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Communication

SEVIER

Anu Ploom, Ants Tuulmets

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A novel insight into the inductive effect in silicon chemistry

It has been established that the inductive effect in silicon chemistry must be expressed by two terms involving the electronegativity of substituents, and additionally, a protocol for correlation analysis in organosilicon chemistry is now available. $logk_{rel} = \rho_I \sigma_I + \zeta \chi + \delta E_S(Si)$

Regular Papers

Rocío García-Bueno, M. Dolores Santana, Gregorio Sánchez, Joaquín García, Gabriel García, José Pérez, Luís García

J. Organomet. Chem. 694 (2009) 316

Spectroscopic and structural characterization of *O*,*O*'-(diphenylphosphineoxide)amidate and acetylacetonate complexes of pentacoordinate nickel(II) Heteroleptic nickel pentacoordinate complexes with the macrocyclic ligands 2,4,4trimethyl-1,5,9-triazacyclododec-1-ene or its 9-methyl derivative, as ancillary ligands, and *O,O'*-(diphenylphosphineoxide)amidate ligands have been prepared as well as related acetylacetonate derivatives. The complexes have been studied by spectroscopic methods (IR, Vis–UV and ¹H NMR) and X-ray diffraction.



Han Vinh Huynh, Jiang Wu

J. Organomet. Chem. 694 (2009) 323

Rotamers of palladium complexes bearing IR active *N*-heterocyclic carbene ligands: Synthesis, structural characterization and catalytic activities A synthetic route for the preparation of mono- and bis(carbene) Pd(II) complexes bearing unsymmetrical IR active NHC ligands has been established. The isomerisation dynamics of *trans-anti-* and *trans-syn-*rotamers in solution have been studied by NMR spectroscopy. A preliminary study revealed a high catalytic activity for selected complexes in the double Mizoroki-Heck reaction of aryl dibromides.



Swee Kuan Yen, Lip Lin Koh, Han Vinh Huynh, T.S. Andy Hor

J. Organomet. Chem. 694 (2009) 332

Formation and structures of Pd(II) *N*,*S*-heterocyclic carbene-pyridyl mixed-ligand complexes

Introduction of an isopropyl substituent on nitrogen in the benzothiazolium ring or an amine at the α -position to the pyridyl provides a motif for double γ -hydrogen interactions with the metal. This results in pseudo-5-membered-ring chelate and a source of stabilization for d^8 carbene structures.



Jun Ni, Li-Yi Zhang, Zhong-Ning Chen

J. Organomet. Chem. 694 (2009) 339

Syntheses, characterization and sensitized lanthanide luminescence of heteronuclear Pt-Ln (Ln = Eu, Nd, Yb) complexes with 2,2'-bipyridyl ethynyl ligands With excitation at absorption region of MLCT/LLCT transitions in the platinum(II) terpyridyl acetylide chromophore, Pt–Ln heteronuclear complexes exhibit lumines-cence characteristic of the corresponding lanthanide(III) ions whereas the Pt-based emission is mostly quenched, revealing unambiguously occurrence of effective Pt \rightarrow Ln energy transfer.



Akinobu Naka, Yoshiaki Matsumoto, Tatsuya Itano, Kei Hasegawa, Tomoaki Shimamura, Joji Ohshita, Atsutaka Kunai, Takae Takeuchi, Mitsuo Ishikawa

J. Organomet. Chem. 694 (2009) 346

Nanosized starlike molecules. Synthesis and optical properties of tris- and tetrakis [oligo(disilanylenebithienylene)dimethyl silyl]benzene Two types of the starlike molecules with the arms consisting of disilanylene–bithienylene unit, such as **18** and **20**, were synthesized by the reaction of 1,3,5-trisand 1,2,4,5-tetrakis(halodimethylsilyl)benzene with the lithiumdisilanylenebithienylene derivatives. UV–Vis absorption and fluorescence spectra of these compounds have been reported.



Taro Tanabe, Yoshiyuki Mizuhata, Nobuhiro Takeda, Norihiro Tokitoh

J. Organomet. Chem. 694 (2009) 353

Syntheses and structures of overcrowded silanedichalcogenols and their applications to the syntheses of silanedichalcogenolato complexes

Overcrowded silanedichalcogenols, Tbt-(Mes)Si(EH)(E'H), were isolated and their molecular structures were fully characterized. Novel silanedichalcogenolato transition metal complexes, [Tbt(Mes)Si(μ -E)(μ -E')ML_n] [ML_n = Pd(PPh₃)₂, Pt(PPh₃)₂, Ru(η^6 benzene), or Ru(PMe₃)₃], were synthesized by utilizing them as key building blocks.



Yang-Jian Hu, Hua Hong Zou, Ming-Hua Zeng, Ng Seik Weng

J. Organomet. Chem. 694 (2009) 366

Two bis-[1-(aryliminomethyleny)-2-oxynaphthalen] nickel catalysts for the polymerization of methyl methacrylate Two bis-(1-arylliminomethylenyl-2-oxynaphthalen) nickel complexes (aryl = 2methylphenyl, 1; 2, 6-diisoproyl-phenyl, 2) were reacted with alkylaluminium in presence of equimolar PPh3, and then found they can catalyst polymerization of methyl methacrylate (MMA), the highest activity reaching 1.1×105 g PMMA/(mol Ni \cdot h) by 1 at 0.8 mol/l of MMA, 400 of Al/Ni ratio.



Philip C. Andrews, Craig M. Forsyth, Peter C. Junk, Iryna Nuzhnaya, Leone Spiccia

J. Organomet. Chem. 694 (2009) 373

Synthesis and structural characterisation of gallium and indium fluoroalkoxide 'ate' complexes

The metathesis reactions of alkali metal hexafluoroalkoxides with GaCl₃ or InCl₃ result in the formation and isolation of group 1/13 "ate" complexes. The stoichiometry of the reaction and the nature of the alkali metal used determines the structural and physical characteristics of the complexes. A variety of inter- and intramolecular interactions give rise to some unexpected and interesting solid-state structures.



Pintu K. Kundu, Rekha Singh, Sunil K. Ghosh

J. Organomet. Chem. 694 (2009) 382

Silicon assisted diversified reaction of a β -silylmethylene malonate with dimethyl-sulfoxonium methylide

Conditions have been established for the reaction of dimethylsulfoxonium methylide with a β -silylmethylene malonate to give a cyclopropane or a cyclobutane or an allylsilane with high selectivity. The silicon group played a crucial role in the reaction either by assisting and/or by participating in the process.



Kiyofumi Inamoto, Jun-ichi Kuroda, Eunsang Kwon, Kou Hiroya, Takayuki Doi

J. Organomet. Chem. 694 (2009) 389

Pincer-type bis(carbene)-derived complexes of nickel(II): Synthesis, structure, and catalytic activity A series of new CNC-type pincer complexes of nickel were successfully synthesized and fully characterized. The catalytic activity of these nickelacycles in the Suzuki–Miyaura coupling reaction also is described.



R = Mesityl (Mes), Diisopropylphenyl (DIPP)

Contents

Farman Ullah, Anca I. Oprea, Markus K. Kindermann, Gabor Bajor, Tamas Veszprémi, Joachim Heinicke

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Homologues of *N*-heterocyclic carbenes: Detection and electronic structure of *N*bridgehead pyrido[*a*]-anellated 1,3,2diazagermol-2-ylidenes Cyclodelocalized *N*-bridgehead pyrido[*a*]anellated *N*-heterocyclic germylenes **1***a*,**b** and the electron-rich, partly delocalized dichloro-pyrido[*a*]-1,3,2-diazasilole **4***a* were prepared from GeCl₂ · dioxane or SiCl₄, respectively, and dilithium reagents, formed from *N*-tert-butyl pyridine-2-aldimines and excess lithium in THF. Quantum chemical investigations of pyrido[*a*]- and benzo-anellated model germylene and homologous silylenes and carbenes illuminate the relative stabilities and electronic properties.



Ching-Shiang Fang, Yao-Jheng Huang, Bijay Sarkar, C.W. Liu

J. Organomet. Chem. 694 (2009) 404

Structural studies of phosphor-1,1diselenoato Mn(I) and Re(I) complexes Facile syntheses and structural characterizations of Mn(I) and Re(I) complexes of dialkyl diselenophosphate are presented. Intermolecular Se...Se interactions revealed in the lattice form supramolecularly bound 1D network and dimeric species.



Luciano Canovese, Fabiano Visentin, Claudio Santo, Alessandro Dolmella

J. Organomet. Chem. 694 (2009) 411

The role of ancillary ligands and of electron poor alkenes and alkynes in stabilizing Pd(0) derivatives: A comparative study

The characteristics of the ligand neocuproine (2,9-dimethylphenathroline) allow

a number of exchange equilibrium studies between the low valence complex [Pd(η^2 nq)(Neocup)] (nq = naphthoquinone; Neocup = neocuproine) and several alkenes and alkynes. A new order of stability which compares differently unsaturated molecules was therefore established. The structures of the complexes [Pd(η^2 dmfu)(DPPQ)] (dmfu = dimethylfumarate) and of the first di-nitrogen palladium(0) alkyne derivative [Pd(η^2 -deta)(Neocup)] (deta = but-2-ynedioc acid diethyl ester) were also reported.



Elena N. Suslova, Alexandr I. Albanov, Bagrat A. Shainyan

J. Organomet. Chem. 694 (2009) 420

Transformations of diallylsilanes under the action of electrophilic reagents

Reactions of dimethyl-, diphenyl-, and (chloromethyl)methyldiallylsilanes with acetic, trifluoroacetic, triflic acids and complex $BF_3 \cdot 2AcOH$ are studied. Depending on the structure of the starting diallylsilane and the nature of the electrophilic reagent the

following processes are realized: addition of an electrophile to one C=C bond; expulsion of one or two molecules of propene with addition of the electrophile residue to the silicon atom; and rearrangement with elimination of one allyl group from silicon and its attachment to the second allyl group of diallylsilane. Quantum chemical calculations of all three types of transformations are performed on the example of the reactions of dimethyl- and bis(chloromethyl)diallylsilanes with HF, CF₃COOH, CF₃SO₃H, as well as of the intermediate carbenium and silylenium cations.



H.J. Breunig, T. Borrmann, E. Lork, O. Moldovan, C.I. Raţ, R.P. Wagner

J. Organomet. Chem. 694 (2009) 427

Syntheses, crystal structures and DFT studies of $[Me_3EM(CO)_5]$ (E = Sb, Bi; M = Cr, W), *cis*-[(Me_3Sb)_2Mo(CO)_4], and $[{}^tBu_3BiFe(CO)_4]$

The syntheses and the molecular structures of $[Me_3EM(CO)_5]$ [E = Sb, Bi; M = Cr, W], *cis*-[(Me_3Sb)_2Mo(CO)_4], and [^tBu_3BiFe-(CO)_4] are reported. The complexes [Me_3EM(CO)_5] [E = Sb, Bi; M = Cr, W] were investigated by DFT methods.



M. Helena Garcia, Pedro Florindo, M. Fátima M. Piedade, M. Teresa Duarte, M. Paula Robalo, Etienne Goovaerts, Wim Wenseleers

J. Organomet. Chem. 694 (2009) 433

Synthesis and structural characterization of ruthenium(II) and iron(II) complexes containing 1,2-di-(2-thienyl)-ethene derived ligands as chromophores Synthesis and characterization of a threelegged piano stool structured organometallic family possessing coordinated chromophores derived from 1,2-di-(2-thienyl)ethene. Spectroscopic and electrochemical studies are compared with other related compounds and discussed under the scope of potential nonlinear optical properties.



E. Tas, A. Kilic, M. Durgun, I. Yilmaz, I. Ozdemir, N. Gurbuz

J. Organomet. Chem. 694 (2009) 446

Mono- and dinuclear Pd(II) complexes of different salicylaldimine ligands as catalysts of transfer hydrogenation of nitrobenzene with cyclohexene and Suzuki-Miyaura coupling reactions In this study, the synthesis, spectroscopic, catalytic, and electrochemical properties of salicylaldimine Schiff-base ligands (L_n) and their dinuclear Pd(II) complexes for L_1 and L_2 ligands with mononuclear Pd(II) complexes for L_3 and L_4 ligands were investigated. The complexes were easily prepared from cheap materials that could be used as versatile and efficient catalysts for different C–C coupling reactions (Suzuki–Miyaura reactions).



Fazia Derridj, Julien Roger, Florence Geneste, Safia Djebbar, Henri Doucet

J. Organomet. Chem. 694 (2009) 455

Palladium-catalyzed direct heteroarylation of chloropyridines and chloroquinolines

Through the use of air-stable PdCl-(dppb)(C_3H_5) as catalyst, a range of chloropyridines or chloroquinolines undergoes coupling via C–H bond activation/functionalization reaction with benzoxazole, thiazoles, furans or thiophenes in low to good yields.

 $\begin{array}{c} \text{N or } C-C \text{ or } N \\ R \underbrace{+}_{O \text{ or } O} \underbrace{+}_{O \text{ or } O} + c C \underbrace{+}_{N} \underbrace{PdCl(dppb)(C_3H_3) 2.5\%}_{base, 120 \text{ or } 150 \text{ }^{\circ}C} & N \text{ or } C -C \text{ or } N \\ R \underbrace{+}_{V} \underbrace{+}_{V} Pyridyl \\ \text{ or } O \end{array}$

Contents

Linda Kaufmann, Alireza Haghiri Ilkhechi, Hannes Vitze, Michael Bolte, Hans-Wolfram Lerner, Matthias Wagner

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Two short Mn–C contacts between the Mn^{II}-ion and the ferrocene cyclopentadienyl ring have been observed in the complex [Fc₂Bpz^{Ph}₂Mn(THF)Cl] indicating multipledecker sandwich character of the (C₅H₅)-Fe(C₅H₄R)Mn fragment (R = Bpz^{Ph}₂Fc).



Note

Jeongju Moon, Sunwoo Lee

J. Organomet. Chem. 694 (2009) 473

Palladium catalyzed-dehalogenation of aryl chlorides and bromides using phosphite ligands

The Pd-phosphite catalyst effectively promoted the dehalogenation of aryl halides to give dehalogenated products in moderate to excellent yields. The aryl chlorides required strong bases such as NaO^tBu for this transformation, whereas the aryl bromides were dehalogenated in the presence of weak bases such as Cs₂CO₃.

cat. Pd2(dba)3/ ph R

condition X = Cl : NaO¹Bu, i-PrOH, 80 °C X = Cl : 8 examples X = Br : Cs₂CO₃, Cyclohexanol, 120 °C X = Br : 22 example



Erratum	 	
Corrigendum	 	



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