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Journal of Organometallic Chemistry

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Contents

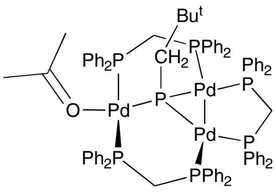
Communication

Christopher D. Andrews, Andrew D. Burrows, Michael Green, Jason M. Lynam, Mary F. Mahon

J. Organomet. Chem. 691 (2006) 2859

Transformation of an η^1-coordinated phosphaalkyne into a bridging phosphinidene ligand

Reaction of the tripalladium cluster $[Pd_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3](PF_6)_2$ with ^{t}BuCP results in formation of $[Pd_3(\mu\text{-}dppm)_3(\eta^1\text{-}PCBu^t)_2](PF_6)_2$ in which the phosphaalkyne ligands exhibit the unusual η^1-coordination mode. In acetone solution this complex is transformed into the remarkable phosphinidine complex $[Pd_3(\mu\text{-}dppm)_3(\eta^1\text{:}\mu_3\text{-}PCH_2Bu^t)(OCMe_2)](PF_6)_2$.



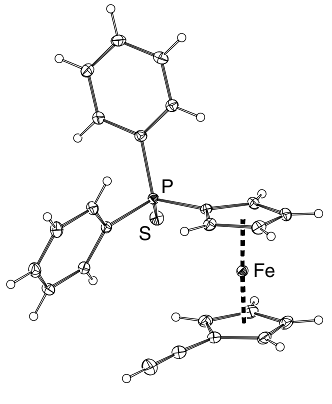
Regular papers

Petr Štěpnička, Ivana Císařová

J. Organomet. Chem. 691 (2006) 2863

Synthesis of [1′-(diphenylthiophosphoryl)-ferrocenyl]ethyne and alkyne-metal complexes thereof

The novel functionalized ferrocene alkyne, $Ph_2P(S)fcC{\equiv}CH$ (**1**; fc = ferrocene-1,1′-diyl), was prepared from $Ph_2P(S)fcCHO$ (**6**) via dibromide $Ph_2P(S)fcCH{=}CBr_2$ (**7**). The alkyne reacts with $K_2[HgI_4]$/KOH to give the σ-acetylide $Hg\{Ph_2P(S)fcC{\equiv}C\}_2$ (**8**), and with $[Co_2(CO)_8]$ yield the ferrocenylated metallatetrahedrane complex $[(\mu\text{-}\eta^2\text{:}\eta^2\text{-}\mathbf{1})\{Co(CO)_3\}_2](Co\text{–}Co)$ (**9**). The structures of **1**, Ph_2PfcBr (**5**), **6**, **7**, and **9** have been determined by single-crystal X-ray diffraction.

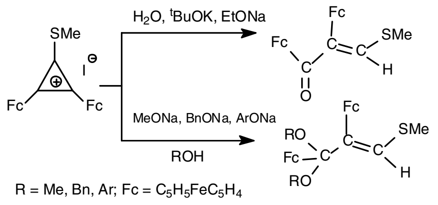


Tatiana Klimova Berestneva, Marcos Martínez García, Luis Ortiz-Frade, Simon Hernández Ortega, Ruben A. Toscano, Elena Klimova

J. Organomet. Chem. 691 (2006) 2872

Synthesis, structures and some chemical and electrochemical properties of *E*-1,2-diferrocenyl-3-methylthioprop-2-enone and its ketals

2,3-Diferrocenyl-1-methylthiocyclopropenylium iodide reacts with water, metal alkoxides, phenolates and with alcohols in the presence of Et_3N to give *E*-1,2-diferrocenyl-3-methylthioprop-2-enone **8** or its ketals. Their structures were established based on data from ^{1}H and ^{13}C NMR spectroscopy and X-ray diffraction analysis. Electrochemical properties of obtained compounds have been studied.



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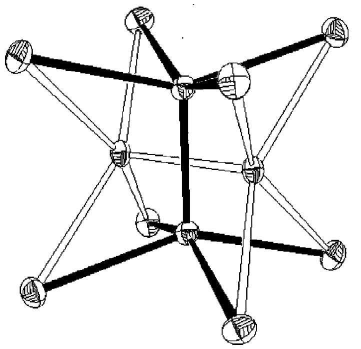
doi:10.1016/S0022-328X(06)00352-4

Paul W. Dickinson, Gregory S. Girolami

J. Organomet. Chem. 691 (2006) 2883

Synthesis, characterization, and X-ray crystal structure of the octabromodiosmate(III) salt $[(C_5Me_4H)_2OsBr]_2[Os_2Br_8]$ and its conversion to $[(C_5Me_4H)_2OsBr][Os_2HBr_4(cod)_2]$

The salt $[(C_5Me_4H)_2OsBr]_2[Os_2Br_8]$ has been synthesized and the $Os_2Br_8^{2-}$ anion shown to adopt an eclipsed (D_{4h}) conformation. Treatment of $[(C_5Me_4H)_2OsBr]_2[Os_2Br_8]$ with 1, 5-cyclooctadiene in ethanol affords octamethylosmocene, $(C_5Me_4H)_2Os$, and the salt $[(C_5Me_4H)_2OsBr][Os_2HBr_4(cod)_2]$, which is a rare example of a diosmium complex containing a bridging hydride.

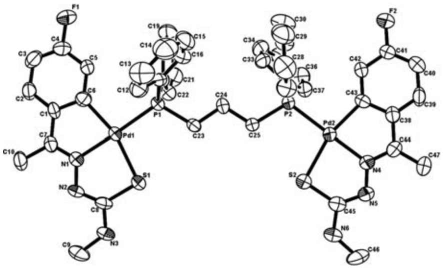


Javier Martínez, Luis A. Adrio, José M. Antelo, Juan M. Ortigueira, Mª Teresa Pereira, Margarita López-Torres, José M. Vila

J. Organomet. Chem. 691 (2006) 2891

Synthesis, characterization and solid state structures of thiosemicarbazone palladacycles: Influence of hydrogen bonding in the molecular arrangement

Dinuclear cyclometallated palladium thiosemicarbazone compounds with tertiary diphosphines may adopt *cisoid* or *transoid* geometries depending on the *inter*- or *intramolecular* nature of the hydrogen bonding established between atoms.

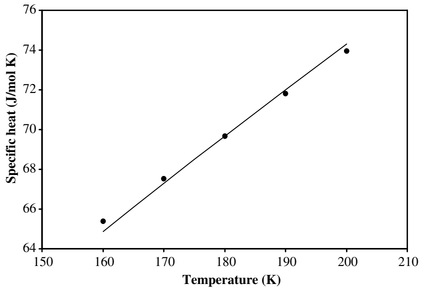


Ruchi Agarwal, Poonam Tandon, Vishwambhar Dayal Gupta

J. Organomet. Chem. 691 (2006) 2902

Phonon dispersion in poly(dimethylsilane)

In the present communication we report normal modes and their dispersion in polydimethylsilane (PDMS) $[-Si(CH_3)_2-]_n$ using Urey–Bradley force field, which in addition to valence force field accounts for the non-bonded interactions in the *gem* and *cis* configurations and tension terms. The partially deuterated PDMS (PDMS-d_3), i.e., $(SiCH_3\text{-}CD_3)_n$ and fully deuterated PDMS (PDMS-d_6), i.e., $(SiCD_3CD_3)_n$ are also studied to check the assignments and validity of the force field. Dispersion curves show two interesting features: (1) a divergence of dispersion curves following repulsion of species belonging to the same symmetry; (2) crossing between the two modes. In addition, heat capacity as a function of temperature via density-of-states is evaluated and some of the modes left unassigned by the earlier workers have been assigned.

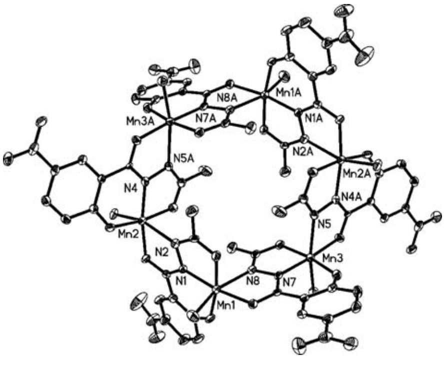


Long-Fei Jin, Feng-Ping Xiao, Gong-Zhen Cheng, Zhen-Ping Ji

J. Organomet. Chem. 691 (2006) 2909

Synthesis, crystal structure and bioactivity of a novel 18-metallacrown-6 $[Mn_6(H_2O)_6(anshz)_6]\cdot 10DMF$

A novel macrocyclic hexanuclear manganese(III) 18-metallacrown-6 compound, $[Mn_6(H_2O)_6\ (anshz)_6]\cdot 10DMF$, has been prepared using a trianionic pentadentate ligand *N*-acetyl-5-nitrosalicylhydrazide (anshz^{3-}) and characterized by X-ray diffraction. Antibacterial screening data showed that the manganese metallacrown has strong antimicrobial activity against *Bacillus subtilis.*

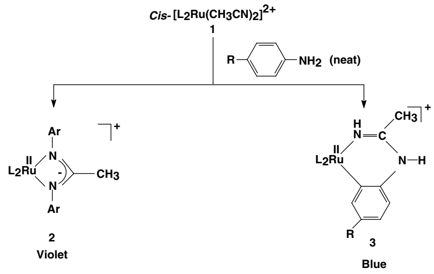


Priyabrata Banerjee, Srijit Das, Phillip E. Fanwick, Sreebrata Goswami

J. Organomet. Chem. 691 (2006) 2915

Unprecedented examples of double-addition of aromatic amines across a ruthenium(II)-coordinated nitrile function: Isolation and X-ray structures of ruthenium complexes of amidinate and cyclometalated amidine

An unprecedented type of nucleophilic double-addition of aromatic monoamines to a Ru(II)-coordinated acetonitrile is described.

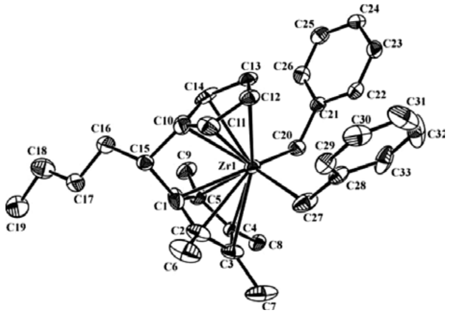


Antonio Antiñolo, Rafael Fernández-Galán, Antonio Otero, Sanjiv Prashar, Iván Rivilla, Ana M. Rodríguez

J. Organomet. Chem. 691 (2006) 2924

Synthesis and reactivity of asymmetrically substituted *ansa*-bridged zirconocene complexes: X-ray crystal structures of [Zr{R(H)-C(η^5-C_5Me_4)(η^5-C_5H_4)}Cl_2] (R = Bu^n, Bu^t) and [Zr{Bu^n(H)C(η^5-C_5Me_4)(η^5-C_5H_4)}(CH_2Ph)$_2$]

The synthesis and structural characterization of *ansa*-zirconocene complexes with asymmetric substitution at the *ansa*-bridging atom is described. Their reactivity in alkylation and isocyanide insertion processes has also been studied.

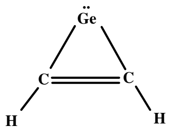


M.Z. Kassaee, S.M. Musavi, M. Ghambarian, M.R. Khalili Zanjani

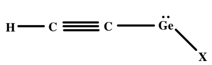
J. Organomet. Chem. 691 (2006) 2933

Switching of global minima of novel germylenic reactive intermediates via halogens (X): C_2GeH_2 vs. C_2GeHX at ab initio and DFT levels

The global minimum among six isomeric C_2GeH_2 germylenes, is singlet (s), aromatic, germacyclopropenylidene (**$1_{s\text{-}H}$**), while among the 24 corresponding halogermylenes C_2GeHX, the global minimum switches to the singlet, acyclic, ethynylhalogermylene (**$2_{s\text{-}X}$**), at eight reasonably high ab initio and DFT levels (X = F, Cl, and Br).



germacyclopropenylidene (singlet, **$1_{s\text{-}H}$**)



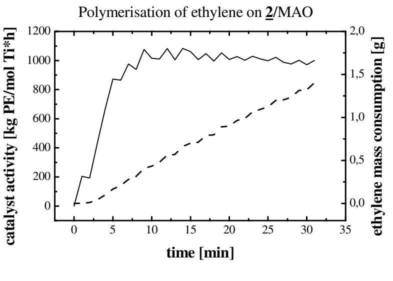
Ethynylhalogermylene (singlet, **$2_{s\text{-}X}$**)

Marc-Stephan Weiser, Marcel Wesolek, Rolf Mülhaupt

J. Organomet. Chem. 691 (2006) 2945

The synthesis and X-ray structure of a phenoxyimine catalyst tailored for living olefin polymerisation and the synthesis of ultra-high molecular weight polyethylene and atactic polypropylene

The living polymerisation behaviour of the catalyst was proven by online monitoring of polymerisation kinetics and SEC analyses.

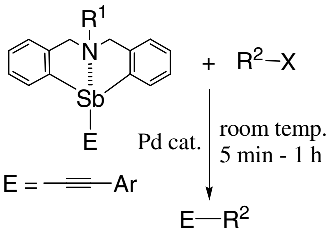


Naoki Kakusawa, Yoshinori Tobiyasu,
Shuji Yasuike, Kentaro Yamaguchi,
Hiroko Seki, Jyoji Kurita

J. Organomet. Chem. 691 (2006) 2953

Hypervalent organoantimony compounds 12-ethynyl-tetrahydrodibenz[c,f][1,5]azastibocines: Highly efficient new transmetallating agent for organic halides

Extremely efficient and high-speed ethynylation of acyl chlorides, aryl iodides and bromides was demonstrated by Pd-catalyzed cross-coupling reaction of *N*-*t*-butyl-*Sb*-ethynyl-5,6,7,12-tetrahydrodibenz[c,f][1,5]azastibocine under mild conditions (room temperature, 5 min to 1 h). Single-crystal X-ray analysis of the *N*-methyl-1,5-azastibocine revealed that the remarkable reactivity enhancement of the azastibocine was derived from elongation of the antimony–ethynyl carbon bond originated from Sb–N intramolecular non-bonding interaction.



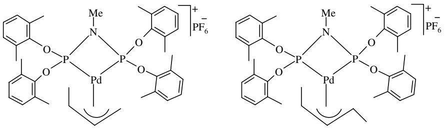
Ar = C_6H_5, *p*-CH_3-C_6H_4, *p*-F-C_6H_4
R^1 = Me, *i*-Pro, *t*-Bu etc.
R^2-X = Acyl-Cl, Ar-I, Ar-Br

Swadhin K. Mandal,
Thengarai S. Venkatakrishnan,
Arindam Sarkar,
Setharampattu S. Krishnamurthy

J. Organomet. Chem. 691 (2006) 2969

Steric and electronic effects in stabilizing allylpalladium complexes of “P–N–P” ligands, $X_2PN(Me)PX_2$ (X = OC_6H_5 or $OC_6H_3Me_2$-2,6)

The difference in the reactivity of the two ligands, $X_2PN(Me)PX_2$ [X = OC_6H_5 (**1**) or $OC_6H_3Me_2$-2,6 (**2**)] towards (allyl)palladium dimers [Pd(η^3-1,3-R′-R″-C_3H_3)(μ-Cl)]$_2$ (R′ = R″ = H, Me or Ph; R′ = H, R″ = Me) is brought out.Ligand **1** gives the dipalladium(I) complex in all reactions; only with [Pd(η^3-1,3-R′-R″-C_3H_3)(μ-Cl)]$_2$ (R′ = R″ = Ph), a cationic allyl palladium complex is also formed. By contrast, ligand **2** gives only cationic allyl palladium complexes; for two of these complexes, isomers with less favourable allylic arrangements (*anti*- or *syn*/*anti*) are present in solution to a significant extent.



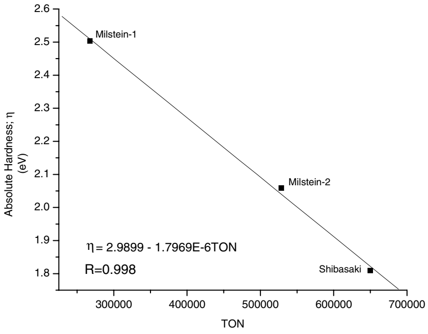
Anti-isomer (25%) *Syn*/*anti*-isomer (40%)

Carolina Tabares-Mendoza,
Patricia Guadarrama

J. Organomet. Chem. 691 (2006) 2978

Predicting the catalytic efficiency by quantum-chemical descriptors: Theoretical study of pincer metallic complexes involved in the catalytic Heck reaction

A tool to predict the catalytic activity by interpolation was constructed, correlating a quantum chemical descriptor like absolute hardness with the catalytic activity experimentally measured in turnover numbers for pincer metallic complexes.

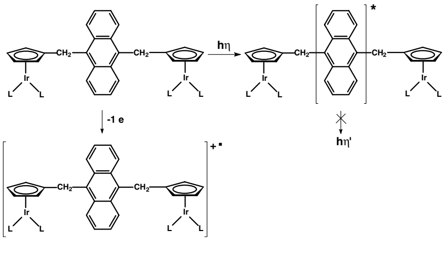


Federica Bertini, Lucia Calucci,
Francesca Cicogna, Benedetta Gaddi,
Giovanni Ingrosso, Massimo Marcaccio,
Fabio Marchetti, Demis Paolucci,
Francesco Paolucci, Calogero Pinzino

J. Organomet. Chem. 691 (2006) 2987

Electronic properties of new homobimetallic anthracene-bridged η^5-cyclopentadienyl derivatives of iridium(I) and of the corresponding cation radicals [$L_2Ir\{C_5H_4CH_2$(9,10-anthrylene)-$CH_2C_5H_4\}IrL_2]^{+\cdot}$

A study is reported aimed to investigate how the active sites of new homobimetallic anthracene-bridged cyclopentadienyl derivatives of iridium(I) interact in those conditions (chemical, photophysical, and electrochemical) which can induce the intramolecular transmission of electronic effects.

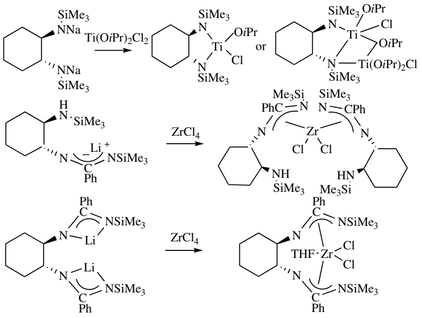


JianFeng Li, ShuPing Huang, LinHong Weng, DianSheng Liu

J. Organomet. Chem. 691 (2006) 3003

Synthesis and structural studies of some titanium and zirconium complexes with chiral bis(amide), amidinate or bis(amidinate) ligands

Some new results of Group 4 metal complexes liganded by bis(amide), amine-amidinate, amido-amidinate, unbridged and bridged bis(amidinate) are reported. Their synthesis methods and characterization are described. Structural studies show some new features and detailed comprehension is given by comparing with relevant compounds.

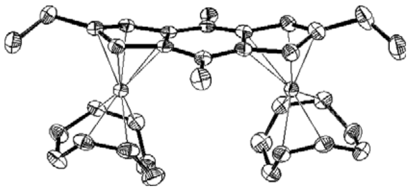


Edgardo Esponda, Christopher Adams, Francisco Burgos, Ivonne Chavez, Juan M. Manriquez, Fabien Delpech, Annie Castel, Heinz Gornitzka, Monique Rivière-Baudet, Pierre Rivière

J. Organomet. Chem. 691 (2006) 3011

New Rh derivatives of *s*-indacene active in dehydrogenative silylation of styrene

The synthesis and the characterization of mono and bimetallic rhodium complexes are described. The crystal structure of *syn*-[(2, 6-diethyl-4,8-dimethyl-*s*-indacenediide){Rh-(COD)}$_2$] confirms the ^{13}C and ^{103}Rh NMR studies which suggest a bonding mode of the indacenediide ligand in between η^3 and η^5. The complexes were shown to be highly active for the catalytic dehydrogenative silylation.

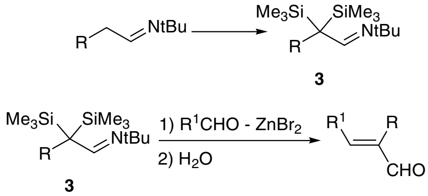


Nour Lahmar, Jamaa Aatar, Taïcir Ben Ayed, Hassen Amri, Moncef Bellassoued

J. Organomet. Chem. 691 (2006) 3018

A general route to α-alkyl (*E*)-α,β-unsaturated aldehydes

The bisilyated reagents **3** react with aldehydes to give α-alkyl α,β-ethylenic aldehydes in good yield and with very high *E* stereoselectivity.

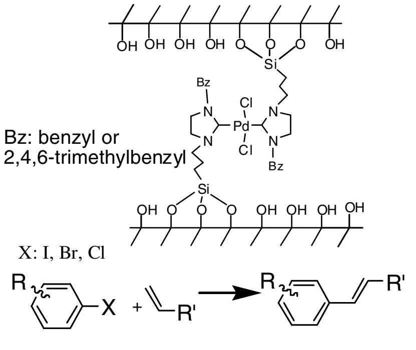


Özge Aksın, Hayati Türkmen, Levent Artok, Bekir Çetinkaya, Chaoying Ni, Orhan Büyükgüngör, Erhan Özkal

J. Organomet. Chem. 691 (2006) 3027

Effect of immobilization on catalytic characteristics of saturated Pd-N-heterocyclic carbenes in Mizoroki–Heck reactions

A highly thermally stable saturated Pd–NHC acts only as a catalyst precursor in Mizoroki Heck catalysis to highly active Pd species when it is immobilized.

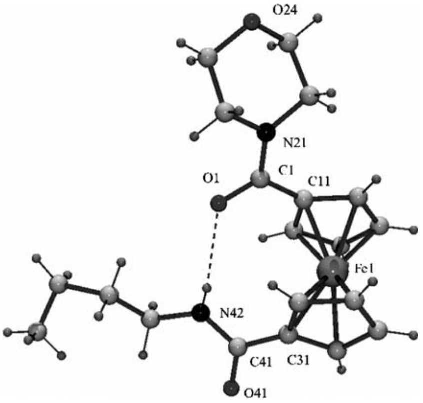


Árpád Kuik, Rita Skoda-Földes, Attila C. Bényei, Gábor Rangits, László Kollár

J. Organomet. Chem. 691 (2006) 3037

Formation of intramolecular hydrogen bonds in heterodisubstituted ferrocene diamides with a secondary and a tertiary amido group: X-ray structure of 1′-(*N*′-butyl-carbamoyl)-morpholino ferrocenecarboxamide

Unsymmetrical ferrocene 1,1′-diamides with one secondary and one tertiary amido group form intramolecular hydrogen bonds both in the solid state and in solution. The structure of (BuNHCOC$_5$H$_4$)Fe(C$_5$H$_4$CON(CH$_2$CH$_2$)$_2$O) (**1a**) is determined by X-ray crystallography, as well as solution-phase ^{1}H NMR and infrared spectroscopy. The hydrogen bond can be cleaved upon addition of chloride ions.

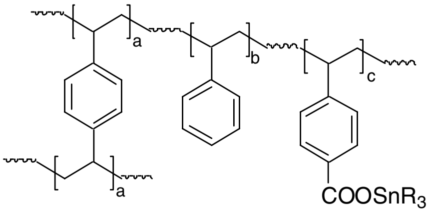


Luigi Angiolini, Daniele Caretti, Laura Mazzocchetti, Elisabetta Salatelli, Rudolph Willem, Monique Biesemans

J. Organomet. Chem. 691 (2006) 3043

Cross-linked polystyrene resins containing triorganotin-4-vinylbenzoates: Assessment of their catalytic activity in transesterification reactions

Cross-linked polystyrene resins bearing different organotin carboxylates were prepared and characterized by NMR spectroscopy. Their catalytic activity in transesterification was evaluated and related to the nature of the organotin substituent. Triphenyltin substituted polymers show comparable to better catalytic activity with respect to similar organotin resins as well as model compounds.

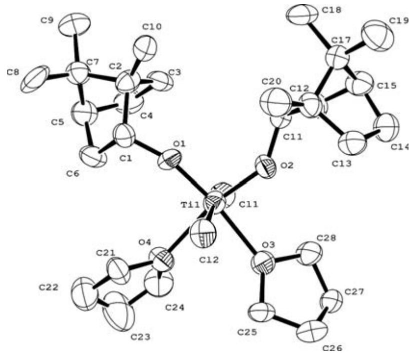


Yolanda Pérez, Isabel del Hierro, Isabel Sierra, Pilar Gómez-Sal, Mariano Fajardo, Antonio Otero

J. Organomet. Chem. 691 (2006) 3053

Polymerization of ε-caprolactone using bulky alkoxo-titanium complexes and structural analysis of [Ti(OBorneoxo)$_2$Cl$_2$(thf)$_2$]

A variety of bisalkoxo titanium dichloride THF adducts [Ti(OR)$_2$Cl$_2$(thf)$_2$] have been prepared. The molecular structure of hexacoordinated titanium dichloride with alkoxo units derived from borneol has been determined by single-crystal X-ray diffraction studies. The parent Lewis acid bisalkoxo titanium dichloride derivatives [Ti(OR)$_2$Cl$_2$] and related alkoxo complexes [Ti(OR)$_2$(OPr^i)$_2$]$_2$ have been tested as initiators in ring-opening polymerization of ε-caprolactone and L-lactide.

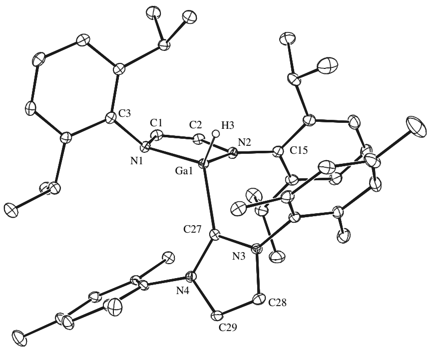


Cameron Jones, David P. Mills, Richard P. Rose

J. Organomet. Chem. 691 (2006) 3060

Oxidative addition of an imidazolium cation to an anionic gallium(I) *N*-heterocyclic carbene analogue: Synthesis and characterisation of novel gallium hydride complexes

The reaction of an anionic gallium(I) heterocycle, [:Ga{[N(Ar)C(H)]$_2$}]$^-$, Ar = C$_6$H$_3$Pr$^i_2$-2,6, with an imidazolium salt, [HC{N(Mes)-C(H)}$_2$]Cl, IMesHCl, Mes = C$_6$H$_2$Me$_3$-2,4,6, leads to oxidative insertion of the gallium(I) centre into the imidazolium C–H bond and the formation of an *N*-heterocyclic carbene coordinated gallium hydride complex.

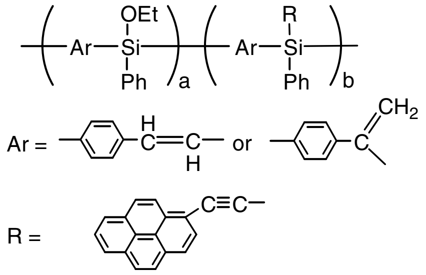


Joji Ohshita, Ryosuke Taketsugu, Koichi Hino, Atsutaka Kunai

J. Organomet. Chem. 691 (2006) 3065

Synthesis and reactions of poly[(ethoxysilylene)phenylenevinylene]s and chain-to-pendant energy transfer in the resulting polymer

Synthesis of poly[(ethoxysilylene)phenylenevinylene]s, followed by their reactions with nucleophiles provides a route to variously substituted poly(silylenephenylenevinylene)s. Of the resulting polymers, pyrenylethynyl-substituted one exhibited energy transfer from the backbone to the substituent in the photo-excited state.

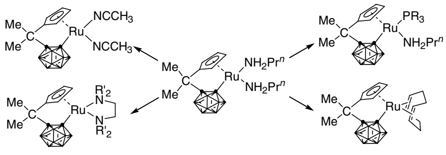


Yi Sun, Hoi-Shan Chan, Pierre H. Dixneuf, Zuowei Xie

J. Organomet. Chem. 691 (2006) 3071

Reactions of $[\eta^5:\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]$-Ru(COD) with Lewis bases: Synthesis, structure, and electrochemistry of ruthenium amine, nitrile, carbene, phosphite and phosphine complexes

Ruthenium amine and acetonitrile complexes bearing a constrained-geometry carboranyl ligand are much more labile than the corresponding COD analogue, allowing the introduction of a variety of new ligands on the Ru site. Thus, they may be good candidates as catalyst precursors.

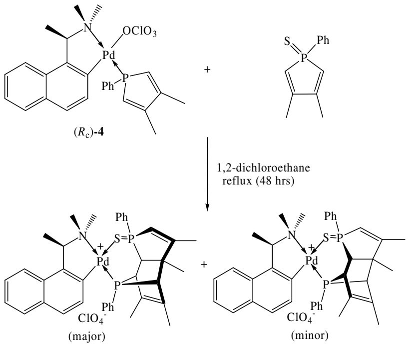


Sumod A. Pullarkat, Kien-Wee Tan, Mengtao Ma, Geok-Kheng Tan, Lip Lin Koh, Jagadese J. Vittal, Pak-Hing Leung

J. Organomet. Chem. 691 (2006) 3083

Asymmetric synthesis of a P-chiral heteroditopic $\widehat{P\ P}$=S ligand via chiral metal template promoted cycloaddition between 3,4-dimethyl-1-phenylphosphole and its sulfonated analog

A novel chiral heteroditopic $\widehat{P\ P}$=S ligand has been synthesized via asymmetric [4+2] Diels-Alder reaction involving 3,4-dimethyl-1-phenylphosphole, and its P-sulfonated analogue utilizing the palladium(II) template complex containing *ortho*-metalated (*R*)-(1-(dimethylamino)ethyl)naphthalene as the chiral auxiliary.

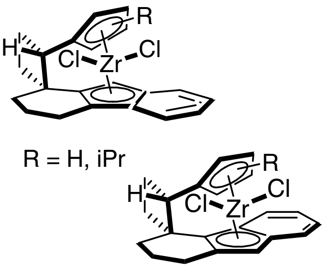


Geir Langli, Christian Rømming, Kjell Undheim

J. Organomet. Chem. 691 (2006) 3089

Spirane-bridged *ansa* η^5-cyclopentadienyl-η^5-fluorenyl-zirconocene precatalysts

Rigid zirconocene precatalysts with a C_2-bridge embedded in spirane scaffolds have been prepared from 1- and 4-fluorenones. The intermediate ligands were lithiated and zirconated to afford η^5-cyclopentadienyl-η^5-fluorenyl-zirconocenes. Isopropyl homologues resulted from regioselective substitution in the cyclopentadienyl ring. The catalytic properties of the zirconocenes were investigated in propene polymerisations. X-ray analysis has been used for zirconocene structure confirmation.



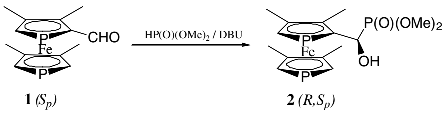
Notes

Damian Plażuk, **Janusz Zakrzewski**, **Agnieszka Rybarczyk-Pirek**

J. Organomet. Chem. 691 (2006) 3098

Diastereoselective addition of dimethyl phosphite to 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene-2-carboxaldehyde

Addition of dimethyl phosphite to racemic 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene-2-carboxaldehyde gives almost exclusively one diastereomer of the corresponding α-hydroxyphosphonate (d.r. ⩾ 96:4). Its absolute configuration (S, R_p)–(R, S_p) was established by X-ray diffraction.



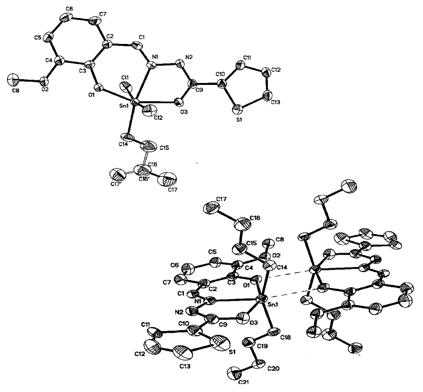
(only one enantiomer is shown)

Han Dong Yin, **Shao Wen Chen**

J. Organomet. Chem. 691 (2006) 3103

Synthesis and characterization of organotin(IV) compounds with Schiff base of *o*-vanillin-2-thiophenoylhydrazone

Seven Schiff base adducts of organotin(IV), $RSnLCl_2$, which L is *o*-vanillin-2-thiophenoylhydrazone, and R is *n*-C_4H_9 (**1**), Me (**2**), Ph (**3**), and $[R_2SnL]$, which L is *o*-vanillin-2-thiophenoylhydrazone, R is *n*-C_4H_9 (**4**), Me (**5**), Ph (**6**), $PhCH_2$ (**7**) have been synthesized. Those products were characterized by elemental analysis, IR, ^1H, ^{13}C and ^{119}Sn NMR spectra. The crystal and molecular structures of compounds **1**, **4**, and **6** have been determined by X-ray single crystal diffraction.



Robert F. Cunico, **Adalie R. Motta**

J. Organomet. Chem. 691 (2006) 3109

Structural and electronic effects on the reactivity of carbamoylsilanes towards acrylonitrile addition

The rates of addition to acrylonitrile of a series of carbamoylsilanes were found to increase with an increase in the size of alkyl groups attached to silicon and nitrogen. X-ray structural parameters indicated that steric compression within the carbamoylsilanes was not a factor in determining reactivity, but the ionization potentials of the carbamoylsilanes roughly paralleled the reactivity pattern observed.