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Journal of Organometallic Chemistry

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Contents

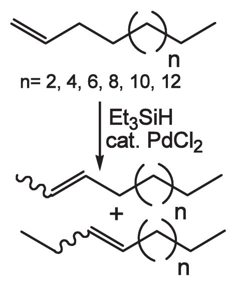
Communication

Maryam Mirza-Aghayan, Rabah Boukherroub, Mohammad Bolourtchian, Maryam Hoseini, Kourosh Tabar-Hydar

J. of Organomet. Chem. 678 (2003) 1

A novel and efficient method for double bond isomerization

Isomerization of carbon–carbon double bond of 1-alkenes was carried out in the presence of triethylsilane and catalytic amounts of palladium (II) chloride at room temperature. This method was found to be very efficient and gave high yields of the corresponding 2- and 3-isomers.



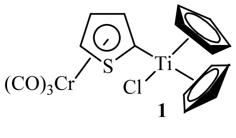
Regular Papers

Marilé Landman, Thomas Waldbach, Helmar Görls, Simon Lotz

J. of Organomet. Chem. 678 (2003) 5

Titanium complexes of π-coordinated thiophene derivatives

The activation of π-coordinated tricarbonylchromium complexes of thiophene and benzothiophene to titanocene dichloride resulted in the formation of the complexes [Ti{(η^1,η^5-thienyl)Cr(CO)$_3$}Cp$_2$Cl] (**1**) and [Ti{(η^1,η^6-benzothienyl)Cr(CO)$_3$}Cp$_2$Cl] (**5**). The chlorine ligand of both complexes is susceptible to substitution by other nucleophiles.



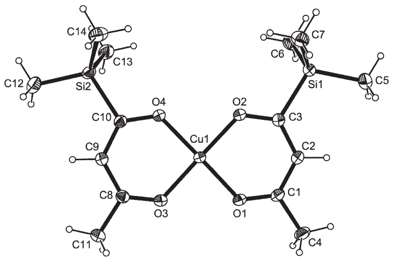
1

Kulbinder K. Banger, Silvana C. Ngo, Seiichiro Higashiya, Rolf U. Claessen, Kenneth S. Bousman, Poay N. Lim, Paul J. Toscano, John T. Welch

J. of Organomet. Chem. 678 (2003) 15

Facile synthesis of a novel class of organometalloid-containing ligands, the sila-β-diketones: preparation and physical and structural characterization of the copper(II) complexes, Cu[R′C(O)CHC(O)SiR$_3$]$_2$

Sila-β-diketones, R′C(O)CH$_2$C(O)SiR$_3$, were obtained in good yield by the condensation of the lithium enolate of an acetyltrialkylsilane with an acyl chloride. Homoleptic copper(II) complexes of the new diketonate ligands were prepared and subsequently studied by thermal and X-ray diffraction techniques in order to assess the effect of silicon substitution on volatility.

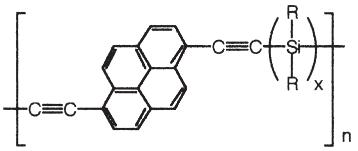


Joji Ohshita, Kazuhiro Yoshimoto, Yosuke Tada, Yutaka Harima, Atsutaka Kunai, Yoshihito Kunugi, Kazuo Yamashita

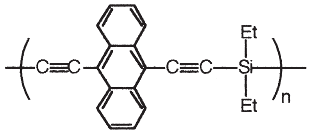
J. of Organomet. Chem. 678 (2003) 33

Hole-transporting properties of organosilanylene–diethynylpyrene and diethynylanthracene alternating polymers. Applications to patterning of light-emitting images

Polymers **1** and **2** were prepared and their applications to hole-transport of double layer electroluminescent (EL) devices were studied, in comparison with those of **3**, reported previously. Polymers **1**–**3** were photoactive and UV-irradiation of the films led to a drastic drop of the luminance of the device, being applicable to the patterning of EL images.



1 R = Et, x = 1
2 R = Me, x = 2



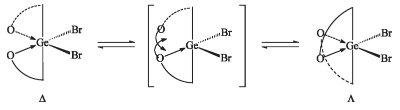
3

Vadim V. Negrebetsky, Sergey Yu. Bylikin, Alexander G. Shipov, Yuri I. Baukov, Alan R. Bassindale, Peter G. Taylor

J. of Organomet. Chem. 678 (2003) 39

Stereochemical rearrangements of dibromides of hexacoordinated germanium containing amidomethyl and lactamomethyl chelate ligands

For the first time a slow (on the NMR time scale) dynamic exchange between two diastereomers of hexacoordinated dibromogermanes **3a**–**c**, **4** containing two amidomethyl and lactamomethyl C,O-chelate ligands has been observed at room temperature in solution. Based on the dynamic NMR and quantum-chemical calculations (ab initio FR 3-21G), as well as on the structures determined for these compounds in the solid state, a *cis*-configuration of monodentate ligands was proposed for one of the diastereomers and an all-*trans*-configuration for the other. At low temperatures interconversion of enantiomers in the *cis*-diastereomer was observed.



Talal A.K. Al-Allaf, Harry Schmidt, Kurt Merzweiler, Christoph Wagner, Dirk Steinborn

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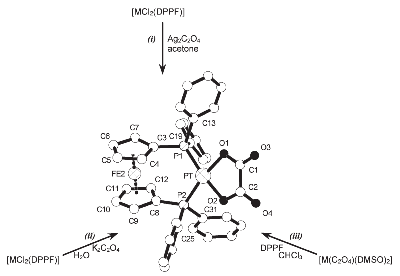
Carboxylation of (DPPF)-MCl$_2$ [DPPF = 1,1′-bis(diphenylphosphino)ferrocene; M = Pt or Pd] in aqueous and non-aqueous solution
Crystal and molecular structures of [Pt-(C$_2$O$_4$)(DPPF)] and of [PtCl(NO$_3$)(DPPF)]

Dechlorination of the precursor [MCl$_2$-(DPPF)] (M = Pt or Pd), DPPF = 1,1′-bis(diphenylphosphino)ferrocene, by AgNO$_3$ in H$_2$O did not give the expected cation [M(DPPF)(H$_2$O)$_2$]$^{2+}$ but rather the unusual complex [{M(μ-OH)(DPPF)}$_2$]-(NO$_3$)$_2$ as insoluble solid. Carboxylation of the precursor can be achieved by treatment with K- or Ag-carboxylates in aqueous or non-aqueous solutions or by ligand exchange of [M(Carboxylato)(DMSO)$_2$] with DPPF in CHCl$_3$. The complexes were characterized physicochemically and spectroscopically. X-ray analyses of two complexes were determind.

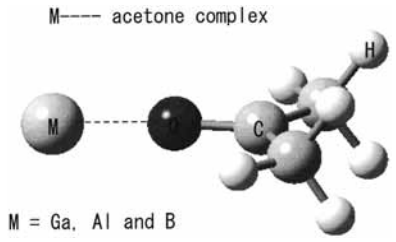


Hiroto Tachikawa, Hiroshi Kawabata

J. of Organomet. Chem. 678 (2003) 56

Structures and electronic states of gallium–acetone complexes: ab-initio DFT study

The structures and electronic states of acetone–metal complexes (Ac–M, where M = Ga, Al, and B) have been investigated using ab-initio DFT and CI calculations in order to elucidate the mechanism of the electron conductivity and doping effects. It was found that the electronic states of Ac–Ga and Ac–Al at the ground state are composed of ion-pair state expressed approximately by (Ac$^{\delta-}$)(M$^{\delta+}$).

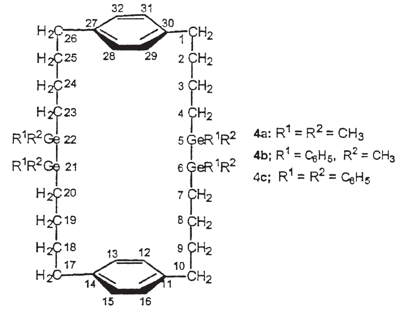


Yoshito Takeuchi, Yoshitake Suzuki, Fumiyasu Ono, Kenji Manabe

J. of Organomet. Chem. 678 (2003) 61

Synthesis of 5,5,6,6,21,21,22,22-octamethyl-5,6,21,22-tetragerma[10.10]paracyclophane

A [10,10]paracyclophane, 5,5,6,6,21,21,22,-22-octamethyl-5,6,21,22-tetragerma[10.10]-paracyclophane (**4a**), with two $-R^1R^2Ge-GeR^1R^2-$ moieties in the center of two bridges, was prepared.



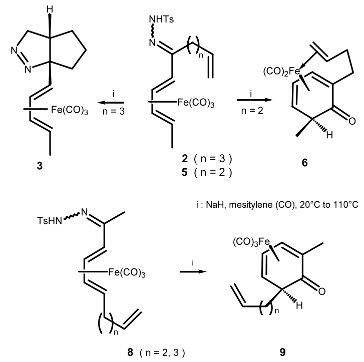
4

Philippe Geoffroy, Dominique Gassmann, Christophe Cénac, Michel Franck-Neumann

J. of Organomet. Chem. 678 (2003) 68

Synthesis of tricarbonyliron cyclohexa-2,4-dienone complexes from tosylhydrazones of acyclic dienone complexes. A novel ansa dicarbonyliron complex by intramolecular trapping of reaction intermediates of the cyclocarbonylation reaction

Tosylhydrazones of tricarbonyliron complexed linear conjugated alicyclic dienones (**5**, **8**) give sodium salts, which are thermally cleaved and cyclocarbonylated to stable complexes of cyclohexa-2,4-dienones. With ω-unsaturated side chains of appropriate length on the ketonic end of the dienone ligand, the non ligated double bond interferes with different reaction intermediates to give 1,3-dipolar cycloadducts of the α-diazodiene complex (**2**→**3**), or, as novel ansa type complex, a chelated $Fe(CO)_2$ cyclohexadienone complex (**5**→**6**).

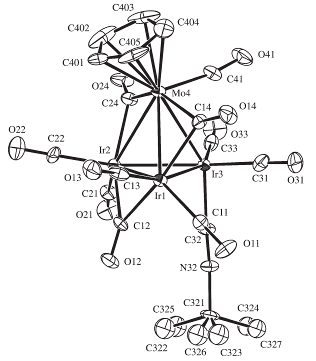


Alistair J. Usher, Mark G. Humphrey, Anthony C. Willis

J. of Organomet. Chem. 678 (2003) 72

Mixed-metal cluster chemistry. 24. Isocyanide derivatives of $[MoIr_3(\mu\text{-}CO)_3(CO)_8(\eta\text{-}C_5H_5)]$ and $[Mo_2Ir_2(\mu\text{-}CO)_3(CO)_7(\eta\text{-}C_5H_5)_2]$; X-ray crystal structures of $[MoIr_3(\mu\text{-}CO)_3(CO)_7(L)(\eta\text{-}C_5H_5)]$ ($L = CNBu^t$, $CNC_6H_3Me_2$-2,6) and $[Mo_2Ir_2(\mu\text{-}CO)_2(CNBu^t)_2(CO)_6(\eta\text{-}C_5H_5)_2]$

Reactions of $MoIr_3(\mu\text{-}CO)_3(CO)_8(\eta\text{-}C_5H_5)$ (**1**) with stoichiometric amounts of isocyanides afford the ligand-substituted clusters $[MoIr_3(\mu\text{-}CO)_3(CO)_{8-n}(L)_n(\eta\text{-}C_5H_5)]$ ($L = CNBu^t$, $n = 1$ (**3**), 2 (**4**), 3 (**5**); $L = CNC_6H_3Me_2$-2,6, $n = 1$ (**6**), 2 (**7**), 3 (**8**)) in moderate to excellent yields (13–75%). Single-crystal X-ray studies of **3** and **6** reveal that the isocyanides occupy coordination sites on an apical cluster core metal atom, a first for ligand-substituted derivatives of **1**.

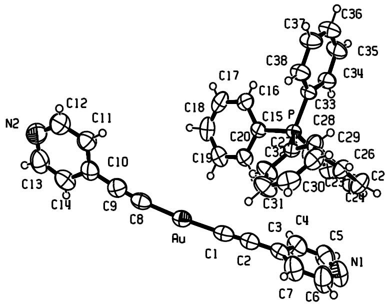


Montserrat Ferrer, Laura Rodríguez, Oriol Rossell, Fernando Pina, João C. Lima, Mercè Font Bardia, Xavier Solans

J. of Organomet. Chem. 678 (2003) 82

Linear ditopic acetylide gold or mercury complexes: synthesis and photophysic studies X-ray crystal structure of $PPh_4[Au(C{\equiv}CC_5H_4N)_2]$

Linear ditopic acetylide gold(I) complexes of the type $[PPh_4][Au(Alk)_2]$ (AlkH = 4-ethynylpyridine, 4-ethynylbenzonitrile and (4-ethynylphenyl)(4-pyridyl)acetylene) and the analogous mercury(II) complexes $[Hg(Alk)_2]$ have been synthesised as potential spacers in self-assembly processes. Photophysic studies revealed that some of these compounds are emissive and their photoluminescence properties have been investigated.



Li Chen, Qinglan Xie, Lijuan Sun, Huiling Wang

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Synthesis and characterization of 1-ferrocenecarboxysilatranes and crystal structures of FcC(CH_3)=CHCOOSi(OCH_2CH_2)$_3$N and *p*-FcC_6H_4COOSi(OCH_2CH_2)$_3$N

A series of novel silatranes containing ferrocenyl carboxylate were obtained by the reaction of 1-ethoxysilatrane with ferrocenyl carboxylic acids, and characterized by elemental analysis, IR and ^{1}H-NMR. The crystal structure of FcC(CH_3)=CHCOOSi(OCH_2CH_2)$_3$N and *p*-FcC_6H_4COOSi(OCH_2CH_2)$_3$N was determined by X-ray diffraction.

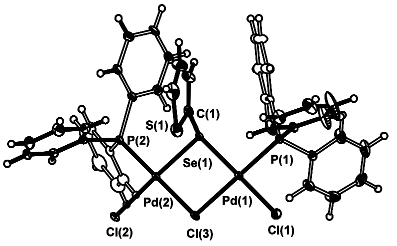
$$\mathrm{FcRCOOH + EtOSi(OCH_2CH_2)_3N} \xrightarrow[\text{reflux}]{\text{chlorobenzene}} \mathrm{FcRCOOSi(OCH_2CH_2)_3N}$$

Raija Oilunkaniemi, Risto S. Laitinen, Milja S. Hannu-Kuure, Markku Ahlgrén

J. of Organomet. Chem. 678 (2003) 95

$C_4H_3SSeCH_2CH_2OC_6H_5$: synthesis, characterization and reaction with palladium(II) and nickel(II)

ThSeCH_2CH_2OPh (Th = 2-thienyl, C_4H_3S; Ph = phenyl) has been prepared by the reaction of BrCH_2CH_2OPh and ThSeLi and characterized by NMR spectroscopy and X-ray crystallography. Upon treating ThSeCH_2CH_2OPh with [PdCl_2(NCPh)$_2$] and [NiCl_2(PPh_3)$_2$] in benzene, [Pd_2Cl_2(μ-Cl)(μ-SeTh)(PPh_3)$_2$] and [PdCl_2(PPh_3)$_2$] were formed together with NiCl_2. The former complex contains a novel asymmetrical arrangement of one bridging chlorido and thienylselenolato ligand.

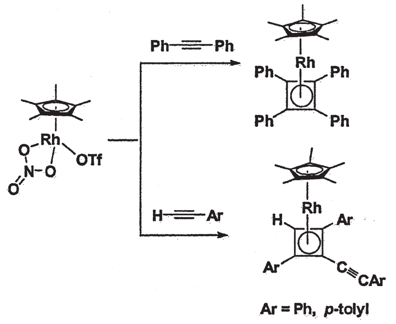


Won Seok Han, Soon W. Lee

J. of Organomet. Chem. 678 (2003) 102

Rhodium(III)-mediated cycloaddition of alkynes: reactivity of [Cp*Rh(η^2-NO_3)(OTf)] bearing two labile ligands

[Cp*Rh(η^2-NO_3)(OTf)] (**1**) mediated cyclodimerization or cyclotrimerization of alkynes and alkynyl esters. In addition, compound **1** reacted with propargyl halides to give triply halide-bridged dinuclear compounds, [Cp*Rh(μ_2-X)$_3$RhCp*](OTf) (X = Cl or Br).



Yingming Yao, Mingqiang Xue, Yunjie Luo, Zhenqin Zhang, Rui Jiao, Yong Zhang, Qi Shen, Wingtak Wong, Kaibei Yu, Jie Sun

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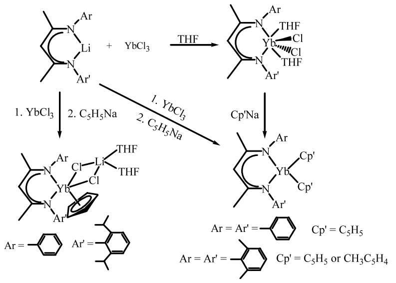
Synthesis and characterization of β-diketiminate lanthanide complexes: the effect of the bulkiness of ancillary ligand on the reaction

The reactions of β-diketiminate ytterbium dichlorides with 1 equiv of Cp′Na were studied. These results reveal that choice suitable bulkiness of β-diketiminate and cyclopentadienyl are both important for the synthesis of mixed-ligand lanthanide chloride supported by β-diketiminate and cyclopentadienyl.



Abdelhay Elarraoui, Josep Ros,
René Mathieu, Ramón Yáñez

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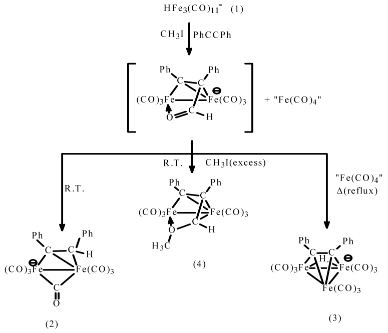
Improved synthesis of di- and trinuclear iron carbonyl complexes containing bridging diphenylethenyl ligand.
X-ray structure of [PPh$_4$][Fe$_2$(CO)$_6$(μ-CO)(μ-PhC=CHPh)]

The reactivity of [PPh$_4$][HFe$_3$(CO)$_{11}$] with diphenylacetylene and CH$_3$I has been checked. Different mononuclear and dinuclear products with diphenylethenyl ligand are obtained according to whether an equivalent or excess of methyl iodide is present. The molecular structure of the complex [PPh$_4$][Fe$_2$(CO)$_6$(μ-CO)(μ-PhC=CHPh)] was determined by X-ray crystallography.



Anjali Gupta, Rajnish K. Sharma,
Rakesh Bohra, Vimal K. Jain,
John E. Drake, Michael B. Hursthouse,
Mark E. Light

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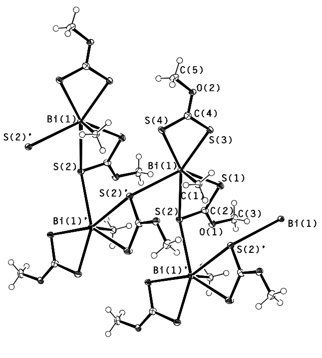
Synthesis and characterization of methylbismuth(III) complexes containing dithio ligands: crystal and molecular structure of [MeBi{S$_2$COMe}$_2$] and transformation of [MeBi{S$_2$CO^{i}Pr}$_2$] to Bi$_2$S$_3$

Reactions of sodium/potassium salts of xanthates, dithiocarbamates and dialkyldithiophosphates with methylbismuth dichloride have been carried out in 1:2 stiochiometric ratio in anhydrous benzene and products of the type [MeBi(S$_2$COR)$_2$] (R = Me, Et, ^{i}Pr), [MeBi(S$_2$CNR$_2$)$_2$] (R = Me, Et, 1/2C$_4$H$_8$N) and [MeBi{S$_2$P(OR)$_2$}$_2$] (R = Me, Et, ^{i}Pr) have been isolated. All of these complexes were characterized by elemental analyses and by IR and NMR (^{1}H, ^{13}C and ^{31}P) spectra. The X-ray structure analysis of [MeBi(S$_2$COMe)$_2$] have been carried out.

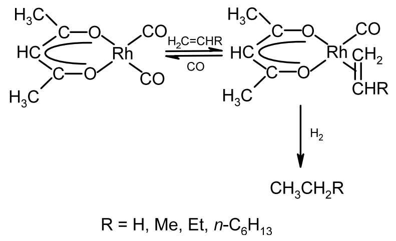


Jie Zhang, Xue-Zhong Sun,
Martyn Poliakoff, Michael W. George

J. of Organomet. Chem. 678 (2003) 128

Study of the reaction of Rh(acac)(CO)$_2$ with alkenes in polyethylene films under high-pressure hydrogen and the Rh-catalysed hydrogenation of alkenes

The thermal reaction of Rh(acac)(CO)$_2$ with alkenes has been studied both in the absence and in the presence of high-pressure hydrogen using a high-pressure cell for in situ FTIR and polymer matrix techniques. A series of rhodium alkenes complexes, Rh(acac)(CO)(alkene), have been characterized using IR, and the catalytic hydrogenation of alkenes has been monitored.



David Owiny, Sean Parkin,
Folami T. Ladipo

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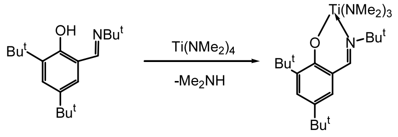
Synthesis, structural determination, and ethylene polymerization chemistry of mono(salicylaldiminato) complexes of titanium(IV)

Monomeric titanium(IV)mono(salicylaldiminato) complexes [L^{1}Ti(NMe$_2$)$_3$] (**1**) and [L^{1}TiCl$_3$] (**2**) (**L^1** = 4,6-Bu$^t_2$-2-(CH=NBu^t)C$_6$H$_3$O$^-$) were synthesized and characterized by spectroscopic methods and X-ray crystallography. Reactions of TiCl$_4$ with one equivalent of $[4,6-\mathrm{Bu}^t_2-2-(\mathrm{CH{=}NCH_2Ph})\mathrm{C_6H_3OH}]$ (**L^{2}H**) and $[4,6-\mathrm{Bu}^t_2-2-\{\mathrm{CH{=}N(2-C_6H_4OH)}\}\mathrm{C_6H_3OH}]$ (**L^{3}H$_2$**) produced dimeric [L^{2}TiCl$_2$(μ-Cl)]$_2$ (**3**) and [L^{3}TiCl$_2$]$_2$ (**4**), respectively. The structure of **4** contained a rare face to face π–π stacking interaction. With methylalumoxane as co-catalyst, **1** and **2** showed modest activities in ethylene polymerization.



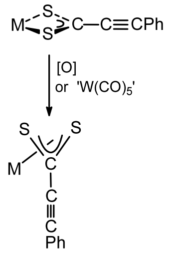
[L^{1}Ti(NMe$_2$)$_3$] (**1**)

Pradeep Mathur, Abhijit K. Ghosh, Sarbani Mukhopadhyay, Chimalakonda Srinivasu, Shaikh M. Mobin

J. of Organomet. Chem. 678 (2003) 142

Insertion of CS_2 into a metal acetylide bond and conversion of the bonding mode of $S_2CC{\equiv}CPh$ from η^2 to η^3

Carbon disulfide inserts into a metal–acetylide bond to give either (η^2-S_2C–$C{\equiv}CPh$) or (η^3-S_2C–$C{\equiv}CPh$) groups. The η^2 form can be converted to the η^3 form by either oxidation at the metal center or by addition of '$W(CO)_5$' units to the S atoms.



Chunlin Ma, Qin Jiang, Rufen Zhang

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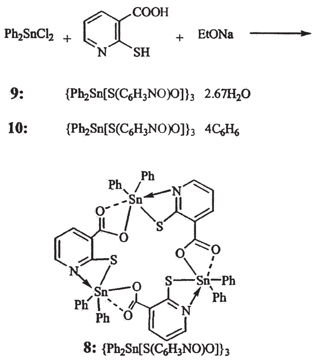
Synthesis and structure of a novel trinuclear 18-membered macrocycle of diphenyltin complexes with 2-mercaptonicotinic acid

The 18-membered stereoregular diphenyltin macrocycles: $\{Ph_2Sn[S(C_6H_3NO)O]\}_3$ (**8**), $\{Ph_2Sn[S(C_6H_3NO)O]\}_3 \cdot 2.67H_2O$ (**9**) and $\{Ph_2Sn[S(C_6H_3NO)O]\}_3 \cdot 4C_6H_6$ (**10**) have been synthesized by the reaction of diphenyltin dichloride with 2-mercaptonicotinic acid. All three complexes were characterized by elemental, IR, ^{1}H-NMR analyses. Single crystal structures of complexes **9** and **10** were determined by X-ray diffraction studies.



8: $\{Ph_2Sn[S(C_6H_3NO)O]\}_3$

Xiaojing Wang, Lv Chen, Akira Endou, Momoji Kubo, Akira Miyamoto

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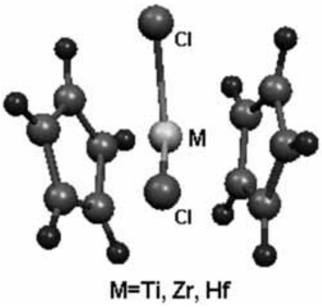
A study on the excitations of ligand-to-metal charge transfer in complexes Cp_2MCl_2 ($Cp = \pi$-C_5H_5, M = Ti, Zr, Hf) by density functional theory

The excitations of ligand-to-metal charge transfer and the main electronic spectral features of the complexes Cp_2MCl_2 ($Cp = \pi$-C_5H_5, M = Ti, Zr, Hf) were described by the time-dependent density functional theory and the differential self-consistent-field density functional theory (ΔSCF–DFT).



Julien Pytkowicz, Sylvain Roland, Pierre Mangeney, Gilbert Meyer, Anny Jutand

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Chiral diaminocarbene palladium(II) complexes: synthesis, reduction to Pd(0) and activity in the Mizoroki–Heck reaction as recyclable catalysts

A preparation of chiral Pd^{II} bis-diaminocarbene or mixed diaminocarbene-phosphine complexes is reported. Crystal structure details of Pd^{II} *trans*-diiodo bis-carbene complex are presented. These two families of complexes where tested in the Mizoroki–Heck reaction as recyclable catalysts. Their ability to be reduced into Pd^0 was investigated as well as the ability of the Pd^0 complexes formed to undergo oxidative addition with aryl halides.