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Contents

Communication

Qi-Ying Lv, Wei Li, Shu-Zhong Zhan, Jian-Ge Wang, Jia-Yin Su, An Ding

J. Organomet. Chem. 693 (2008) 1155

Chemistry of tetracyanoethylene (TCNE): From TCNE to dicyanomethylacetate In the presence of CoCl₂ · 6H₂O, the reaction of TCNE (tetracyanoethylene) with CH₃OH forms a dicyanomethylacetate molecule, which has been obtained as one solvent molecule in one new compound {[Co(bpy)₂CN₂][(NC)₂C-CO₂CH₃]} · 2H₂O (1). It was characterized by IR spectra, UV–Vis spectra, and cyclic voltammogram. Its structure was determined by X-ray crystallography: 1 crystallizes in *P*2(1)/*n* with *a* = 13.3368(17), *b* = 12.5299(16), *c* = 16.074(2) Å, α = 90, β = 94.6320(10), γ = 90°, and *Z* = 2.



Regular Papers

Priyadarshi Satpati

J. Organomet. Chem. 693 (2008) 1159

Structure and bonding of MCB_5H_7 and its sandwiched dimer $CB_5H_6M-MCB_5H_6$ (M = Si, Ge, Sn): Isomer stability and preference for slip distorted structure Theoretically, consecutive substitution of two boron atoms in $B_7 H^{-2}{}_7$ by M (Si, Ge, Sn) and carbon leads to slip-distorted neutral MCB_5H_7 which upon dehydrogenation may produce more distorted neutral dimer $CB_5H_6M-MCB_5H_6.$



Arkadiusz Kłys, Agnieszka Rybarczyk-Pirek, Janusz Zakrzewski

J. Organomet. Chem. 693 (2008) 1166

Reaction of 3,3',4,4'-tetramethyl-1,1'-diphosphaferrocene with $[Re_2(CO)_8(CH_3CN)_2]$ afforded two trimetallic complexes in which the heterometallocene is ligated across the Re–Re bond through P,P and P,Fe atoms.



Ari Lehtonen, Hynek Balcar, Jan Sedláček, Reijo Sillanpää

J. Organomet. Chem. 693 (2008) 1171

Synthesis and ROMP activity of aminophenolsubstituted tungsten(VI) and molybdenum(VI) complexes Air-stable tungsten(VI) and molybdenum(VI) complexes with tridentate aminobis(phenolate) and bidentate aminophenolate ligands catalyse ROMP of 2-norbornene derivatives when activated by Et₂AlCl. Activity increases when coming from dichlorido complexes [MO- $(L^1)Cl_2$] (L^1 = methylamino-*N*,*N*-bis(2-methylene-4,6-dimethylphenolate)] to the trichlorido complexes [M(X)(L²)Cl₃] (X = O, NPh; L^2 = 2,4-di-*tert*-butyl-6-((dimethylamino)methyl)-phenolate).



Shinobu Sato, Shigeori Takenaka

J. Organomet. Chem. 693 (2008) 1177

Linker effect of ferrocenylnaphthalene diimide ligands in the interaction with double stranded DNA

Synthetic ferrocenylnaphthalene diimide ligands 1–7 showed the redox peak current at varied potential depending on their linker types. Binding affinity of 1–7 with double stranded DNA was showed the good correlation with the current increasing based on their ligands after DNA duplex formation on the electrode.



Atanu Jana, Arijit Kumar De, Amit Nag, Debabrata Goswami, Parimal K. Bharadwaj

J. Organomet. Chem. 693 (2008) 1186

Diaza-18-crown-6 based chromophores for modulation of two-photon absorption crosssection by metal ions Two novel aza-crown ether based chromophores have been synthesized in good yields which show large two-photon absorption cross-sections in presence of metal ions. Theoretical calculations also support the experimental findings.



Tingting Xiao, Jianhui Wang, Yuetao Zhang, Wei Gao, Ying Mu

J. Organomet. Chem. 693 (2008) 1195

Synthesis, structures, and catalytic properties for ethylene polymerization of bridged $[\eta^5, \eta^1-C_5H_4CHPhArO]TiCl_2$ complexes

A number of bridged half-sandwich titanium complexes $[\eta^5:\eta^{1}-2-C_5H_4CHPh-4-R^{1}-6-R^2C_6H_2O]TiCl_2 [R^1 = H (5), Me (6), 'Bu (7, 8);$ $R^2 = H (6, 7), 'Bu (5, 8)] were synthesized and$ characterized by elemental analyses, ¹H, ¹³CNMR. Molecular structures of complexes 5and 8 were determined by single crystal X-raydiffraction analysis. Upon activation withAl'Bu₃/Ph₃CB (C₆F₅)₄, complexes 5–8 exhibitreasonable catalytic activity for ethylenepolymerization and copolymerization with1-hexene.





Hariklia Papadaki, Aristides Christofides, Evangelos G. Bakalbassis, John C. Jeffery

J. Organomet. Chem. 693 (2008) 1203

An experimental and a DFT study on the synthesis, spectroscopic characterization, and reactivity of the adducts of dimethyl- and diphenyltin(IV) dichlorides with γ -pyrones [4*H*-pyran-4-one (PYR) and 2,6-dimethyl-4*H*-pyran-4-one (DMP)]: Crystal structure of Ph₂SnCl₂(PYR)

An experimental and a DFT theoretical study on the adducts of $R_2Sn(IV)Cl_2$ (R = methyl or phenyl) with γ -pyrones (PYR = 4*H*-pyran-4one or DMP = 2,6-dimethyl-4*H*-pyran-4-one). The molecular structure of Ph₂SnCl₂(PYR) was established by X-ray diffraction analysis, and the reactivity of Me₂SnCl₂(PYR)₂ towards bipy, Ph₃PO, QNO (Q = quinoline) was investigated.



Elena Klimova, Tatiana Klimova Berestneva, Simon Hernandez-Ortega, Luis Ortiz-Frade, Leon V. Backinowsky, Marcos Martínez García

J. Organomet. Chem. 693 (2008) 1215

Synthesis of 1,2-diferrocenyl-3-(diacylmethylidene)cyclopropenes and 1,1-diacyl-2,3diferrocenyl-4-methylsulfanylbuta-1,3-dienes, their structures and electrochemical properties 2,3-Diferrocenyl-1-morpholinocyclopropenylium tetrafluoroborate reacts with 1,3-diketones in the presence of triethylamine to give 3-diacylmethylidene-1,2-diferrocenylcyclopropenes (8a–d). Under similar conditions, 2,3diferrocenyl-1-methylsulfanylcyclopropenylium iodide affords (8a–c) and 1,1-diacyl-2,3diferrocenyl-4-methylsulfanylbuta-1,3-dienes (10a–c). Electrochemical properties of several (diacylmethylidene)diferrocenylcyclopropenes (8a–c) and 1,1-diacyl-2,3-diferrocenyl-4methylsulfanylbuta-1,3-dienes (10a–c) are studied.



Toru Isobe, Yoshiyuki Mizuhata, Norihiro Tokitoh

J. Organomet. Chem. 693 (2008) 1225

Acyclic tetrachalcogenoether ligands tethered with bulky substituents: Their syntheses and coordination chemistry New tetrachalcogenoether ligands, [TbtE-(*o*-phenylene)Se]₂(*o*-phenylene) (E = S or Se), and their dichloropalladium(II) complexes were synthesized. Although the X-ray crystallographic analysis for the complexes indicated the existence of interaction between the palladium and the terminal chalcogen atoms in the crystalline state, the ⁷⁷Se NMR spectrum suggested no interaction between them in solution.



E = S or Se $\label{eq:E} Tbt = C_6H_2\mbox{-}2,4,6\mbox{-}\{CH(SiMe_3)_2\}_3$

Janet Braddock-Wilking, Yan Zhang, Joyce Y. Corey, Nigam P. Rath

J. Organomet. Chem. 693 (2008) 1233

Preparation of 1,1-disubstituted silacyclopentadienes A series of 1,1-disubstituted silacyclopentadienes has been prepared by a variety of reactions utilizing the known 1,1-(diethylamino)-2,5-bis(trimethylsilyl)-3,4-diphenylsilole or related 1,1-bis(diethylamino)-2,5-dimethyl-3,4-diphenylsilole. Several other new siliconcontaining byproducts were produced from reactions of the siloles that took unexpected pathways. The first molecular structure of a 1,1-dibromo-substituted silole was determined by X-ray crystallography.



Bing Mu, Tiesheng Li, Jingya Li, Yangjie Wu

J. Organomet. Chem. 693 (2008) 1243

The highly efficient Suzuki–Miyaura crosscoupling reaction using cyclopalladated *N*alkylferrocenylimine as a catalyst in aqueous medium at room temperature under ambient atmosphere A series of *N*-alkyl-substituted cyclopalladated ferrocenylimines were used in palladium-catalyzed Suzuki–Miyaura cross-coupling reactions of aryl halides in room temperature and CH₃OH/H₂O media under aerobic conditions. Good to excellent yields were obtained with lower catalyst loading and short reaction time.



Margaret M. Gallagher, A. Denise Rooney, John J. Rooney

J. Organomet. Chem. 693 (2008) 1252

Variable temperature ${}^{1}H$ NMR studies on Grubbs catalysts

Variable temperature ¹H NMR studies were conducted on (1,3-dimesityl-4,5-dihydroimidazol-2-ylidene)(PCy₃)(Cl)₂Ru=CHPh and (PCy₃)₂(Cl)₂Ru=CHPh in solution. The findings include that (1) both mesityl goups rotate around the N-Mes bond at approximately the same rate in a range of solvents, (2) the rotation around the C_{alkylidene}-Ph bond was slower for (IMesH₂)(PCy₃)(Cl)₂Ru=CHPh compared to (PCy₃)₂(Cl)₂Ru=CHPh.



Jesús Jover, Ramón Bosque, José A. Martinho Simões, Joaquim Sales

J. Organomet. Chem. 693 (2008) 1261

Estimation of enthalpies of formation of organometallic compounds from their molecular structures

The QSPR approach allows to derive a model containing nine descriptors, that are easily calculated from the molecular structure, capable to estimate the gas-phase enthalpy of formation, $\Delta_{\rm f} H^0$, of organometallic compounds of the general formula MR_nX_{n-m}, where M is a metal or a semimetal from groups 12 to 16.



Antonio F. Bella, Aurora Ruiz, Carmen Claver, Francisco Sepúlveda, Felix A. Jalón, Blanca R. Manzano

J. Organomet. Chem. 693 (2008) 1269

Pyrazolyl-pyrimidine based ligands in palladium catalyzed copolymerization and terpolymerization of CO/olefins The catalytic behaviour of the cationic complexes [PdMe(NCMe)(N-N')][BAr'₄] in CO/4*tert*-butylstyrene copolymerization and CO/ ethylene/4-*tert*-butylstyrene terpolymerization was investigated. Molecular weights and polydispersity (M_w/M_n) of the obtained polyketones resulted among the best reported for C_s -bisnitrogen planar ligands.



Y=H, Me, Br

Gloria Uccello-Barretta, Federica Balzano, Claudio Evangelisti, Patrizio Raffa, Alessandro Mandoli, Samuele Nazzi, Giovanni Vitulli

J. Organomet. Chem. 693 (2008) 1276

A new platinum vapor-derived highly efficient hydrosilylation catalyst: NMR structural investigation

A new highly efficient Pt-hydrosilylation catalyst has been prepared by co-vaporization of platinum with a mixture of mesitylene and 1,3-divinyl-1,1,3,3-tetramethyldisiloxane. The characterization and the structure around the Pt atoms has been investigated by mono- and bidimensional NMR spectroscopy.



Joerg Harloff, Eckhard Popowski

J. Organomet. Chem. 693 (2008) 1283

Reactions of trimethylsiloxychlorosilanes with lithium metal – On the mechanism of the formation of trimethylsiloxysilyllithium compounds LiSiRR'(OSiMe₃) Depending on substituents the reaction pathways of the formation of $(Me_3SiO)RR'SiLi$ differ. The formation of $(Me_3SiO)RPhSiLi$ $(R = Et, {}^{i}Pr)$ takes place via the intermediates $(Me_3SiO)RPhSi-(RPhSi)_{n}$ -SiPhR $(OSiMe_3)$ (n = 0, 1) which are cleaved by excess lithium. $(Me_3SiO)MesPhSiLi$ is formed via $Me_3SiO-(MesPhSi)_2OSiMe_3$ and its following cleavage by Li. $(Me_3SiO)Mes_2SiLi$ is directly obtained by reductive lithiation without formation of intermediates.

(Me₃SiO)RR'SiCl R/R' = (Et, iPr, Mes)/Ph; Mes/Mes



Chunxiang Li, Weng Kee Leong

J. Organomet. Chem. 693 (2008) 1292

The reaction of triosmium and -ruthenium clusters with bifunctional ligands

The reaction of $[Os_3(CO)_{10}(\mu-H)(\mu-OH)]$, 1, or $[Os_3(CO)_{10}(NCCH_3)_2]$, **2**, with bifunctional ligands carrying –OH, –SH and –COOH groups affords, as the major product, clusters of the general formula $[Os_3(CO)_{10}(\mu-H)(\mu-E^{-}E'H)]$ (E, E' = O, S or COO). In some cases, a minor product with general formula $[Os_3(CO)_{10}(\mu-H)(\mu,\mu-E^{-}E')Os_3(CO)_{10}(\mu-H)]$ was also obtained. With $Ru_3(CO)_{12}$, **3b**, only the first type of products is obtained.



Hongzhi Liu, Shin-ichi Kondo, Ryoji Tanaka, Hiroyuki Oku, Masafumi Unno

J. Organomet. Chem. 693 (2008) 1301

A spectroscopic investigation of incompletely condensed polyhedral oligomeric silsesquioxanes (POSS-mono-ol, POSS-diol and POSStriol): Hydrogen-bonded interaction and hostguest complex Three different incompletely condensed silsesquioxanes (POSS-mono-ol, POSS-diol and POSS-triol) are chosen to investigate the hydrogen-bond interaction by ¹H NMR dilution experiment and FTIR spectra. The possibility of three POSS silanols as anion receptors to form host-guest complexes was also explored in this paper.



Vadim V. Negrebetsky, Peter G. Taylor, Evgeniya P. Kramarova, Aleksander G. Shipov, Sergey A. Pogozhikh, Yuri E. Ovchinnikov, Alexander A. Korlyukov, Allen Bowden, Alan R. Bassindale, Yuri I. Baukov

J. Organomet. Chem. 693 (2008) 1309

Synthesis, structure and dynamic stereochemistry of $(O \rightarrow Si)$ -chelate *N*-(trifluorosilylmethyl)-[*N*-(*S*)-(1-phenylethyl)]-acetamide and 1-(trifluorosilylmethyl)-2-oxoperhydroazepine: Retention of the $O \rightarrow Si$ coordination in the adduct with KF and 18-crown-6

Blanca M. Muñoz, Rosa Santillan, Mario Rodríguez, José Manuel Méndez, Margarita Romero, Norberto Farfán, Pascal G. Lacroix, Keitaro Nakatani, Gabriel Ramos-Ortíz, José Luis Maldonado

J. Organomet. Chem. 693 (2008) 1321

Synthesis, crystal structure and non-linear optical properties of boronates derivatives of salicylideniminophenols

This paper describes the synthesis and (O \rightarrow Si)-chelate structure of the novel compounds *N*-(trifluorosilylmethyl)-[*N*-(*S*)-(1-phenylethyl)]acetamide (1a) and 1-(trifluorosilylmethyl)-2-oxoperhydroazepine (1b). It describes the expansion of the silicon coordination environment upon reaction of the trifluoride (1b) with KF in the presence of 18-crown-6 resulting in adduct 2 with retention of (O \rightarrow Si)-chelation. Based on dynamic ¹⁹F NMR investigations and quantum-chemical calculations, the stereodynamical behavior of the above compounds and the *N*-(trifluorosilylmethyl)-*N*-methylacetamide (1c) are discussed.

The X-ray structure and NMR characterization of a series of boronates is reported. The α - and β -angle between the stilbene skeleton and the aryl or naphthylboronic fragments are indicative of different conformations. Secondand third-order non-linear optical characterization was also performed.





D = H, OMe, N(Et)₂ R = α -naphthyl, β -naphthyl, *o*-tolyl, *o*-formyl

Shinichi Yamabe, Noriko Mizukami, Noriko Tsuchida, Shoko Yamazaki

J. Organomet. Chem. 693 (2008) 1335

A new mechanism for the addition of alcohols to disilenes revealed by DFT and ONIOM calculations Dimers of aliphatic alcohols and phenols were found to react with disilenes via ready proton relays. Monomers may also react but give large activation energies. The effect of four mesityl groups on the addition reactivity was discussed in detail. $Mes_{2}Si{=}SiMes_{2} + (3,5\text{-}(CF_{3})_{2}\text{-}C_{6}H_{3}OH)_{2} \rightarrow \ 1:1 \ adduct + 3,5\text{-}(CF_{3})_{2}\text{-}C_{6}H_{3}OH$



S. Soualmi, L. Ignatovich, E. Lukevics, A. Ourari, V. Jouikov

J. Organomet. Chem. 693 (2008) 1346

Electrochemical oxidation of benzyl germatranes

Electrochemical data and DFT B3LYP/6-311G calculations suggest that the cation radicals obtained by anodic oxidation of bromobenzyl germatranes retain the *endo*-configuration; their fast deprotonation allows anodic substitution at the α -position of germatranes. Oxidation E_p are well described by the additive inductive model including mesomeric interactions.



Halit Kantekin, Elif Çelenk, Hülya Karadeniz

J. Organomet. Chem. 693 (2008) 1353

Synthesis and characterization of new metalfree and metallophthalocyanines containing macrocyclic moieties The synthesis and characterization of new metal-free 7 and metallophthalocyanines 8, 9 carrying macrocyclic $N_2S_2O_4$ donor groups on peripheral positions have been investigated. Phthalonitrile derivative 6 was synthesized according to Rosenmund von Braun procedure from compound 5. The novel compounds were characterized by elemental analysis, IR, ¹H and ¹³C NMR, UV–Vis and MS spectra data.



Zhen-Kang Wen, Yun-Fu Xie, Shu-Bin Zhao, Run-Yu Tan, Liang-Fu Tang

J. Organomet. Chem. 693 (2008) 1359

Functionalized bis(pyrazol-1-yl)methanes by organotin halide on the methine carbon atom and their related reactions

Modification of bis(pyrazol-1-yl)methane by organotin halide has been carried out, and their related reactions have also been investigated. Reaction of these functionalized bis(pyrazol-1-yl)methane with W(CO)₅ THF results in the oxidative addition of the relative electrophilic Sn–X (X = Cl or I) bond to the tungsten(0) atom, yielding new metal–metal bonded complexes R_2 SnCHPz₂W(CO)₃X (R = Ph or *t*-Bu).



Yong-Sheng Xie, Xiao-Hong Pan, Bao-Xiang Zhao, Jin-Ting Liu, Dong-Soo Shin, Jin-Hua Zhang, Liang-Wen Zheng, Jing Zhao, Jun-Ying Miao

J. Organomet. Chem. 693 (2008) 1367

Synthesis, structure characterization and preliminary biological evaluation of novel 5-alkyl-2-ferrocenyl-6,7-dihydropyrazolo[1,5-*a*]-pyrazin-4(5*H*)-one derivatives

A series of novel 5-alkyl-2-ferrocenyl-6,7-dihydropyrazolo[1,5-*a*]pyrazin-4(5*H*)-one derivatives were synthesized by the reaction of ethyl 1-(2-bromoethyl)-3-ferrocenyl-1*H*-pyrazole-5-carboxylate with non-aromatic primary amines in one-pot procedure and characterized by IR, ¹H NMR, ¹³C NMR, HRMS and X-ray diffraction analysis. The effects of all the compounds on A549 cell growth were investigated. The results showed that all compounds had almost inhibitory effects on the growth of A549 cells.



Sonia Pedotti, Angela Patti

J. Organomet. Chem. 693 (2008) 1375

Microwave-assisted synthesis of 1,5-dioxo-3substituted [5]ferrocenophanes Under microwave irradiation the one-pot Claisen–Schmidt reaction between 1,1'-diacetylferrocene and aldheydes was fast and highly selective giving title compounds as main product.



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Notes

Anthony P. Shaw, Hairong Guan, Jack R. Norton

J. Organomet. Chem. 693 (2008) 1382

Synthesis and properties of carboxy-substituted half-sandwich ruthenium complexes with chelating bisphosphine ligands (η^5 -C₅H₄-CO₂H)Ru(η^2 -L)X (X = I, H)

Several Ru(II) complexes $(\eta^5-C_5H_4CO_2H)$ -Ru $(\eta^2-L)I$ have been prepared by the hydrolysis of the ester linkage in $(\eta^5-C_5H_4CO_2t-Bu)Ru(\eta^2-L)Cl$ with trimethylsilyl iodide. The hydrides $(\eta^5-C_5H_4CO_2H)Ru(\eta^2-L)H$ may be prepared by reduction of the iodide complexes in KOH/MeOH solutions followed by acidification. This method has proven amenable to complexes with several chelating bisphosphine ligands.



Kazufumi Kohno, Jun-Chul Choi, Yoshihiro Ohshima, Abulimiti Yili, Hiroyuki Yasuda, Toshiyasu Sakakura

J. Organomet. Chem. 693 (2008) 1389

Reaction of dibutyltin oxide with methanol under CO_2 pressure relevant to catalytic dimethyl carbonate synthesis

Dibutyltin oxide $(Bu_2SnO)_n$ (3) reacts with methanol to give the tetrabutyl(dimethoxy)stannoxane dimer (4). The presence of 2,2dimethoxypropane under a CO₂ pressure accelerates the reaction resulting in nearly quantitative yield.

[Bu ₂ SnO] _n + MeOH 3	+ MeO_OMe
150 °C, 24 h	Bu Bu Bu Bu Sn-O-Sn Bu MeO OMe





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