

Contents

Special Issue: Dedicated to Professor Pascual Royo

Preface	1
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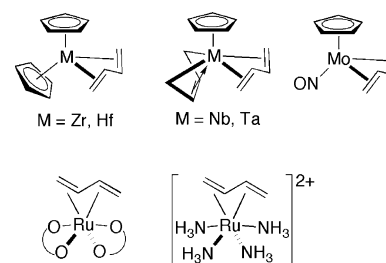
Account

Kazushi Mashima, Akira Nakamura

J. of Organomet. Chem. 663 (2002) 5

Adaptable coordination modes of conjugated 1,3-diene: uniqueness of *s-trans* coordination

In this contribution, we briefly review the general aspects of the mononuclear *s-trans* diene complexes including the recent results.



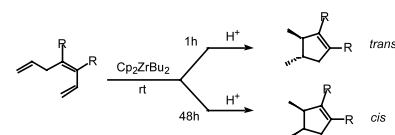
Regular Papers

Zhenfeng Xi, Guohua Gao, Martin Kotora, Tamotsu Takahashi

J. of Organomet. Chem. 663 (2002) 13

Zirconocene mediated cyclization and isomerization of 1,3,6-heptatriene

Cyclization of 1,3,6-heptatrienes with Cp_2ZrBu_2 at room temperature for 1 h afforded predominantly *trans*-dimethylcyclopentenes after hydrolysis. When the mixture was stirred for 48 h, *cis*-dimethylcyclopentenes were obtained with high selectivity after hydrolysis.



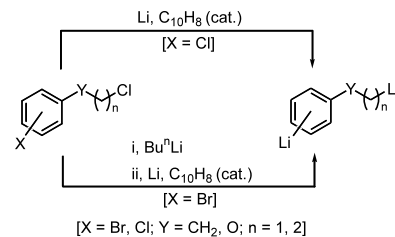
Miguel Yus, Diego J. Ramón, Inmaculada Gómez

J. of Organomet. Chem. 663 (2002) 21

Lithiophenylalkyllithiums: new dilithium reagents having both sp^2 - and sp^3 -hybridised remote carbanionic centres

The use of a naphthalene-catalysed lithiation process let us to obtain dilithiated species, bearing the carbanionic centre on remote sp^2 - and sp^3 -hybridisation carbon atoms, which were trapped by reaction with

different carbonyl compounds to afford the expected diols. The whole process may be seen as a double homologation of the appropriate alcohols through the preparation of dihalogenated material, lithiation of dihalogenated system, reaction of organolithium intermediate with carbonyl compounds and final hydrolysis. The homologation can be a sequential or simultaneous two-directional process depending on the starting halogenated material used, as well as the lithiation methodology chosen.

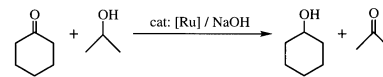


**Victorio Cadierno, Pascale Crochet,
Joaquín García-Álvarez,
Sergio E. García-Garrido, José Gimén**

J. of Organomet. Chem. 663 (2002) 32

Neutral and cationic (η^6 -arene)-ruthenium(II) complexes containing the iminophosphorane–phosphine ligand $\text{Ph}_2\text{P}-\text{CH}_2\text{P}(=\text{N}-p\text{-C}_5\text{F}_4\text{N})\text{Ph}_2$: influence of the arene ring in catalytic transfer hydrogenation of cyclohexanone

The synthesis and catalytic activity in transfer hydrogenation of cyclohexanone by propan-2-ol of ruthenium(II) complexes $[\text{Ru}(\eta^6\text{-arene})\text{Cl}_2\{k^1\text{-}P\text{-Ph}_2\text{PCH}_2\text{P}(=\text{N}-p\text{-C}_5\text{F}_4\text{N})\text{Ph}_2\}]$ and $[\text{Ru}(\eta^6\text{-arene})\text{Cl}\{k^2\text{-}P,N\text{-Ph}_2\text{PCH}_2\text{P}(=\text{N}-p\text{-C}_5\text{F}_4\text{N})\text{Ph}_2\}][\text{SbF}_6]$ (arene = C_6H_6 , 1-*i*-Pr-4- $\text{C}_6\text{H}_4\text{Me}$, 1,3,5- $\text{C}_6\text{H}_3\text{-Me}_3$, 1,2,3,4- $\text{C}_6\text{H}_2\text{Me}_4$, 1,2,4,5- $\text{C}_6\text{H}_2\text{Me}_4$, C_6Me_6) is reported.

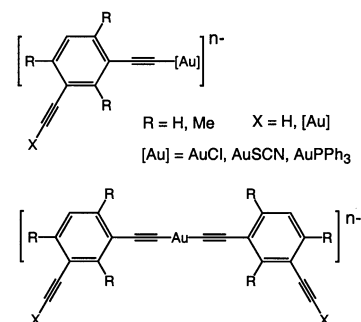


**José Vicente, María Teresa Chicote,
María Dolores Abrisqueta,
Miguel M. Álvarez-Falcón**

J. of Organomet. Chem. 663 (2002) 40

The first anionic arenediethynylgold(I) complexes

Synthetic methods for the preparation of mono-, di-, tri- and polyanionic alkynegold(I) complexes derived from diethynylarenes are reported.

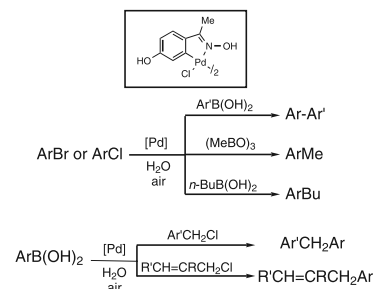


Luis Botella, Carmen Nájera

J. of Organomet. Chem. 663 (2002) 46

Cross-coupling reactions with boronic acids in water catalysed by oxime-derived palladacycles

Oxime-derived palladacycles are a robust source of palladium for the Suzuki coupling of aryl chlorides and bromides with aryl- and alkylboronic acids under aerobic conditions in refluxing water or in aqueous methanol at room temperature. These pre-catalysts are also efficient in the cross-coupling of benzylic and allylic chlorides or acetates with arylboronic acids in aqueous acetone at room temperature.

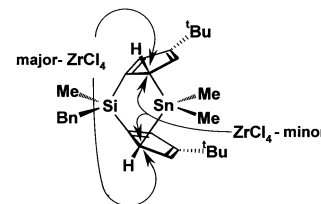


**Mario Hüttenhofer, Armin Weeber,
Hans-Herbert Brintzinger**

J. of Organomet. Chem. 663 (2002) 58

Mechanisms of Sn-to-Zr cyclopentadienyl transfer in the formation of Me_2Si -bridged zirconocenes from sila-stanna-tetrahydro-s-indacenes

Cyclopentadienyl rings are transferred from Sn(IV) to Zr(IV) centers predominantly under inversion but partly also under retention at both of their metal-bound C atoms.

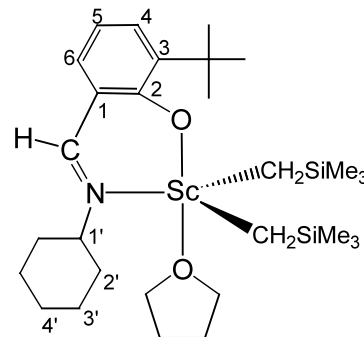


**Agustín Lara-Sanchez, Antonio Rodriguez,
David L. Hughes, Mark Schormann,
Manfred Bochmann**

J. of Organomet. Chem. 663 (2002) 63

Synthesis, structure and catalytic activity of new iminophenolato complexes of scandium and yttrium

2-Iminophenols react with $M(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_3$ ($M = \text{Sc}$ or Y) to give five-coordinate $M(\text{CH}_2\text{SiMe}_3)_2(\text{THF})(\text{L})$. While the scandium compounds are stable, the yttrium derivatives undergo slow ligand rearrangement, depending on the nature of the nitrogen substituents. The scandium complexes are efficient catalysts for the ring-opening polymerisation of ϵ -caprolactone.

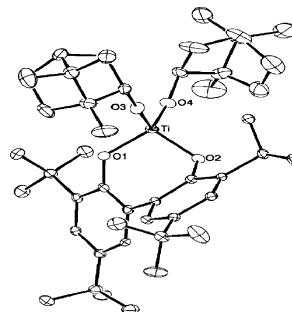


**Timothy J. Davis, Patrick J. Carroll,
Patrick J. Walsh**

J. of Organomet. Chem. 663 (2002) 70

Synthesis and X-ray structures of (biphenoxide)Ti species: four and five coordinate complexes that crystallize as mixtures of diastereomers

A set of novel Ti(IV) crystal structures is described, where two diastereomers crystallize in a 1:1 ratio in the unit cell. The achiral ligand 4,4',6,6'-tetra-*tert*-butyl-2,2'-biphenol reacted with chiral Ti(IV) complexes $\text{Ti}(\text{O}i\text{-Pr})_2(\text{OR}^*)_2$ to give (biphenoxide)Ti(OR^{*})₂ as a mixture of diastereomers. These diastereomers were crystallized to give four and five coordinate titanium complexes as a 1:1 mixture of diastereomers.

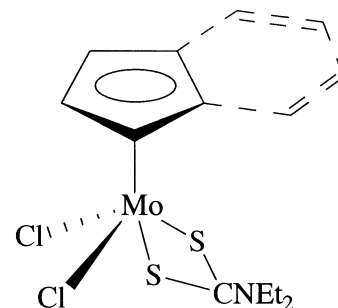


Carlos C. Romão, Beatriz Royo

J. of Organomet. Chem. 663 (2002) 78

Mono-indenyl and cyclopentadienyl derivatives of molybdenum(IV) with a 16 valence-electron configuration

A series of half-sandwich molybdenum (IV) complexes of the type (ring)MoCl₂X [ring = cyclopentadienyl, $\eta^5\text{-C}_5\text{H}_5$ (Cp) or indenyl $\eta^5\text{-C}_9\text{H}_7$ (Ind) and X = S₂CNEt₂, S₂P(OEt)₂, CH(NPh)₂, O₂CCH₃ and acac] have been synthesised and characterised by elemental analysis, IR and ¹H-NMR spectroscopy and magnetic susceptibility.

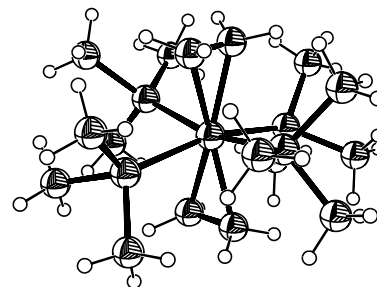


**Diego del Río, Gábor Schubert, Imre Pápai,
Agustín Galindo**

J. of Organomet. Chem. 663 (2002) 83

Theoretical analysis of bis(ethylene) complexes of molybdenum and tungsten

DFT calculations on *trans*-[M(C₂H₄)₂(PH₃)₄] model complexes and the actual *trans*-[M(C₂H₄)₂(PMe₃)₄] (M = Mo, W) compounds were performed. Experimental structures were properly reproduced only when the PMe₃ ligands were used. The low PMe₃ dissociation energies calculated are in agreement with the experimental results. The comparison of PH₃ and PMe₃ data corroborate the hypothesis that phosphine dissociation has a steric origin.

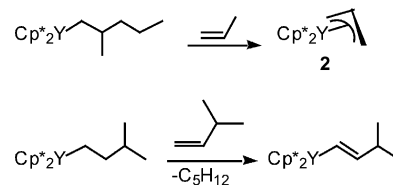


**Charles P. Casey, Jon A. Tunge,
Maureen A. Fagan**

J. of Organomet. Chem. 663 (2002) 91

Why propene is not polymerized by $(Cp^*_2YH)_2$: reactions of yttrium alkyl complexes with alkenes produce allyl and vinyl yttrium complexes

Yttrium alkyl complexes react with C–H bonds of alkenes to form either yttrium allyl complexes or yttrium vinyl complexes. The selectivity of the reaction of Cp^*_2YR with C–H bonds is allylic $CH_3 \gg$ vinyl C–H \gg allylic CH_2 . Propene is metallated by Cp^*_2YR to give an η^3 -allyl complex **2** which does not react further with propene.

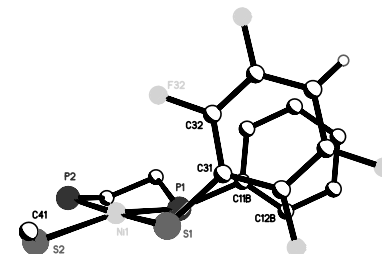


Miguel A. Usón, Jesús M. Llanos

J. of Organomet. Chem. 663 (2002) 98

Synthesis of Group 10 polyfluorothiolate mono- and bi-nuclear complexes. Crystal structures of $[Ni(SC_6HF_4)_2(dppe)]$, $[(dppe)Ni(\mu-SC_6HF_4)_2Pd(C_6F_5)_2]$ and $[(dppe)Ni(\mu-SC_6F_5)_2Pd(C_6F_5)_2]$

Homologous complexes containing the pentafluorothiophenolate or *p*-tetrafluorothiophenolate ligands show very different interfacial π - π interactions between aromatic rings.

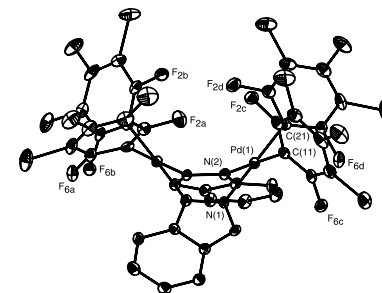


**Raquel de la Cruz, Pablo Espinet,
Ana M. Gallego, Jose M. Martín-Alvarez,
Jesús M. Martínez-Iharduya**

J. of Organomet. Chem. 663 (2002) 108

Structural and dynamic studies in solution of anionic dinuclear azolato-bridged palladium(II) complexes

Detailed analysis of the ^{19}F -NMR spectra of the boat-shaped complexes $(NBu_4)_2[Pd_2(\mu-azolate)_2R_4]$ ($R = 3,5-C_6Cl_2F_3$) and a single-crystal X-ray structure of $HT-(NBu_4)_2-[Pd_2(\mu-indz)_2R_4]$ afford valuable structural information. The substituents of the azolate ligands, which reduce the dihedral angle between the coordination planes of the two metals, place the *endo* F_{ortho} of different PdR_2 fragments at short distances. The study of the dynamic processes for these complexes reveals the involvement of different mechanisms.

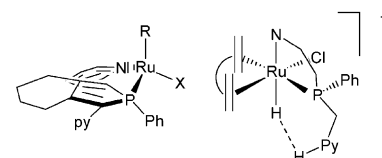


**Agustín Caballero, Félix A. Jalón,
Blanca R. Manzano, Mathieu Sauthier,
Loïc Toupet, Régis Réau**

J. of Organomet. Chem. 663 (2002) 118

A study of the coordination ability of 2,5-di(2-pyridyl)phospholes on Ru centres

A series of ruthenium complexes bearing 1-phenyl-2,5-di(2-pyridyl)phosphole were prepared. The phosphole ligand acts as an 1,4-*P,N* chelate ligand in all cases and in several examples only one of the possible diastereomers was formed. The structural dependence in the formation of a weak dihydrogen bridge was demonstrated for one of the complexes.



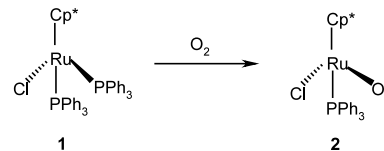
$X = Cl$; $R = \eta^6$ -*p*-cymene, $\eta^6-C_6Me_6$, $n=1$
 $\eta^5-C_5H_5$, $\eta^5-C_5Me_5$.
 $X = \sigma^1$ -2,3-cycloocten-1-yl; $R = \eta^5-C_5Me_5$, $n=0$

**J. Román Torres-Lubián,
M. Esther Sánchez-Castro,
Patricia Juárez-Saavedra,
Javier Hernández-Martínez,
Bárbara Gordillo-Román,
M. Angeles Paz-Sandoval**

J. of Organomet. Chem. 663 (2002) 127

Reaction of $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$ with dioxygen and formation of a neutral complex $\text{Cp}^*\text{RuCl}(\text{O}_2)(\text{PPh}_3)$

Reaction of $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$ (1) with atmospheric oxygen leads to neutral $\text{Cp}^*\text{RuCl}(\text{O}_2)(\text{PPh}_3)$ (2). The activated oxygen molecule, afforded fulvene compound $[\{\eta^6\text{-C}_5\text{Me}_4\text{CH}_2\text{RuCl}_2\}_2]$ (4), along with OPPh_3 , or oxidation of the phosphite $\text{L} = \text{MeOP}[(\text{OCHMe})_2\text{CH}_2]$ to the corresponding phosphate, along with formation of the mono- and disubstituted $\text{Cp}^*\text{RuCl}(\text{PPh}_3)(\text{L})$ (5), $\text{Cp}^*\text{RuCl}(\text{L})_2$ (6) and $[\text{Cp}^*\text{Ru}(\text{PPh}_3)(\text{L})_2]\text{Cl}$ (7) complexes. Structural information of 5 and 6 derivatives has been obtained by X-ray diffraction.

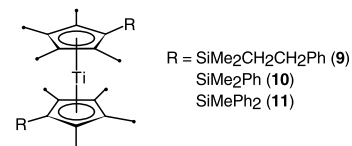


**Lenka Lukešová, Michal Horáček,
Petr Štěpnička, Karla Fejfarová,
Róbert Gyepes, Ivana Císařová,
Jiří Kubišta, Karel Mach**

J. of Organomet. Chem. 663 (2002) 134

Synthesis and crystal structures of thermally stable titanocenes

Reduction of titanocene dichlorides $[\text{TiCl}_2(\eta^5\text{-C}_5\text{Me}_4\text{R})_2]$, where $\text{R} = \text{SiMe}_2\text{CH}_2\text{CH}_2\text{Ph}$ (3), SiMe_2Ph (4), and SiMePh_2 (5) with magnesium in THF proceeds via the respective titanocene monochlorides $[\text{TiCl}(\eta^5\text{-C}_5\text{Me}_4\text{R})_2]$ (6–8) to afford finally the thermally stable titanocenes, $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_4\text{R})_2]$ (9–11). As revealed by X-ray crystallography, titanocenes 9 and 11 possess bent metallocene structures with the cyclopentadienyl rings tilted at an angle of 9.8(1) and 14.4(2)°, respectively.



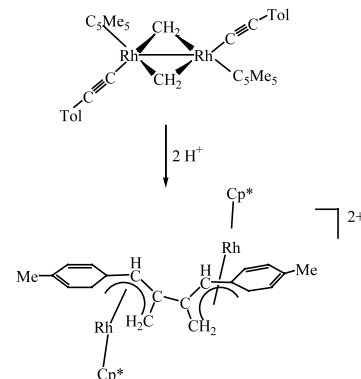
cyclopentadienyl-ring tilt: 9, 9.8(1); 11, 14.4(2)°.

**Aurora Castro, Peter M. Maitlis,
Michael L. Turner, Brian E. Mann,
Harry Adams**

J. of Organomet. Chem. 663 (2002) 145

Proton induced coupling reactions in dinuclear σ -alkynyl- μ -methylene-rhodium complexes

Complexes $[(\text{C}_5\text{Me}_5\text{Rh})_2(\mu\text{-CH}_2)(\text{C}_2\text{C}_6\text{H}_4\text{-X})_2]$ react with acids to give the unexpected products *syn*- and *anti*- $[(\text{C}_5\text{Me}_5)_2\text{Rh}_2\{\mu\text{-}\eta^5, \eta^5\text{-}\{\text{XC}_6\text{H}_4\text{CH}(\text{CH}_2)\text{CC}(\text{CH}_2)\text{CHC}_6\text{H}_4\text{-X}\}][\text{BF}_4]_2$, ($\text{X} = \text{H}$ and *p*-Me). An X-ray determination of the *syn-p*-tolyl complex showed it to contain a hydrocarbon skeleton of two linked η^5 -allylbenzenes; spectroscopy showed that similar hydrocarbon skeletons were in the other complexes.

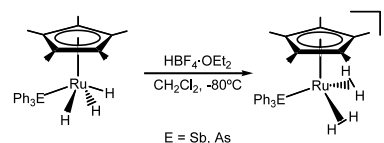


**Halikhedkar Aneetha,
Manuel Jiménez Tenorio,
M. Carmen Puerta, Pedro Valerga**

J. of Organomet. Chem. 663 (2002) 151

Ruthenium hydrides bearing SbPh_3 and AsPh_3 ligands: characterization of the bis(dihydrogen) complexes $[\text{Cp}^*\text{Ru}(\text{H}_2)_2(\text{EPh}_3)]^+$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$; $\text{E} = \text{Sb}, \text{As}$)

The protonation of the trihydrides $[\text{Cp}^*\text{RuH}_3(\text{EPh}_3)]$ ($\text{E} = \text{Sb}, \text{As}$) with $\text{HBF}_4 \cdot \text{OEt}_2$ in CD_2Cl_2 at -80°C afforded the corresponding bis(dihydrogen) complexes $[\text{Cp}^*\text{Ru}(\text{H}_2)_2(\text{EPh}_3)][\text{BF}_4]$, which were characterized in solution by T_1 and $^1J_{\text{HD}}$ measurements. Protonation of the monohydride $[\text{Cp}^*\text{RuH}(\text{SbPh}_3)_2]$ at -80°C yields the dihydrogen complex $[\text{Cp}^*\text{Ru}(\text{H}_2)(\text{SbPh}_3)_2][\text{BF}_4]$, which rearranges to its dihydride tautomer $[\text{Cp}^*\text{RuH}_2(\text{SbPh}_3)_2][\text{BF}_4]$ when the temperature is raised.



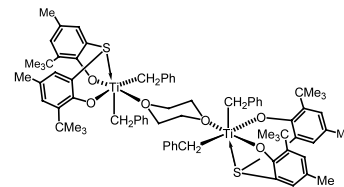
**Stefan Fokken, Frank Reichwald,
Thomas P. Spaniol, Jun Okuda**

J. of Organomet. Chem. 663 (2002) 158

Dialkyl titanium complexes that contain a sulfur-linked bis(phenolato) ligand:

The structure of an olefin polymerization catalytic precursor

Reaction of the dichloro complex $[\text{Ti}(\text{tbmp})\text{Cl}_2]_2$ (tbmp = 2,2'-thiobis(2-*tert*-butyl-4-methylphenoxy) with methyllithium at low temperature gave the unexpectedly thermally robust, yellow dimethyl complex $[\text{Ti}(\text{tbmp})\text{Me}_2]$. The reaction of the dichloro complex with benzyl Grignard reagent in pentane afforded the crystallographically characterized dibenzyl complex $[\text{Ti}(\text{tbmp})\text{-(CH}_2\text{Ph)}_2]$ as a 1,4-dioxane adduct.

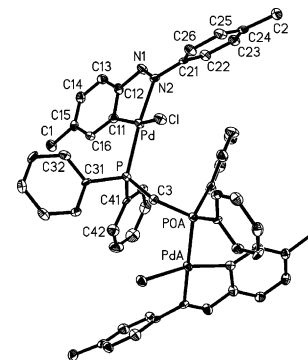


**José Vicente, Aurelia Arcas, Delia Bautista,
M. Carmen Ramirez de Arellano**

J. of Organomet. Chem. 663 (2002) 164

Mono- and di-nuclear complexes of *ortho*-palladated and -platinated 4,4'-dimethylazobenzene with bis(diphenylphosphino)methane. More data on *transphobia*

Palladium and platinum complexes containing $\kappa^2\text{-C,N'}$ - $\text{C}_6\text{H}_3(\text{N}=\text{NC}_6\text{H}_4\text{-Me-4'})\text{-2-Me-5}$, $\kappa^1\text{-dppm}$, $\mu\text{-dppm}$, and/or $\kappa^2\text{-dppm}$ have been prepared. The new species include mono- and di-, homo- and hetero-nuclear complexes.



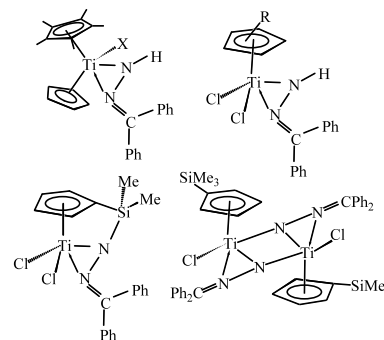
**Vanessa Taberner, Tomás Cuenca,
Eberhardt Herdtweck**

J. of Organomet. Chem. 663 (2002) 173

Hydrazonide titanium derivatives

Synthesis, characterization and catalytic activity in olefin polymerization. Molecular structure of $[\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}(\mu\text{-N}_2\text{CPh}_2)]_2$

Dicyclopentadienyl hydrazonide titanium derivatives are prepared by reaction of $\text{Ti}(\text{C}_5\text{Me}_5)(\text{C}_5\text{H}_5)\text{Cl}_2$ with $\text{LiN}(\text{H})\text{NCPH}_2$. Monocyclopentadienyl hydrazonide titanium complexes have also been synthesized by the Ti-Cl bond aminolysis reaction of $\text{Ti}(\text{CpR})\text{Cl}_3$ with hydrazone $[\text{H}_2\text{N}=\text{N}=\text{CPh}_2]$ in the presence of amine. When an excess of amine is used, the dinuclear complex $[\text{Ti}(\text{C}_5\text{H}_4\text{SiMe}_3)\text{Cl}(\mu\text{-N}_2\text{CPh}_2)]_2$ or the cyclopentadienyl-amido derivative $\text{Ti}[\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2-\eta^1\text{-NNCPH}_2)]\text{Cl}_2$ could be prepared, depending on the nature of the cyclopentadienyl substituent.

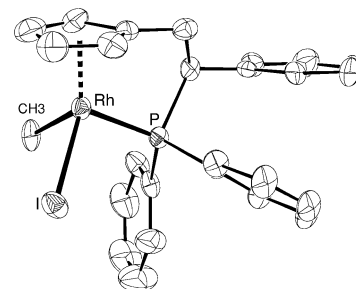


**Santiago Ciruelos, Angelino Doppiu,
Ulli Englert, Albrecht Salzer**

J. of Organomet. Chem. 663 (2002) 183

New optically active 'constrained-geometry' cyclopentadienyl-phosphine ligands and their metal complexes

Bidentate Cp-PR₂ ligands with a chiral linker induce high stereoselectivity at rhodium on oxidative addition reactions with methyl iodide.



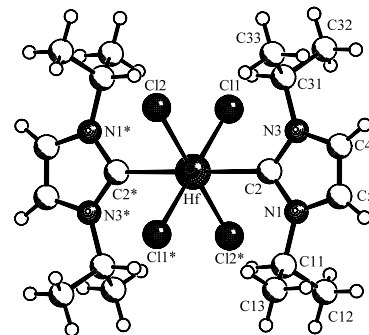
**Martin Niehues, Gerald Kehr,
Gerhard Erker, Birgit Wibbeling,
Roland Fröhlich, Olivier Blacque,
Heinz Berke**

J. of Organomet. Chem. 663 (2002) 192

Structural characterization of Group 4 transition metal halide bis-Arduengo carbene complexes MCl_4L_2 :

X-ray crystal structure analyses and DFT calculations

Treatment of a series of 'Arduengo carbenes' with the Group 4 metal halides $ZrCl_4$ or $HfCl_4$ gave the *trans*-bis(carbene ligand) MCl_4 adducts that were characterized by X-ray diffraction and a theoretical analysis (DFT). The carbene adducts form moderately active ethene polymerization catalysts when treated with methylalumoxane.

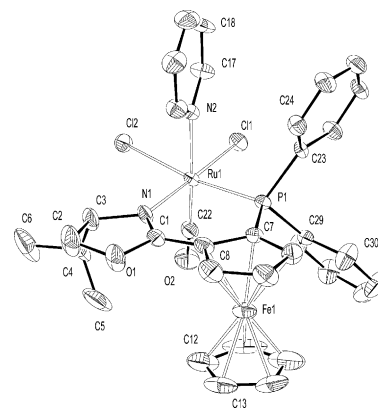


**José Gimeno, Elena Lastra, César Madrigal,
Claudia Graiff, Antonio Tiripicchio**

J. of Organomet. Chem. 663 (2002) 204

New ruthenium(II) complexes containing the chiral ligand (4*S*)-2-[(*S_p*)-2-(diphenylphosphino)ferrocenyl]-4-(methylethyl)oxazoline (FcPN). X-ray structures of *mer-trans*-[$RuCl_2(dppm)(FcPN)$] (*dppm* = bis(diphenylphosphino)methane) and *cis*-[$RuCl_2(CO)(py)(FcPN)$]

Fac-mer isomerizations of octahedral ruthenium (II) complexes [RuCl₂(dppm)(FcPN)] are described to occur through a five-coordinate intermediate [RuCl(dppm)(FcPN)]-[Cl] which is isolated as its hexafluorophosphate salt. Synthesis of carbonyl complex [RuCl₂(CO)(L)(FcPN)] (L=PPh₃, py) and [RuCl(CO)(dppm)(FcPN)][PF₆] are also described. X-ray crystal structures of complexes *mer-trans*-[RuCl₂(dppm)(FcPN)] (**1**) and *cis*-[RuCl₂(CO)(Py)(FcPN)] (**8**) are reported.

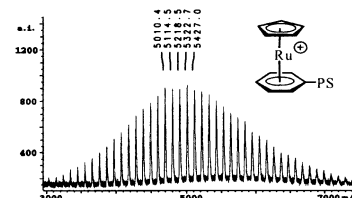


Eva Royo, Hans-Herbert Brintzinger

J. of Organomet. Chem. 663 (2002) 213

Mass spectrometry of polystyrene and polypropene ruthenium complexes. A new tool for polymer characterization

Formation of organometallic ruthenium allows observation of polystyrene ions with $M_n = 1430-135000$ and of polypropene ions with $M_n = 2700-6100$ by MALDI-TOF-MS.

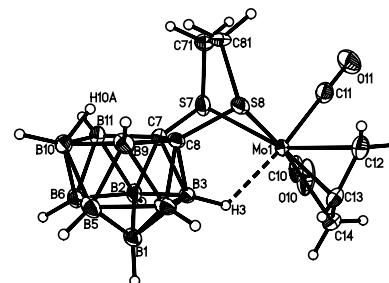


**Gemma Barberà, Clara Viñas,
Francesc Teixidor, Georgina M. Rosair,
Alan J. Welch**

J. of Organomet. Chem. 663 (2002) 221

Synthesis and characterisation of the *exo-nido* molybdacarborane complex $Mo(\eta-C_3H_5)(CO)_2(7,8-\mu-SCH_2CH_2S-7,8-nido-C_2B_9H_{10})$. Strong B-H-Mo 3-centre bonding

Reaction of [7,8- μ -SCH₂CH₂S-7,8-*nido*-C₂B₉H₁₀]⁻ and MoBr(η -C₃H₅)(CO)₂(MeCN)₂ in THF affords the zwitterionic *exo-nido* molybdacarborane complex Mo(η -C₃H₅)(CO)₂(7,8- μ -SCH₂CH₂S-7,8-*nido*-C₂B₉H₁₀), characterised by ¹H- and ¹¹B-NMR spectroscopy and by a crystallographic study. Deprotonation of [7,8- μ -SCH₂CH₂S-7,8-*nido*-C₂B₉H₁₀]⁻ with Li-NⁱPr₂ followed by reaction with MoBr(η -C₃H₅)(CO)₂(MeCN)₂ affords Li[1,2- μ -SCH₂CH₂S-3-(η -C₃H₅)-3,3-(CO)₂-3,1,2-*closo*-MoC₂B₉H₉] for which ¹H- and ¹¹B-NMR data are reported.

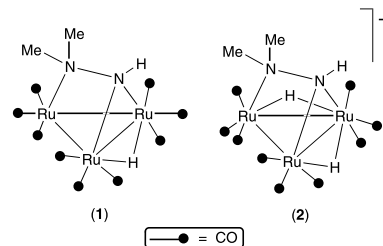


**Javier A. Cabeza, Ignacio del Río,
Santiago García-Granda,
Lorena Martínez-Méndez, Víctor Riera**

J. of Organomet. Chem. 663 (2002) 227

Carbonyl substitution chemistry of neutral and cationic triruthenium cluster complexes derived from 1,1-dimethylhydrazine. Incorporation of two and three phosphane ligands

The carbonyl substitution chemistry of the hydrazido-bridged cluster compounds **1** and **2** with excess PPh_3 and dppm is described. Di- and trisubstituted derivatives have been isolated and characterized. The regiochemistry of the reactions is discussed and compared with those of other related systems.

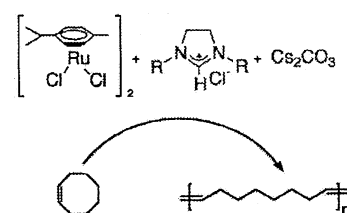


**Ricardo Castarlenas, David Sémeril,
Alfred F. Noels, Albert Démonceau,
Pierre H. Dixneuf**

J. of Organomet. Chem. 663 (2002) 235

Allenyldiene-ruthenium-arene precatalyst for ring opening metathesis polymerisation (ROMP)

The ruthenium allenylidene complex $[\text{RuCl}(\text{=C=C=CPh}_2)(\text{PCy}_3)(p\text{-cymene})][\text{OTf}]$ constitutes an excellent precatalyst for the ring opening metathesis polymerisation of norbornene and cyclooctene. The activation of the precatalyst by initial heating at 60°C generates a catalytic species that operates at room temperature to polymerise cyclooctene in 90% yield.

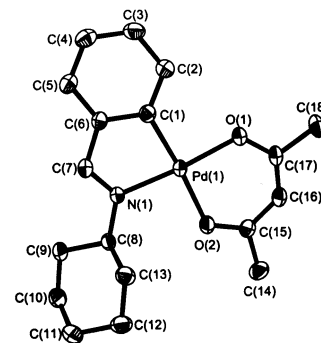


**José M. Vila, Teresa Pereira,
Juan M. Ortigueira, Adriana Amoedo,
María Graña, Gemma Alberdi,
Margarita López-Torres, Alberto Fernández**

J. of Organomet. Chem. 663 (2002) 239

C–Br versus C–H bond activation in palladium(II) cyclopalladated compounds. Crystal and molecular structure of $[\text{Pd}\{\text{C}_6\text{H}_4\text{C}(\text{H})=\text{NCy}\}(\text{MeCOCHCOMe})]$

Cyclometallation of 2-bromobenzylideneimines with $\text{Pd}(0)$ and $\text{Pd}(\text{II})$ salts proceeds via activation of C–H or C–Br bonds, to give mono-, di- or tetranuclear compounds. The phosphine derivatives show *trans* N–Pd–P and C–Pd–P geometries.

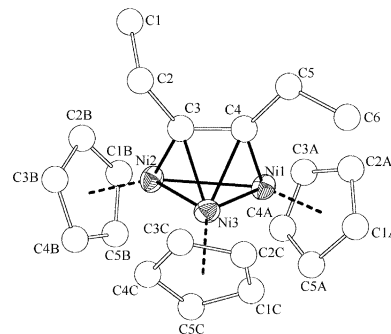


**Antoni Pietrzykowski, Piotr Buchalski,
Stanisław Pasynekiewicz, Janusz Lipkowski**

J. of Organomet. Chem. 663 (2002) 249

The activation of C–H bonds in internal alkenes and dienes by $\{\text{NiCp}\}$ species formed in the reaction of nickelocene with alkali metals

Nickelocene reacts with alkali metals and internal alkenes or dienes forming variety of organonickel products: π -allyl, alkene or alkyne complexes and cyclopentadienylnickel clusters. Depending on the structure of alkene different pathways of the reaction occur: dehydrogenation of alkenes to alkynes, activation of C–H alkyl bond or intramolecular stabilisation.

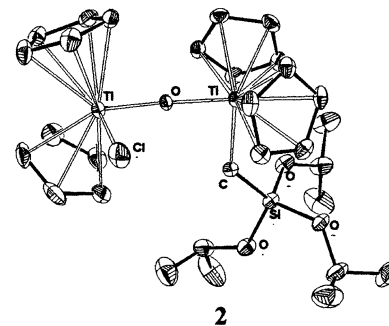


**Daniele Cauzzi, Claudia Graiff,
Marianna Marazzi, Giovanni Predieri,
Antonio Tiripicchio**

J. of Organomet. Chem. 663 (2002) 256

Preparation of Ti(IV), Zr(IV) and Sn(IV) metal alkyls containing the $(Pr^fO)_3SiCH_2$ fragment

By reaction of $(Pr^fO)_3SiCH_2MgCl$ ($RMgCl$) with Cp_2TiCl_2 , Cp_2ZrCl_2 and $SnCl_4$, the stable metal alkyls Cp_2TiClR (**1**) Cp_2TiR_2 , Cp_2ZrR_2 and SnR_4 , were obtained. The reactivity of **1** versus Cl abstraction was investigated. The crystal structures of the new compounds **1** and **2** ($Cp_2ClTi-O-TiRCP_2$) have been determined by X-ray diffraction.

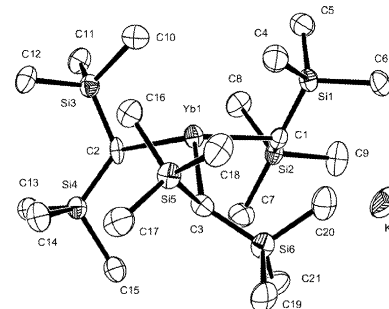


**Peter B. Hitchcock, Alexei V. Khvostov,
Michael F. Lappert**

J. of Organomet. Chem. 663 (2002) 263

Synthesis and structures of crystalline bis(trimethylsilyl)methanido complexes of potassium, calcium and ytterbium

Crystalline $[K(\mu-R)(thf)]_\infty$ (**1**) was obtained from equivalent portions of *n*-butyllithium, bis(trimethylsilyl)methane (=RH) and potassium *t*-butoxide in thf. Desolvation of **1** in a vacuum led to KR. The first three-coordinate metallate(II) alkyls of calcium and ytterbium(II) $[K(MR_3)]_\infty$ [$M = Ca$ (**2**), $M = Yb$ (**3**)] and $[Li(thf)_4][YbR_3]$ (**4**) were prepared using KR and characterised by multinuclear NMR and X-ray data.

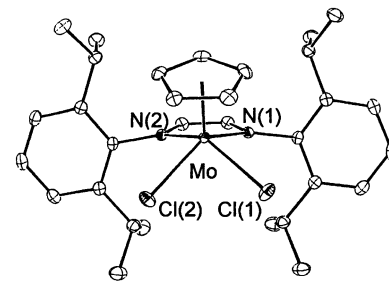


**François Stoffelbach, Rinaldo Poli,
Philippe Richard**

J. of Organomet. Chem. 663 (2002) 269

Half-sandwich molybdenum(III) compounds containing diazadiene ligands and their use in the controlled radical polymerization of styrene

A few members of the $CpMoCl_2(dad)$ ($dad = RN=CH-CH=NR$) family have been synthesized and characterized by analytical, spectroscopic, and electrochemical methods, including an X-ray structure for the $R = C_6H_3Pr_2 - 2,6$ member. They are capable of controlling the radical polymerization of styrene by both ATRP and SFRP mechanisms simultaneously.

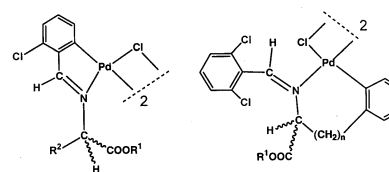


**Joan Albert, J. Magali Cadena,
Asensio González, Jaume Granell,
Xavier Solans, Mercè Font-Bardia**

J. of Organomet. Chem. 663 (2002) 277

Cyclopalladation of Schiff bases from phenylalanine and 2-phenylglycine

New five- and six-membered palladacycles can be obtained by metallation of Schiff bases derived from amino acids.

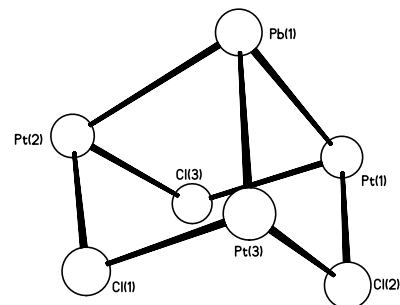


Irene Ara, Larry R. Falvello, Juan Forniés,
Julio Gomez-Cordón, Elena Lalinde,
Rosa I. Merino, Isabel Usón

J. of Organomet. Chem. 663 (2002) 284

A luminescent Pt₃Pb cluster with three
Pt(II) → Pb(II) bonds

The structure of tetranuclear (NBu₄)-
[Pb{Pt(μ-Cl)(C₆F₅)₂}₃], obtained by reaction
of (NBu₄)₂[Pt₂(μ-Cl)₂(C₆F₅)₄] and Pb(ClO₄)₂
(1.5:1) reveals the presence of three Pt → Pb
metal-metal bonds. This complex shows lu-
minescence at low temperature.



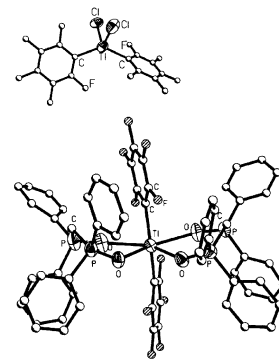
Aranzazu Mendia, Elena Cerrada,
Eduardo J. Fernandez, Antonio Laguna,
Mariano Laguna

J. of Organomet. Chem. 663 (2002) 289

Four- five- and six-co-ordinated pentafluor-
ophenylthallium(III) complexes.

Crystal structures of [Tl(C₆F₅)₃(OPPh₃)],
[Tl(C₆F₅)₂Cl(OPPh₃)₂] and
[Tl(C₆F₅)₂(OdppmO)₂][Tl(C₆F₅)₂Cl₂]

An improved synthesis of [NBu₄][Tl(C₆F₅)₄]
and [Tl(C₆F₅)₃(diox)] is described by two or
one C₆F₅ transfer reaction from [NBu₄]-
[Ag(C₆F₅)₂] or [Ag(C₆F₅)] to [Tl(C₆F₅)₂Cl].
However, [Ag(C₆F₅)L] does not transfer the
pentafluorophenyl group and only [Tl-
(C₆F₅)₂Cl]₂ complexes are obtained. The
X-ray structures of [Tl(C₆F₅)₃(OPPh₃)],
[Tl(C₆F₅)₂Cl(OPPh₃)₂] and [Tl(C₆F₅)₂-
(OdppmO)₂][Tl(C₆F₅)₂Cl₂] show thallium-
(III) centres in a peculiar versatility of co-
ordination forms as tetrahedral, trigonal bi-
pyramidal or octahedral arrangements, re-
spectively.



Author Index of Volume 663	297
Subject Index of Volume 663	299
Contents of Volume 663	305

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