Available online at www.sciencedirect.com

SCIENCE DIRECT®

Volume 691, issue 15, 15 July 2006

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Contents

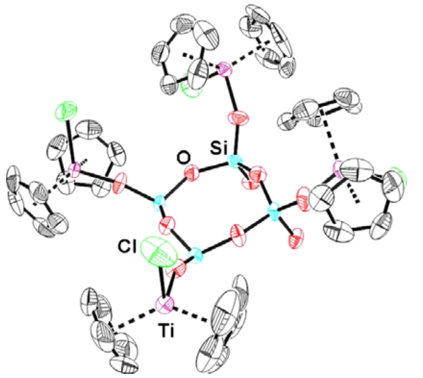
Regular papers

Jason C. Clark, Suree Saengkerdsub,
Geoff T. Eldridge, C. Campana,
Craig E. Barnes

J. Organomet. Chem. 691 (2006) 3213

Synthesis and structure of functional spherosilicate building block molecules for materials synthesis

The syntheses and structures of a number of functionalized spherosilicate building block compounds are described including Si_8O_{20}-$(Cp_2TiCl)_8$.

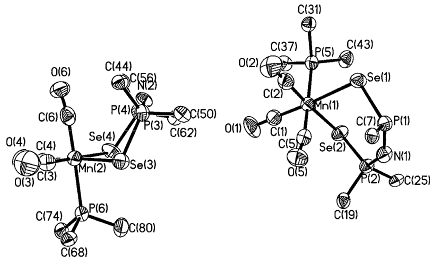


Juan Manuel Germán-Acacio,
Marisol Reyes-Lezama, Noé Zúñiga-Villarreal

J. Organomet. Chem. 691 (2006) 3223

Synthesis and structural studies of phosphorus carbonyl manganacycles containing the tetraphenyldiselenoimidodiphosphinato ligand

Two routes for the preparation of manganacycles $[Mn(CO)_{4-x}(L)\{Ph_2P(Se)NP(Se)Ph_2$-$\kappa^2 Se\}]$, where $x = 1$ for $L = PPh_3$ and $PMePh_2$, and $x = 2$ for $L = Ph_2PCH_2CH_2$-PPh_2 (diphos), are reported. The new complexes were characterized either in solution or in the solid state.

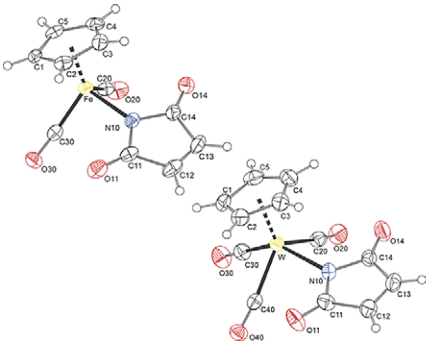


Marcin Palusiak, Bogna Rudolf,
Janusz Zakrzewski, Arno Pfitzner,
Manfred Zabel, Sławomir J. Grabowski

J. Organomet. Chem. 691 (2006) 3232

Intramolecular carbonyl···carbonyl interactions in W, Mo and Fe complexes containing the η^1-*N*-maleimidato ligand: X-ray, DFT and AIM studies

The intramolecular carbonyl···carbonyl interaction in W, Mo and Fe organometallic derivatives of maleimide is investigated. It was found that this interaction can play the essential role in the reaction mechanism of nucleophilic addition to the maleimidato moiety.



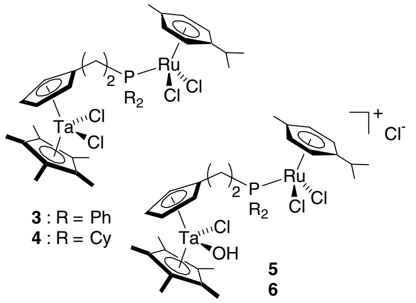
Elsevier B.V.
doi:10.1016/S0022-328X(06)00422-0

Jérôme Goux, Pierre Le Gendre, Philippe Richard, Claude Moïse

J. Organomet. Chem. 691 (2006) 3239

Bimetallic complexes with ruthenium and tantalocene moieties: Synthesis and use in a catalytic cyclopropanation reaction

The synthesis of the heterobimetallic compounds (p-cymene)[(η^5-C_5H_5)(μ-η^5:η^1-C_5H_4-$(CH_2)_2PR_2$)$TaCl_2$]$RuCl_2$ (**3**–**4**) is described. The air oxidation of these bimetallic species **3**–**4**, leads to the cationic hydroxo tantalum ruthenium derivatives **5**–**6**. The latter are easily deprotonated to afford the oxo analogues **7**–**8**. These bimetallic complexes **3**–**8** have been involved in catalytic cyclopropanation of styrene.



3 : R = Ph
4 : R = Cy

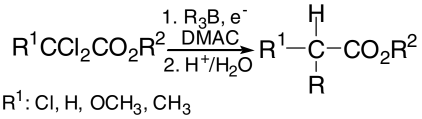
5
6

Sylvie Condon, Chunhai Zou, Jean-Yves Nédélec

J. Organomet. Chem. 691 (2006) 3245

Electrochemical alkyl transfer reaction from trialkylboranes to polyhalo compounds

Reduction of decyl dichloro- and trichloroacetate, under mild electrolysis conditions by using the sacrificial anode process, affords α-chlorocarbanions which readily react with trialkylboranes to give alkylated products in a one step reaction.



$$R^1CCl_2CO_2R^2 \xrightarrow[2.\ H^+/H_2O]{1.\ R_3B,\ e^-\ \ DMAC} R^1-\overset{H}{\underset{R}{C}}-CO_2R^2$$

R^1: Cl, H, OCH_3, CH_3

R^2: CH_3, $C_{10}H_{21}$

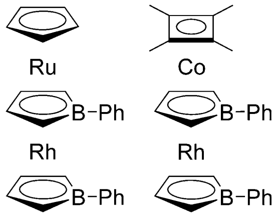
R: Et, *n*-Bu, *n*-Oct, *sec*-Bu, *c*-C_6H_{11}

Dmitry V. Muratov, Pavel V. Petrovskii, Zoya A. Starikova, Gerhard E. Herberich, Alexander R. Kudinov

J. Organomet. Chem. 691 (2006) 3251

Rhodium-containing triple-decker complexes with a central borole ligand

New triple-decker complexes (C_4H_4BPh)Rh(μ-C_4H_4BPh)ML with a bridging borole ligand were synthesized by stacking reactions of anion $[(C_4H_4BPh)_2Rh]^-$ with cationic fragments $[ML]^+$. Structures of three compounds were determined by X-ray diffraction study.

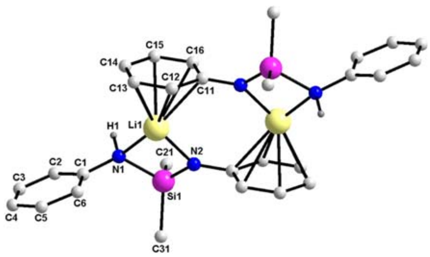


Nallasamy Palanisami, Ramaswamy Murugavel

J. Organomet. Chem. 691 (2006) 3260

Synthesis and spectral characterization of diorganodiaminosilanes $[(ArNH)_2SiPhMe]$ (Ar = 2,6-$^iPr_2C_6H_3$; 2,4,6-$Me_3C_6H_2$) and lithium silylamide $[(2,6\text{-}Et_2C_6H_3NLi)(2,6\text{-}Et_2C_6H_3NH)\text{-}SiPh_2]$

A rare monolithium salt of a diorganodiaminosilane has been synthesized and structurally characterized; the lithium ion in this compound forms an unusual half-sandwich complex through the interaction of all six carbon atoms an adjacent aryl ring emanating from the –NHAr group on the central silicon.

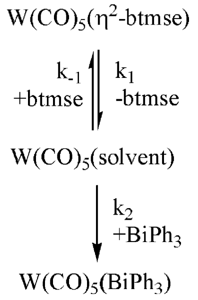


Ercan Bayram, Saim Özkar

J. Organomet. Chem. 691 (2006) 3267

Substitution kinetics of $W(CO)_5(\eta^2$-bis(trimethylsilyl)ethyne) with triphenylbismuthine

The labile complex $W(CO)_5(\eta^2$-btmse) undergoes replacement of bis(trimethylsilyl)ethyne, btmse, by triphenylbismuthine in cyclohexane solution at an observable rate in the temperature range of 35–50 °C yielding almost solely $W(CO)_5(BiPh_3)$ as the final product. The cleavage of metal–alkyne bond is the rate determining step. The activation enthalpy (106 ± 2 kJ mol^{-1}) and the activation entropy (111 ± 6 J K^{-1} mol^{-1}) were determined for this rate determining step from the evaluation of k_1 values at different temperatures, consistent with the dissociative nature of reaction.

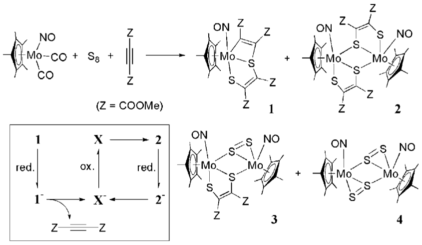


**Mitsushiro Nomura, Souichi Sakaki,
Chikako Fujita-Takayama,
Yoshimasa Hoshino, Masatsugu Kajitani**

J. Organomet. Chem. 691 (2006) 3274

Formations and electrochemical behavior of mononuclear and binuclear molybdenum dithiolene complexes with nitrosyl ligands: Evidence for the formation of a coordinatively unsaturated species [Cp*Mo(NO)(dithiolene)]

The reaction of $[Cp^*Mo(NO)(CO)_2]$ with S_8 and DMAD gave the molybdenum dithiolene complexes $[Cp^*Mo(NO)(S_2C_2Z_2)(C_2Z_2)]$ (**1**, Z = COOMe), $[Cp^*Mo(NO)(S_2C_2Z_2)]_2$ (**2**), $[Cp^*_2Mo_2(NO)_2S_2(S_2C_2Z_2)]$ (**3**) and $[Cp^*Mo(NO)S_2]_2$ (**4**). The reduction of complexes **1** and **2** formed the monomeric complex $[Cp^*Mo(NO)(S_2C_2Z_2)]^-$ ($\mathbf{X}^-$). When the anion $\mathbf{X}^-$ was oxidized, the oxidant reformed complex **2**.

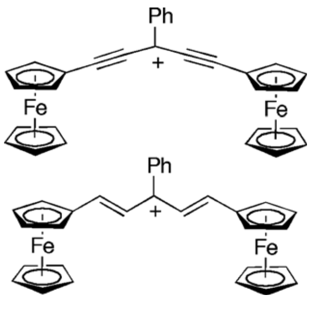


**Christofer Arisandy, Elizabeth Fullam,
Stephen Barlow**

J. Organomet. Chem. 691 (2006) 3285

Comparison of the bis(ferrocenylethynyl)phenylmethylium cation with bis(ferrocenylethenyl)methylium analogues

Attempts to synthesize a bis(ferrocenylethynyl)stabilised carbocation from $(FcCC)_2CHOH$ were unsuccessful. However, the $[(FcCC)_2CPh]^+$ cation could be observed by ^1H and ^{13}C NMR, and by UV–Vis–NIR spectroscopy. Although $[(FcCC)_2CPh]^+$ is much less stable than $[(FcCHCH)_2CPh]^+$, spectroscopic properties could be compared.

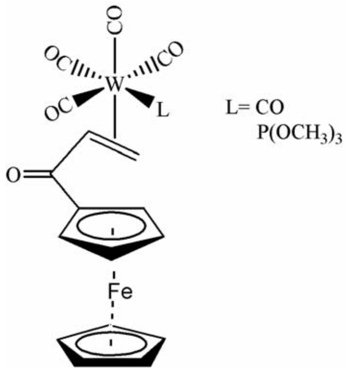


Dilek Ayşe Boğa, Saim Özkar

J. Organomet. Chem. 691 (2006) 3293

Carbonyltungsten(0) complexes of acryloylferrocene: Synthesis and characterization

Photolysis of $W(CO)_6$ or $W(CO)_5[P(OCH_3)_3]$ in the presence of acryloylferrocene in *n*-hexane solution yields pentacarbonyl(η^2-acryloylferrocene)tungsten(0) or *cis*-$W(CO)_4$-$[P(OCH_3)_3](\eta^2$-acryloylferrocene), respectively, as the only photo-substitution product. Both η^2-acryloylferrocene complexes could be isolated and characterized by MS, IR and NMR spectroscopy. Both complexes are found to be labile in solution towards decomposition to the parent carbonyltungsten(0) and free acryloylferrocene.

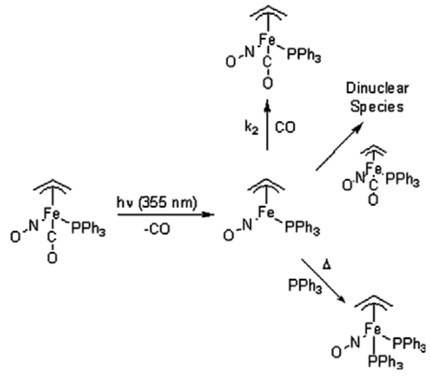


Conor Long, Kieran Maher, Mary T. Pryce

J. Organomet. Chem. 691 (2006) 3298

The photochemistry of (η^3-2-R-C_3H_4)Fe(CO)-(NO)(X) (R = H or Cl; X = CO or PPh_3) in room temperature solution or frozen gas matrixes

A study of allyl iron complexes of the type, (η^3-2-R-C_3H_4)Fe(CO)(NO)(X) (R = H or Cl; X = CO or PPh_3) revels that the predominant photochemical process is loss of a CO ligand. UV irradiation of (η^3-2-R-C_3H_4)Fe(CO)-(NO)(PPh_3) induced a haptotropic shift of the allyl group from η^3 to η^1 coordination.

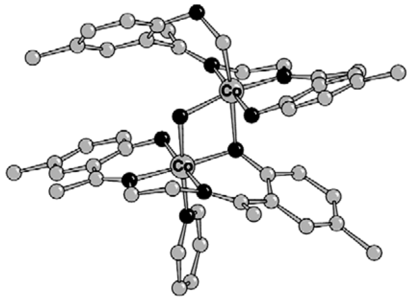


Renata Dreos, Lassaad Mechi, Lucio Randaccio, Patrizia Siega, Ennio Zangrando, Rached Ben Hassen

J. Organomet. Chem. 691 (2006) 3305

Synthesis and X-ray crystal structure of a new μ-hydroxo dinuclear cobalt complex containing one *cis*-β folded and one planar salen moiety

The reduction and successive alkylation of [Co(III)(tmsalen)$(py)_2$]$^+$ at neutral pH lead to a novel and unexpected μ-hydroxo dinuclear cobalt complex, formed by an octahedral [Co(III)(tmsalen)(py)(OH)] unit connected to a β-folded [Co(III)(tmsalenCH_2)] fragment.

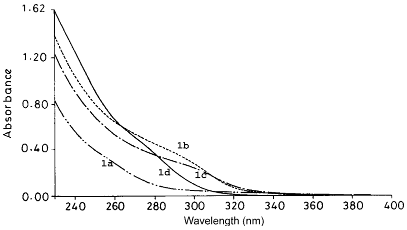


Ravi Shankar, Arti Joshi

J. Organomet. Chem. 691 (2006) 3310

Synthesis of poly(hydrosilane)s, $-[R^1(H)Si]_n-$ ($R^1 = (CH_2)_3SiRR'_2$; R, R′ = Me, Et or Ph) and their reactivity studies towards allyl/vinylsilanes

The synthesis of new poly(hydrosilane)s, $-[RR'_2Si(CH_2)_3SiH]_n-$ (R = R′ = Et (**1a**); R = Ph, R′ = Me (**2a**); R = Me, R′ = Ph (**3a**)) and their reactivity towards allyl/vinylsilanes are described. A comparison of UV spectral data of these polysilanes is included.

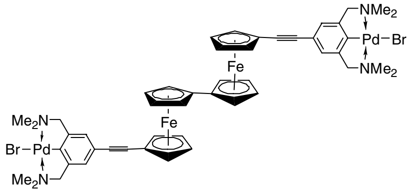


Stefan Köcher, Gerard P.M. van Klink, Gerard van Koten, Heinrich Lang

J. Organomet. Chem. 691 (2006) 3319

Biferrocene NCN pincer metal-d^8 complexes: Synthesis, reaction chemistry and cyclovoltammetric studies

The synthesis, reaction chemistry and chemical properties of biferrocene pincer complexes of general type [(η^5-C_5H_4)Fe(η^5-$C_5H_4C\equiv C$-4-NCN-1-X)$]_2$ (X = H, Br, PdBr, PtBr; NCN = $[C_6H_2(CH_2NMe_2)_2\text{-}2,6)]^-$ is discussed. Their electrochemical behaviour is reported as well.

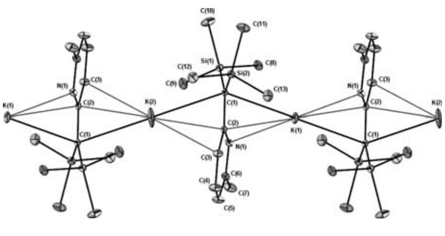


Philip C. Andrews, Colin L. Raston, Brett A. Roberts, Brian W. Skelton, Allan H. White

J. Organomet. Chem. 691 (2006) 3325

Heavier alkali metal complexes of the bulky alkyl ligand 2-(bis(trimethylsilyl)methyl)-6-methylpyridine: Crystal structures of [{6-Me(2 Pyr)}(Me$_3$Si)$_2$CNa(pmdta)] and [{6-Me(2-Pyr)}(Me$_3$Si)$_2$CK]$_\infty$

Two heavier alkali metal complexes of the bulky alkyl ligand 6-Me(2-Pyr)(Me$_3$Si)$_2$CH have been synthesised and characterised by single crystal X-ray diffraction. Monomeric [{6-Me(2-Pyr)}(Me$_3$Si)$_2$CNa(pmdta)] has six coordinate Na bonded to the ligand in an η^3 1-aza-allyl manner, while [{6-Me(2-Pyr)}(Me$_3$Si)$_2$CK]$_\infty$ is an unsolvated polymer displaying both η^3 1-aza-allyl and allylic interactions.

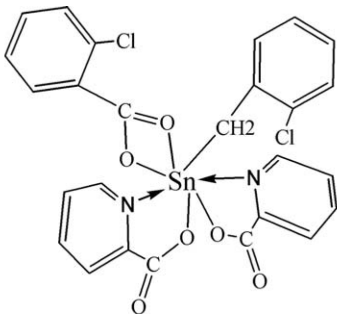


Hao Long Xu, Han Dong Yin, Zhong Jun Gao, Gang Li

J. Organomet. Chem. 691 (2006) 3331

Catalytic oxidation of diorganotin(IV) carboxylates to mixed-ligand monoalkyltin(IV) carboxylates by Ag$^+$ and structure characterization of the mixed-ligand monoalkyltin(IV) 2-pyridinecarboxylate (2-*Cl*PhCH$_2$)Sn(2-*Cl*PhCO$_2$)(O$_2$CC$_5$H$_4$N-2)$_2$

The complexes of the type (ArCH$_2$)$_2$SnO were catalytic-oxygenated by Ag$^+$ and yielded mixed-ligand organotin(IV) complexes (ArCH$_2$)(2-C$_5$H$_4$NCO$_2$)$_2$(ArCOO)tin(IV) (Ar = C$_6$H$_5$ (**1**), 2-*Cl*C$_6$H$_4$ (**2**), 2-*CN*C$_6$H$_4$ (**3**), 4-*Cl*C$_6$H$_4$ (**4**), 4-*CN*C$_6$H$_4$ (**5**), 2-*F*C$_6$H$_4$ (**6**)). The complexes **1**–**6** are characterized by elemental analyses, IR and NMR (^{1}H, ^{13}C, ^{119}Sn) spectroscopies. Single X-ray crystal structure analysis has been determined, which reveals that the center tin atom of complex **2** is seven-coordinated geometry.

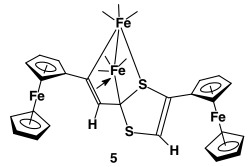


Pradeep Mathur, Vinay K. Singh, Amrendra K. Singh, Shaikh M. Mobin, Carsten Thöne

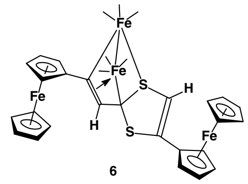
J. Organomet. Chem. 691 (2006) 3336

Photochemical reactions of Fe(CO)$_5$ with FcC≡CH in the presence of S-powder and CS$_2$: Synthesis and characterization of [{μ-SC(H)=C(Fc)S}(CO)$_6$Fe$_2$], [μ-SC(O)C(H)=C(Fc)S}(CO)$_6$Fe$_2$]; *cis*-[μ-η^1:η^2:η^1:η^1-{C(Fc)=C(H)CS$_2$C(H)=C(Fc)}(CO)$_6$Fe$_2$] and *trans*-[μ-η^1:η^2:η^1:η^1-{C(Fc)=C(H)CS$_2$C(Fc)=C(H)}(CO)$_6$Fe$_2$]

Unusual S-containing ligands have been obtained under mild conditions from coupling of ferrocenylacetylene with S, CO and CS$_2$ on iron carbonyl framework. Photolysis of a hexane solution containing Fe(CO)$_5$, ferrocenylacetylene and S-powder yielded [{μ-SC(H)=C(Fc)S}(CO)$_6$Fe$_2$] (**1**) and [μ-SC(O)C(H)=C(Fc)S(CO)$_6$Fe$_2$] (**2**). In presence of CS$_2$, formation of *cis*-[μ-η^1:η^2:η^1:η^1-{C(Fc)=C(H)CS$_2$C(H)=C(Fc)}(CO)$_6$Fe$_2$] (**5**) and *trans*-[μ-η^1:η^2:η^1:η^1-{C(Fc)=C(H)CS$_2$C(Fc)=C(H)}(CO)$_6$Fe$_2$] (**6**) was observed.



5



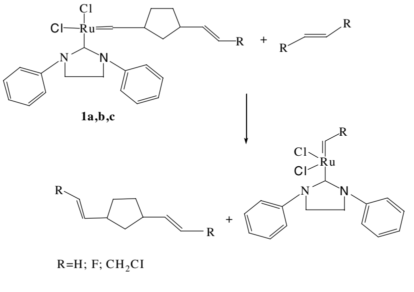
6

Serguei Fomine, Joel Vargas Ortega, Mikhail A. Tlenkopatchev

J. Organomet. Chem. 691 (2006) 3343

Difluoroethylene as a chain transfer agent during ring-opening metathesis polymerization (ROMP) of norbornene by a ruthenium alkylidene complex: A computational study

The polynorbornene chain transfer reaction pathways to ethylene (**2a**), *trans*-1,2-difluoroethylene (**2b**) and *trans*-1,4-dichloro-2-butene (**2c**) by (1,3-diphenyl-4,5-dihydroimidazol-2-ylidene) (PCy$_3$)Cl$_2$Ru=CHPh (**I**) have been studied at B3LYP/LACVP* level of theory. The calculations show that the free Gibbs activation energy of metathesis reaction is dependent on the volume of substituents directly linked to the double bond of an olefin. Highest activation energy is observed for **2c** with highest molecular volume.

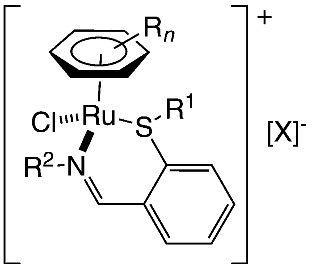


Dominic P. Halbach, Christopher G. Hamaker

J. Organomet. Chem. 691 (2006) 3349

Synthesis, characterization, and X-ray structural analysis of some half-sandwich ruthenium(II) arene complexes with new N,S-donor Schiff base ligands

Several cationic ruthenium(II) half-sandwich complexes with chelating N,S-donor ligands derived from the condensation of 2-(thioalkyl)benzaldehydes with anilines have been synthesized and characterized spectroscopically. Three of the ruthenium complexes and one of the ligands have been characterized by X-ray crystallography.

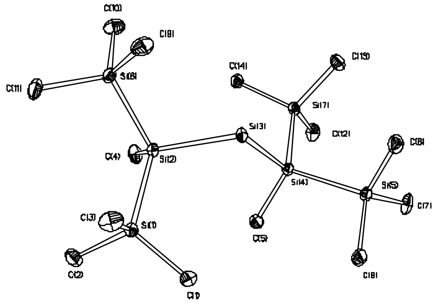


A. Dzambaski, J. Baumgartner, M. Flock, G. Tekautz, K. Hassler, W. Hassler

J. Organomet. Chem. 691 (2006) 3362

Unusual conformational properties of 1,3-dimethyl-1,1,3,3-tetrakis(trimethylsilyl)trisilane: A preparative, X-ray, Raman spectroscopic and ab initio study

The stabilities of various conformers of $(Me_3Si)_2MeSiSiH_2SiMe(SiMe_3)_2$ have been calculated by ab initio methods and examined experimentally with temperature dependent Raman spectroscopy in solution. The solid state structure was examined with X-ray crystallography.

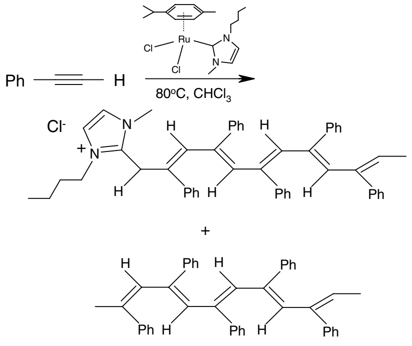


Péter Csabai, Ferenc Joó, Anna M. Trzeciak, Józef J. Ziółkowski

J. Organomet. Chem. 691 (2006) 3371

Catalytic activity of a half-sandwich Ru(II)-N-heterocyclic carbene complex in the oligomerization of alkynes

The ruthenium(II)-N-heterocyclic carbene complex, $[RuCl_2$(1-butyl-3-methylimidazol-2-ylidene)(*p*-cymene)] selectively catalyzes oligomerization of phenylacetylene (PA) and its derivatives to linear oligomers, containing positively charged imidazolium end-group and uncharged ones. The charged oligomer chain consists of maximum 9–11 PA monomer units after 36 h reaction at 80 °C whereas mainly pentamers are formed as other products.

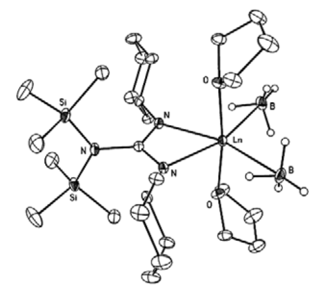


Fugen Yuan, Yan Zhu, Lifeng Xiong

J. Organomet. Chem. 691 (2006) 3377

Syntheses and molecular structures of mono(guanidinate) lanthanide borohydrides and their catalytic activity for MMA-polymerization

The mono(guanidinate) lanthanide borohydride complexes of **1** and **2** have been synthesized by the reactions of $Ln(BH_4)_3(THF)_3$ with sodium guanidinate of $[(Me_3Si)_2NC(NCy)_2]Na$ in a 1:1 molar ratio in THF. They were characterized by elemental analysis, infrared spectrum and X-ray diffraction analysis. The lanthanide ion was bonded by an η^2-guanidinate ligand, two η^3-BH_4^- ligands and two THF molecules as a distorted octahedron. The structure of solvated sodium guanidinate of $\{[(Me_3Si)_2NC(NCy)_2]Na(THF)\}_2$ (**3**) was also presented. **1** and **2** displayed moderate high catalytic activity for the polymerization of methyl methacrylate.



$$Ln(BH_4)_3(THF)_3+[(Me_3Si)_2NC(NCy)_2]Na \xrightarrow{THF} [(Me_3Si)_2NC(NCy)_2]Ln(BH_4)_2(THF)_2+NaBH_4$$

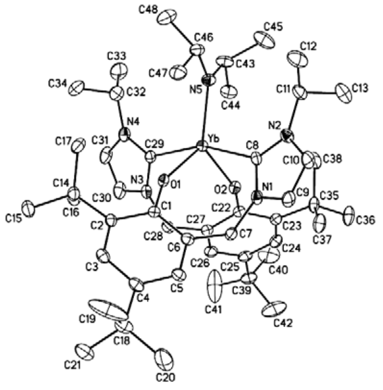
$(Ln=Yb(\mathbf{1}), Er(\mathbf{2}))$

Zhi-Guo Wang, Hong-Mei Sun, Hai-Sheng Yao, Ying-Ming Yao, Qi Shen, Yong Zhang

J. Organomet. Chem. 691 (2006) 3383

Bis-aryloxo-functionalized NHC complexes of ytterbium(III): Syntheses and structures of $Yb[O\text{-}4,6\text{-}{}^tBu_2\text{-}C_6H_2\text{-}2\text{-}CH_2\{C(RNCHCHN)\}]_2\text{-}N({}^iPr)_2$ (R = ^{i}Pr, Me)

The first bis-aryloxo-functionalized NHC ytterbium complexes monoamido were conveniently prepared in high yield by the transamination of $LiYb[N(i\text{-}Pr)_2]_4$ with the corresponding aryloxo-functionalized imidazoliums and BuLi.

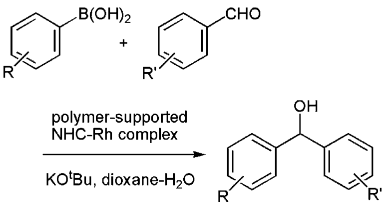


Chun Yan, Xiaoming Zeng, Weifeng Zhang, Meiming Luo

J. Organomet. Chem. 691 (2006) 3391

Polymer-supported *N*-heterocyclic carbene–rhodium complex catalyst for the addition of arylboronic acids to aldehydes

A novel polymer-supported *N*-heterocylic carbene (NHC)–rhodium complex (**2**) was prepared from chloromethyl polystyrene (CM PS) resin and used as a catalyst for the addition of arylboronic acids to aldehydes affording arylmethanols in excellent yields.



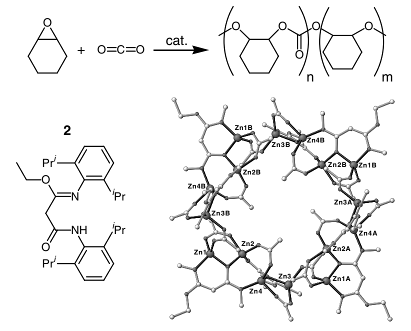
Notes

Mario Kröger, Cristina Folli, Olaf Walter, Manfred Döring

J. Organomet. Chem. 691 (2006) 3397

A new amidoimidomalonate zinc complex with a sedecameric solid state structure catalyzing the copolymerization of CO_2 and cyclohexene oxide

The zinc acetate complex of a newly developed amidoimidomalonate ligand formed an unprecedented solid state structure which included sixteen zinc atoms. Furthermore, this complex catalyzed the copolymerization of CO_2 and cyclohexene oxide to give aliphatic polyethercarbonates.



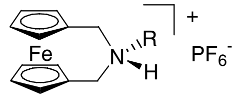
cat. = $[(\mathbf{2})_2Zn_4(OAc)_4]_4$

Yuji Suzaki, Masaki Horie, Tatsuaki Sakano, Kohtaro Osakada

J. Organomet. Chem. 691 (2006) 3403

Structure and properties of protonated *N*-alkyl-2-aza[3]ferrocenophanes

Treatment of *N*-alkyl-2-aza[3]ferrocenophanes with HCl and NH_4PF_6 forms corresponding cationic aza[3]ferrocenophanes having PF_6 as a counter anion. These new cationic aza[3]-ferrocenophanes cause a slow inversion of stereochemistry at nitrogen atom in solution.



R = *p*-methylbenzyl, hexyl