M. Arif, Richard D. Ernst

J. Organomet. Chem. 692 (2007) 4460

Edge-bridged half-open zirconocenes: Synthesis, characterization, and reaction with diphenylacetylene

The synthesis and characterization of the half-open zirconocene, $Zr(C_5H_5)(c\text{-}C_8H_{11})(PEt_3)$ ($c\text{-}C_8H_{11}$ = cyclooctadienyl), is described. The compound shows shorter Zr–C distances for the cyclooctadienyl ligand, in accord with expectations of stronger Zr–C bonding relative to C_5H_5. This compound reacts with two equivalents of diphenylacetylene to yield a bicyclic coupling product.

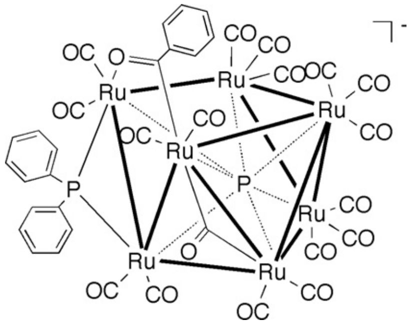


Michael D. Randles, Anthony C. Willis, Marie P. Cifuentes, Mark G. Humphrey

J. Organomet. Chem. 692 (2007) 4467

High-nuclearity ruthenium carbonyl cluster chemistry. 8: Phosphine activation, CO insertion, and deruthenation at a phosphido cluster – X-ray structures of $[ppn][Ru_8(\mu_8\text{-}P)(\mu\text{-}CO)_2(CO)_{20}]$ and $[ppn][Ru_7(\mu_7\text{-}P)(\mu\text{-}\eta^2\text{-}OCPh)(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_{17}]$

Reaction of $[ppn][Ru_8(\mu_8\text{-}P)(\mu\text{-}CO)_2(CO)_{20}]$ with triphenylphosphine proceeds by loss of one cluster core vertex, phosphine P–C cleavage, and CO insertion into the putative Ru–phenyl bond to afford $[ppn][Ru_7(\mu_7\text{-}P)(\mu\text{-}\eta^2\text{-}OCPh)(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_{17}]$ in low yield.

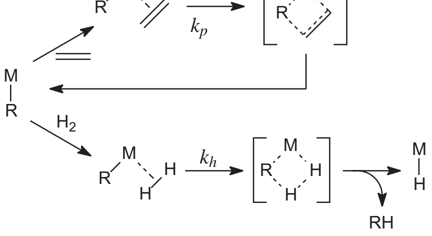


Peter H.M. Budzelaar, Betty B. Coussens, Nic Friederichs

J. Organomet. Chem. 692 (2007) 4473

Hydrogen sensitivity – A systematic computational study of electronic effects

DFT studies for model polymerization catalysts indicate hydrogen sensitivity decreases with increasing electrophilicity (measured as NH_3 complexation energy) of the metal centre.

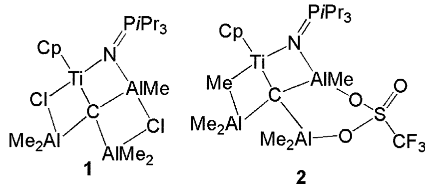


Todd W. Graham, Christopher Ong, Pingrong Wei, Douglas W. Stephan

J. Organomet. Chem. 692 (2007) 4481

Reactions of the titanium-carbide species $CpTi(\mu^2\text{-}Me)(\mu^2\text{-}NP\textit{i}\text{-}Pr_3)(\mu^4\text{-}C)(AlMe_2)_3$

Reaction of $CpTi(\mu^2\text{-}Me)(\mu^2\text{-}NP\textit{i}\text{-}Pr_3)(\mu^4\text{-}C)(AlMe_2)_3$ with $ClSnMe_3$ and MeO_3SCF_3 afford the species $[CpTi(\mu^2\text{-}Cl)(\mu^2\text{-}NP\textit{i}\text{-}Pr_3)(\mu^4\text{-}C)(\mu^2\text{-}Cl)(AlMe)(AlMe_2)_2]$ **1** and $[CpTi(\mu^2\text{-}Me)(\mu^2\text{-}NP\textit{i}\text{-}Pr_3)(\mu^4\text{-}C)(\mu^2\text{-}O_3SCF_3)(AlMe)(AlMe_2)_2]$ **2**, respectively.

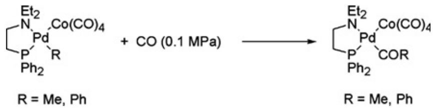


Nobuyuki Komine, Susumu Tsutsuminai, Masafumi Hirano, Sanshiro Komiya

J. Organomet. Chem. 692 (2007) 4486

Synthesis and reactions of heterodinuclear organopalladium complex having an unsymmetrical PN ligand

Reactions of novel heterodinuclear organopalladium–cobalt complexes having an unsymmetrical PN ligand ($Et_2NC_2H_4PPh_2\text{-}\kappa^2N,P$)RPd–$ML_n$ (ML_n = $Co(CO)_4$; R = Me, Ph) with CO yield corresponding acyl complexes ($Et_2NC_2H_4PPh_2\text{-}\kappa^2N,P$)(RCO)Pd–$Co(CO)_4$ (R = Me, Ph). Rate of CO insertion was significantly faster than those for mononuclear methylpalladium complex, PdMeI($Et_2NC_2H_4PPh_2\text{-}\kappa^2N,P$) and methylpalladium–cobalt complex with a 1,2-bis(diphenylphosphino)ethane (dppe) ligand, (dppe-κ^2P,P')MePd–$Co(CO)_4$.

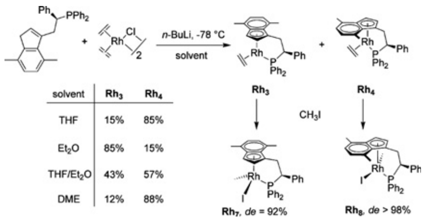


Angelino Doppiu, Ulli Englert, Vera Peters, Albrecht Salzer

J. Organomet. Chem. 692 (2007) 4495

Optically active rhodium complexes with indenyl-linked phosphane ligands

The complexation of (*S*)-[2-(4,7-dimethyl-3*H*-inden-1-yl)-1-phenylethyl]diphenylphosphane with $[Rh(\mu\text{-}Cl)(\eta^2\text{-}CH_2CH_2)_2]_2$ affords the two diastereomers (*S*,R_{pl})-$\mathbf{Rh_3}$ and (*S*,S_{pl})-$\mathbf{Rh_4}$ in a ratio that depends strongly on the solvent. The complexes undergo oxidative addition of CH_3I with high diastereoselectivity.



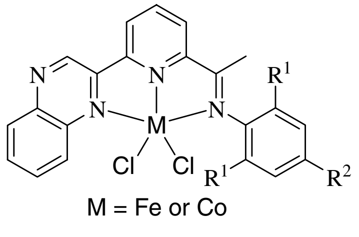
solvent	Rh_3	Rh_4
THF	15%	85%
Et_2O	85%	15%
THF/Et_2O	43%	57%
DME	12%	88%

Wen-Hua Sun, Peng Hao, Gang Li, Shu Zhang, Wenqing Wang, Jianjun Yi, Maliha Asma, Ning Tang

J. Organomet. Chem. 692 (2007) 4506

Synthesis and characterization of iron and cobalt dichloride bearing 2-quinoxalinyl-6-iminopyridines and their catalytic behavior toward ethylene reactivity

The 2-quinoxalinyl-6-iminopyridines and their iron(II) and cobalt(II) complexes were synthesized and full characterized. The molecular structures of (*E*)-*N*-(1-(6-(quinoxalin-2-yl)pyridin-2-yl)ethylidene)benzenamine and their metal complexes indicates rotations of the quinoxalinyl and imino-groups of ligand backbone during coordination, which suggests that the ligands form sterically-favored coordination with the metal center with the distorted trigonal-bipyramidal geometry. Upon activation with MAO, all iron complexes showed good catalytic activity for ethylene reactivity; while their cobalt analogues gave moderate to good activity for ethylene reactivity in the presence of MMAO.

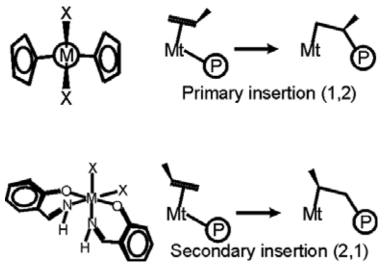


Andrea Correa, Giovanni Talarico,
Luigi Cavallo

J. Organomet. Chem. 692 (2007) 4519

Regiochemistry of propene insertion with group 4 polymerization catalysts from a theoretical perspective

Steric and electronic effects in the regiochemistry of monomer insertion in propene polymerization promoted by various metallocene, CGC and octahedral group 4 metal catalysts has been investigated by using DFT methods.

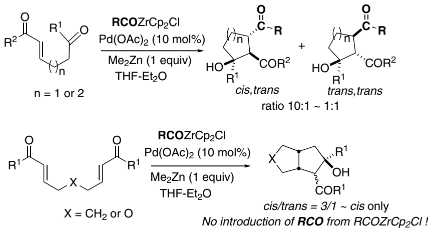


Yuji Hanzawa, Yusuke Oka, Masaya Yabe

J. Organomet. Chem. 692 (2007) 4528

Acylzirconocene chloride: Formation of carbocycles by palladium-catalyzed cascade reaction

Acylzirconocene chloride complex as an acyl group donor reacts with ω-carbonyl α,β-enones or with bis-enones to give carbocyclic compounds under 10 mol% $Pd(OAc)_2$-catalyzed conditions, and each reaction was accelerated by the addition of a stoichiometric amount of Me_2Zn.

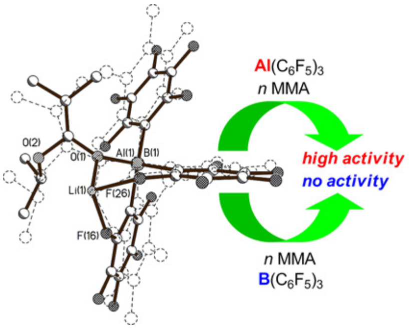


Yalan Ning, Hongping Zhu, Eugene Y.-X. Chen

J. Organomet. Chem. 692 (2007) 4535

Remarkable Lewis acid effects on polymerization of functionalized alkenes by metallocene and lithium ester enolates

Drastic Lewis acid effects on polymerization of functionalized alkenes mediated by metallocene and lithium ester enolates are observed as well as elucidated.

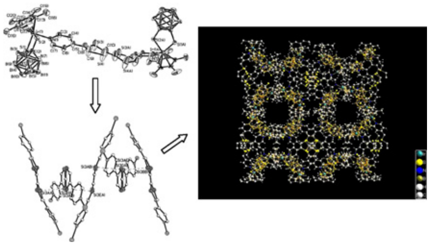


Ying-Feng Han, Jia-Sheng Zhang,
Yue-Jian Lin, Jie Dai, Guo-Xin Jin

J. Organomet. Chem. 692 (2007) 4545

Synthesis and characterization of half-sandwich iridium complexes containing 2,6(7)-bis(4-pyridyl)-1,4,5,8-tetrathiafulvalene and ancillary ortho-carborane-1,2-dichalcogenolato ligands

Binuclear half-sandwich dichalcogenolate carborane iridium complexes **5a** and **5b**, connected with 2,6(7)-bis(4-pyridyl)-1,4,5,8-tetrathiafulvalene ligands, have been synthesized and characterized structurally.



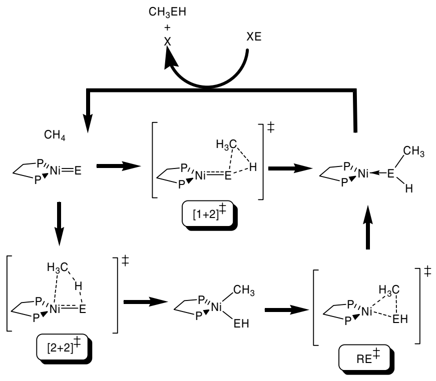
Thomas R. Cundari, Aaron W. Pierpont, Sridhar Vaddadi

J. Organomet. Chem. 692 (2007) 4551

Computational study of methane functionalization by a multiply bonded, Ni-bis-(phosphine) complex

Theoretical study of methane functionalization by a multiply bonded, Ni-bis(phosphine) complex: [2+2] vs [1+2] pathways.

A computational chemistry study of nickel-catalyzed group transfer to methane is presented. Analysis of the reaction energetics implies a possible competition between two mechanisms for carbene transfer, while for nitrene transfer, the [1+2] pathway is predicted to be the preferred route. For phosphinidene transfer, a $[2_\pi + 2_\sigma]$ mechanism is preferred. Regeneration of the active species via a group transfer reagent XE is highly exothermic. The calculations indicate that (P ~ P)Ni=E complexes deserve consideration as plausible starting points in the search for improved hydrocarbon functionalization catalysts.

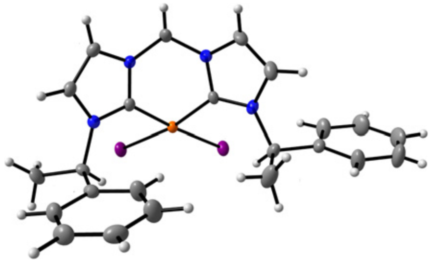


Sabine K. Schneider, Jürgen Schwarz, Guido D. Frey, Eberhardt Herdtweck, Wolfgang A. Herrmann

J. Organomet. Chem. 692 (2007) 4560

Chiral, bridged bis(imidazolin-2-ylidene) complexes of palladium

A systematic study of chiral bis(imidazolin-2-ylidene)palladium(II) complexes is presented, bearing the chiral group on the ring nitrogens. A structural proof of the chiral palladium(II) complexes is represented by a X-ray diffraction study.

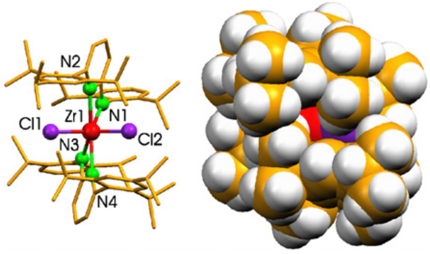


Winfried P. Kretschmer, Bart Hessen, Awal Noor, Natalie M. Scott, Rhett Kempe

J. Organomet. Chem. 692 (2007) 4569

Highly active/selective and adjustable zirconium polymerization catalysts stabilized by aminopyridinato ligands

Sterically very demanding aminopyridinato ligands stabilize thermally robust, highly active and selective zirconium ethylene polymerization catalysts. Small changes in the bulky ligand periphery can be used to fine tune the nature of the formed polymers and even "living" ethylene polymerization at elevated temperatures (50 °C) can be observed.

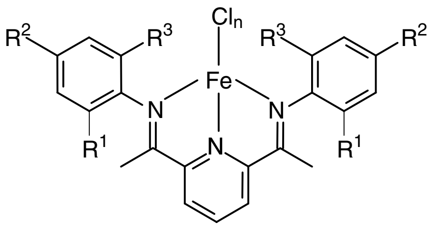


Christian Görl, Helmut G. Alt

J. Organomet. Chem. 692 (2007) 4580

Influence of the *para*-substitution in bis(arylimino)pyridine iron complexes on the catalytic oligomerization and polymerization of ethylene

A series of nine iron complexes with halogen or alkynyl functionalized bis(arylimino)pyridine ligands was synthesized and characterized. After activation with methylalumoxane (MAO), these catalysts oligomerize or polymerize ethylene to give highly linear products. The influence of substituents in the *para*-position of the iminophenyl rings was investigated.



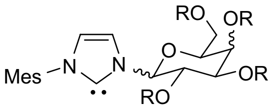
R^2 = halogen, alkynyl
R^1, R^3 = H, methyl
n = 2, 3

Friederike Tewes, Andreas Schlecker, Klaus Harms, Frank Glorius

J. Organomet. Chem. 692 (2007) 4593

Carbohydrate-containing N-heterocyclic carbene complexes

Novel carbohydrate bearing imidazolium salts have been synthesized and used for the in situ generation of the corresponding N-heterocyclic carbenes **1**. These compounds were successfully used as catalysts of the conjugate umpolung of cinnamaldehyde to form γ-butyrolactones. In addition, silver and palladium complexes of these N-heterocyclic carbenes were synthesized and structurally characterized.



1

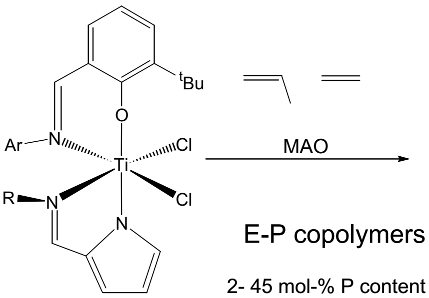
R= Ac, Piv

Lewis M. Broomfield, Yann Sarazin, Joseph A. Wright, David L. Hughes, William Clegg, Ross W. Harrington, Manfred Bochmann

J. Organomet. Chem. 692 (2007) 4603

Mixed-ligand iminopyrrolato-salicylaldiminato group 4 metal complexes: Optimising catalyst structure for ethylene/propylene copolymerisations

Mixed-ligand titanium (iminopyrrolato)(salicylaldiminato) complexes activated with MAO are highly effective ethylene/propylene copolymerisation catalysts. Activities and comonomer incorporation significantly exceeds those of either (N–N)$_2$Ti or (N–O)$_2$Ti systems.

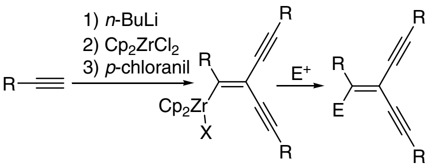


Chanjuan Xi, Yuanyuan Liu, Xiaoyu Yan, Chao Chen

J. Organomet. Chem. 692 (2007) 4612

Zirconocene-promoted coupling reaction of terminal acetylenes to geminal enediynes in the presence of *p*-chloranil

Zirconocene-promoted trimerization of terminal acetylenes to zirconoenediynes in the presence of *p*-chloranil. Moreover, the resulting zirconoenediynes could be transformed into a variety of geminal enediynes through coupling reaction with electrophiles.

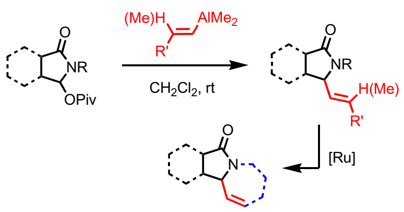


Joshua G. Pierce, David L. Waller, Peter Wipf

J. Organomet. Chem. 692 (2007) 4618

Synthesis of functionalized isoindolinones: Addition of *in situ* generated organoalanes to acyliminium ions

Addition of *in situ* generated di- or trisubstituted alkenylalanes to *N*-acyliminium ions provides rapid access to functionalized isoindolinones. Subsequent ring closing metathesis leads to tricyclic products. These transformations proceed under mild conditions and allow for the convergent synthesis of biologically significant scaffolds from readily available starting materials.

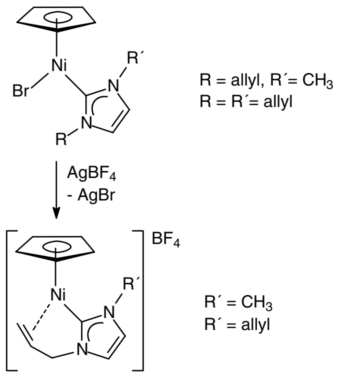


Ekkehardt F. Hahn, Beate Heidrich, Alexander Hepp, Tania Pape

J. Organomet. Chem. 692 (2007) 4630

Coordination compounds of *N*,*N*′-olefin functionalized imidazolin-2-ylidenes

Palladium and nickel complexes with imidazolin-2-ylidene ligands bearing *N*-olefin substituents have been prepared from $Pd(OAc)_2$ or $[Ni(NCCH_3)_6](BF_4)_2$. X-ray diffraction studies revealed formation of *cis* or *trans* square-planar complexes. Bromine abstraction from monocarbene cyclopentadienyl nickel complexes gave the trigonal-pyramidal nickel(II) complexes featuring *N*-allyl double bond coordination.

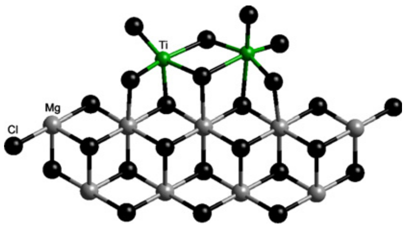


Jin Woo Lee, Won Ho Jo

J. Organomet. Chem. 692 (2007) 4639

Theoretical investigation on the model active site for isotactic polypropylene in heterogeneous Ziegler–Natta catalyst: A density functional study

The reaction mechanism of the stereoselective insertion of propylene monomer into the model active site created by Ti_2Cl_7 adsorption on the (1 0 0) surface of $MgCl_2$ has been investigated by using DFT calculations.

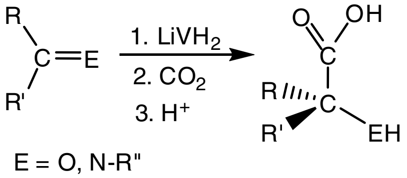


John J. Eisch, Paul O. Fregene, John N. Gitua

J. Organomet. Chem. 692 (2007) 4647

The epimetallation and carbonation of carbonyl and imino derivatives: Epivanadation route to 2-amino and 2-hydroxy acids

The feasibility of hydrocarboxylating carbonyl and imino derivatives by a two-step process of epimetallation and carbonation has been demonstrated with 9-fluorenone and 9-fluorenone anil. With $LiVH_2$ as the epimetallating agent, the process yielded 75% of 9-hydroxy-9-fluorenecarboxylic acid and 65% of 9-(*N*-phenylamino)-9-fluorenecarboxylic acid. Epimetallating reagents of vanadium and titanium also show promise.

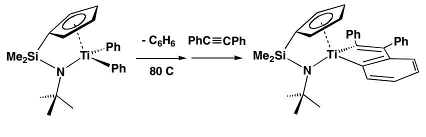


Shawn M. Nettles, Jeffrey L. Petersen

J. Organomet. Chem. 692 (2007) 4654

Synthesis and structural characterization of $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]Ti[(o\text{-}C_6H_4)C(Ph){=}C(Ph)]$, generated via an alkyne-Ti benzyne coupling reaction

The thermolysis of $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]TiPh_2$ in the presence of diphenylacetylene proceeds at 80 °C in cyclohexane solution with the formation of the titanacyclic complex $[(C_5H_4)SiMe_2(N\text{-}t\text{-}Bu)]Ti[(o\text{-}C_6H_4)\text{-}C(Ph){=}C(Ph)]$, which has been characterized by NMR and X-ray crystallography.

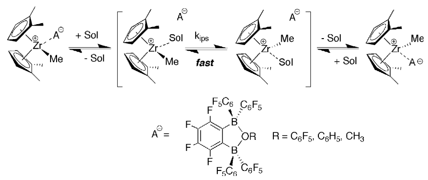


Lee D. Henderson, Warren E. Piers

J. Organomet. Chem. 692 (2007) 4661

Ion pair symmetrization in metallocenium cations partnered with diborane derived borate counteranions

The thermodynamics of ion pair symmetrization in a series of metallocenium species generated from Cp''_2ZrMe_2 ($Cp'' = 1,2\text{-}Me_2C_5H_3$) were studied using a variety of dynamic NMR techniques.

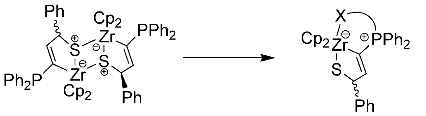


Esteban Ortega, Nadine Pirio,
Philippe Richard, Philippe Meunier

J. Organomet. Chem. 692 (2007) 4669

Exploring reactivity of a bis-sulfonium zirconocene-ate dimer: Synthesis of various zwitterionic phosphonium anionic zirconocene complexes

A new class of stable zwitterionic phosphonium anionic zirconocene complexes containing at least one group 16 atom directly bonded to zirconium was prepared from reactions of a bis-sulfonium zirconocene-ate dimer with methylpropiolate, benzaldehyde, carbon disulfide and more simply with elemental sulfur and heavier chalcogens.

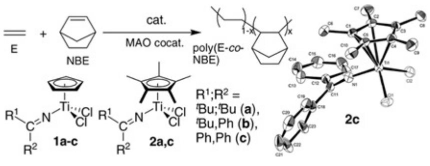

X = C, O, S, Se, Te

Kotohiro Nomura, Junji Yamada, Wei Wang, Jingyu Liu

J. Organomet. Chem. 692 (2007) 4675

Effect of ketimide ligand for ethylene polymerization and ethylene/norbornene copolymerization catalyzed by (cyclopentadienyl)-(ketimide)titanium complexes–MAO catalyst systems: Structural analysis for $Cp^*TiCl_2(N{=}CPh_2)$

Effects of the ketimide substituents for ethylene polymerization and ethylene/norbornene (NBE) copolymerization by $Cp'TiCl_2(N{=}CR^1R^2)$ [Cp' = Cp (**1**), Cp^* (**2**); R^1,R^2 = ^{t}Bu,^{t}Bu (**a**), ^{t}Bu,Ph (**b**), Ph,Ph (**c**)]–MAO catalysts were investigated, and the structure of **2c** was determined by X-ray crystallography.

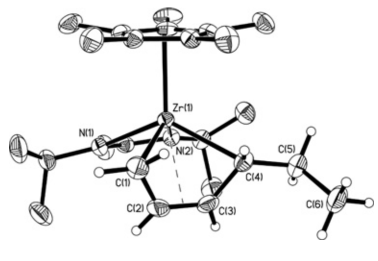


Philip P. Fontaine, Albert Epshteyn,
Peter Y. Zavalij, Lawrence R. Sita

J. Organomet. Chem. 692 (2007) 4683

Regio- and stereospecific syntheses and structural characterization of alkyl-substituted 1,3-diene complexes of cyclopentadienylzirconium amidinates of the general formula: $(\eta^5\text{-}C_5Me_5)Zr[N(^iPr)C(Me)N(^iPr)](\sigma^2,\pi\text{-}C_4H_5R)$ (R = Me or Et)

New synthetic methods have been developed that provide several derivatives of the titled family of compounds in regio- and stereospecific fashion and for which structural characterization support a Zr(IV) σ^2,π-metallacyclopent-3-ene limiting resonance form.

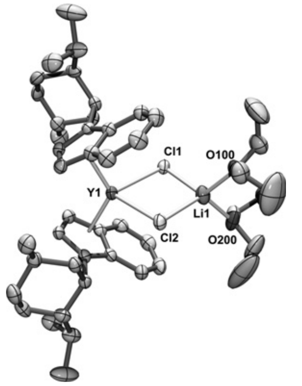


Daniela V. Vitanova, Frank Hampel, Kai C. Hultzsch

J. Organomet. Chem. 692 (2007) 4690

(+)-Neomenthyl- and (−)-phenylmenthyl-substituted cyclopentadienyl and indenyl yttrocenes as catalysts in asymmetric hydroamination/cyclization of aminoalkenes (AHA)

The synthesis of chiral terpenoid-substituted yttrocene complexes, in particular the yttrium analogue of Erker's neomenthylindenyl zirconocene is reported. The application of these complexes in asymmetric hydroamination/cyclization of aminoalkenes was investigated.

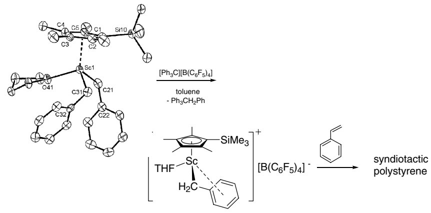


Julia Hitzbleck, Klaus Beckerle, Jun Okuda

J. Organomet. Chem. 692 (2007) 4702

Half-sandwich dibenzyl complexes of scandium: Synthesis, structure, and styrene polymerization activity

Half-sandwich dibenzyl complexes of scandium have been synthesized, structurally characterized and tested as syndiospecific styrene polymerization catalysts upon cationization.

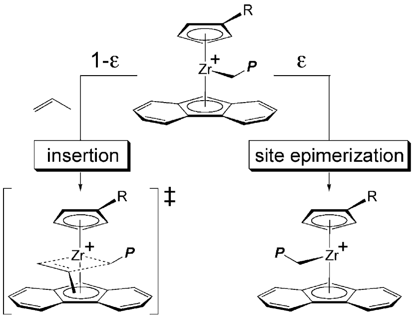


Stephen A. Miller

J. Organomet. Chem. 692 (2007) 4708

Insertion vs. site epimerization with singly-bridged and doubly-bridged metallocene polymerization catalysts

A statistical model has been employed to determine the unidirectional site epimerization probability, , during propylene polymerization with singly-bridged and doubly-bridged C_1-symmetric metallocenes activated with methylaluminoxane. Generally, the probability of site epimerization increased as follows: carbon singly-bridged catalysts < doubly-bridged catalysts < silicon singly-bridged catalysts.

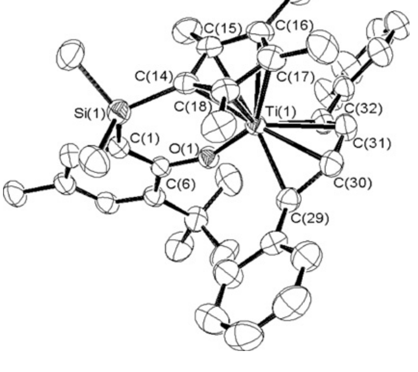


Hidenori Hanaoka, Takahiro Hino, Masaaki Nabika, Tetsuya Kohno, Kazunori Yanagi, Yoshiaki Oda, Akio Imai, Kazushi Mashima

J. Organomet. Chem. 692 (2007) 4717

Synthesis and characterization of titanium alkyl, oxo, and diene complexes bearing a $SiMe_2$-bridged phenoxy-cyclopentadienyl ligand and their catalytic performance for copolymerization of ethylene and 1-hexene

A series of titanium alkyl, oxo, and diene complexes bearing a $SiMe_2$-bridged phenoxy-cyclopentadienyl ligand were synthesized and characterized, and their catalytic behavior for copolymerization of ethylene and 1-hexene was investigated. X-ray analysis of 1,4-diphenyl-1,3-butadiene complex revealed that the diene ligand coordinates in *s-cis* fashion to titanium with a prone orientation. Polymerization study revealed that the alkyl complexes and the diene complexes showed higher activities than the starting dichloride at 130 °C.

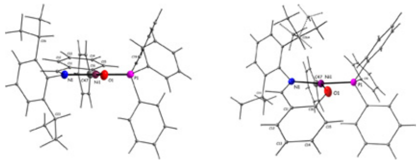


Alexander Zeller, Georg Eickerling, Eberhardt Herdtweck, Martin U. Schmidt, Thomas Strassner

J. Organomet. Chem. 692 (2007) 4725

Polymorphism of a nickel polymerization catalyst

Polymorphism of a nickel(II)salicylaldiminato polymerization catalyst is reported, the two structures differ significantly in the coordination geometry of the central metal atom. Lattice energy calculations were used to analyze the different solid state structures.

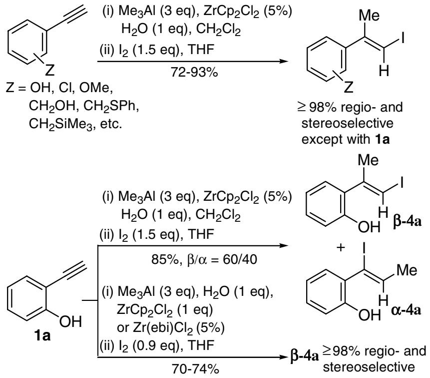


Guangwei Wang, Gangguo Zhu, Ei-ichi Negishi

J. Organomet. Chem. 692 (2007) 4731

Zirconium-catalyzed methylalumination of heterosubstituted arylethynes: Factors affecting the regio-, stereo-, and chemoselectivities

The Zr-catalyzed methylalumination of heterosubstituted arylethynes containing O, S, Cl, and Si can proceed in high yields (>70%) and in a highly regio- and stereoselective manner (⩾ 98–99%), although SO_2Ph, Br, and Cl in a benzylic position present serious chemoselectivity-related problems. The low regioselectivity of 60% initially observed with *o*-ethynylphenol (**1a**) has been elevated to ⩾ 98% through the use of either a catalytic amount of $Zr(ebi)Cl_2$ or $Zr(2\text{-}Me\text{-}Ind)_2Cl_2$ or, more conveniently, the stoichiometric amount of $ZrCp_2Cl_2$, $ZrCp_2MeCl$, or $ZrCp_2Me_2$ in conjunction with the use of a deficient amount (0.9 molar equiv.) of I_2.

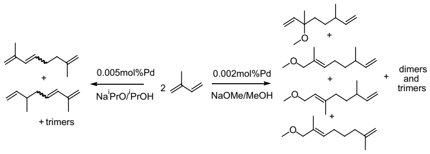


Ralf Jackstell, Anne Grotevendt, Dirk Michalik, Larbi El Firdoussi, Matthias Beller

J. Organomet. Chem. 692 (2007) 4737

Telomerization and dimerization of isoprene by *in situ* generated palladium–carbene catalysts

The palladium-catalyzed telomerization of isoprene with methanol and dimerization of isoprene has been studied in presence of palladium and imidazolium salts, which form *in situ* carbene ligands. A selectivity switch from the telomerization to the dimerization product occurred by using different substituted ligands.

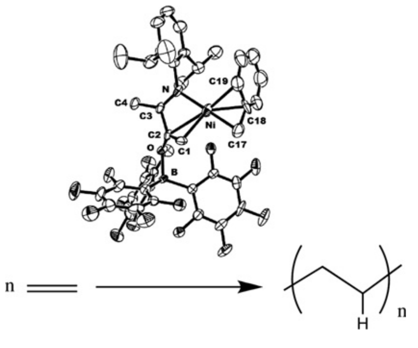


Yaofeng Chen, Brycelyn M. Boardman, Guang Wu, Guillermo C. Bazan

J. Organomet. Chem. 692 (2007) 4745

A zwitterionic nickel–olefin initiator for the preparation of high molecular weight polyethylene

Addition of 2 equiv. $B(C_6F_5)_3$ to [3-(2,6-diisopropylphenylimino)-but-1-en-2-olato](η^1-benzyl)(trimethylphosphine)nickel (**1**) results in the formation of 2-tris(pentafluorophenyl)borate-3-(2,6-diisopropylphenylimino)-but-1-ene(η^3-benzyl)nickel (**2**), in which the borane coordinates to the oxygen of the ligand and forces binding of the olefin to nickel. Compound **2** can be used to initiate the homopolymerization of ethylene to obtain high molecular weight materials.

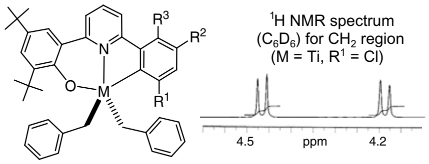


Ka-Ho Tam, Jerry C.Y. Lo, Zhengqing Guo, Michael C.W. Chan

J. Organomet. Chem. 692 (2007) 4750

Cyclometalated group 4 complexes supported by tridentate pyridine-2-phenolate-6-(σ-aryl) ligands: Catalysts for ethylene polymerization and comparisons with fluorinated analogues

The pictured post-metallocene complexes (M = Ti, Zr, Hf) bearing the aromatic σ-carbanion as a chelating group have been prepared as olefin polymerization catalysts. The impact of different substituents on the σ-aryl moiety, especially at the R^1 position, upon spectroscopic and polymerization characteristics have been examined.

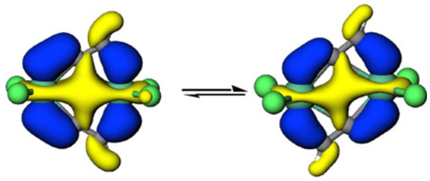


Shuqiang Niu, Agnes Derecskei-Kovacs, Michael B. Hall

J. Organomet. Chem. 692 (2007) 4760

A unique coplanar multi-center bonding network in doubly acetylide-bridged binuclear zirconocene complexes: A density functional theory study

A unique π-conjugative six-center-six-electron bonding network was revealed in the doubly acetylide-bridged binuclear group 4 metallocene complexes. The coplanar multi-center bonding interaction between the metal centers and acetylide ligands not only significantly stabilizes the doubly acetylide-bridged complexes but also lowers the isomerization barrier.

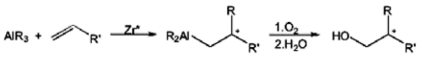


Robby A. Petros, James M. Camara, Jack R. Norton

J. Organomet. Chem. 692 (2007) 4768

Enantioselective methylalumination of α-olefins

The ability of various enantiopure zirconocenes to catalyze the asymmetric methylalumination of allylbenzene has been tested. The enantioselectivity of an ethylene(Ind)$_2$-ZrCl$_2$/MAO system is the same as that of authentic methyl cation generated with Ph_3C^+ from ethylene(Ind)$_2$ZrMe$_2$, confirming that the methyl cation is the active catalyst from ethylene(Ind)$_2$ZrCl$_2$/MAO.

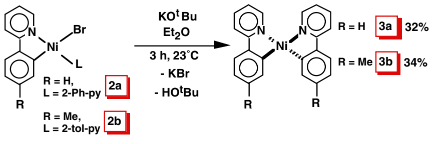


Emily C. Volpe, Andrew R. Chadeayne, Peter T. Wolczanski, Emil B. Lobkovsky

J. Organomet. Chem. 692 (2007) 4774

Heterolytic CH-bond activation in the synthesis of Ni{(2-aryl-κC^2)pyridine-κN}$_2$ and derivatives

When subjected to KO^{t}Bu in Et$_2$O, the bromides (2-aryl-pyridine)BrNi{(2-aryl-κC^2)pyridine-κN} (aryl = phenyl, **2a**; tolyl, **2b**) generated the entitled bis-cyclometalated compounds, Ni{(2-aryl-κC^2)pyridine-κN}$_2$ (aryl = phenyl, **3a**; tolyl, **3b**), whose low spin configuration and rippled geometry were confirmed by X-ray crystallography and a DFT study.

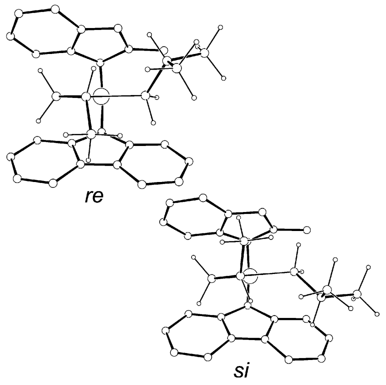


**Pierluigi Mercandelli, Angelo Sironi,
Luigi Resconi, Isabella Camurati**

J. Organomet. Chem. 692 (2007) 4784

Comparing propene polymerization with 1-butene polymerization catalyzed by MAO-activated C_2- and C_1-symmetric zirconocenes: An experimental and computational study on the influence of olefin size on stereoselectivity

The propene and 1-butene polymerization behavior of a series of C_2- and C_1-symmetric zirconocenes has been reexamined. An attempt at rationalizing the observed influence of the olefin size on stereoselectivity on the basis of QM/MM calculations is reported.



**Shun Ohta, Yasuhiro Ohki, Yohei Ikagawa,
Rie Suizu, Kazuyuki Tatsumi**

J. Organomet. Chem. 692 (2007) 4792

Synthesis and characterization of heteroleptic iron(II) thiolate complexes with weak iron–arene interactions

Selective preparation of a series of heteroleptic thiolate complexes of iron(II) have been achieved using acid–base reactions of an iron–amide complex Fe$\{N(SiMe_3)_2\}_2$ with various bulky thiols. All new complexes have been identified by X-ray crystallography. The iron center weakly interacts with the aromatic ring of thiolate ligands.