

Available online at www.sciencedirect.com





Volume 692, issue 5, 1 February 2007

www.elsevier.com/locate/jorganchem

Contents

Regular Papers

Tal Gueta-Neyroud, Boris Tumanskii, Mark Botoshansky, Moris S. Eisen

J. Organomet. Chem. 692 (2007) 927

Synthesis, characterization and catalytic activity of the complex titanium bis(dimethylmalonate)-bis(diethylamido) in the polymerization of propylene The synthesis, characterization and catalytic activity of bis(dimethylmalonate)titanium bis(diethylamine) complex (1) is presented. Complex 1 undergoes a Bailar isomerization in solution. With methylalumoxane (MAO), the complex yields a cationic closed (4) and opened (5) forms of the cationic complex, each of which is responsible for the formation of a different polypropylene.



H. Yasemin Yenilmez, Ali İhsan Okur, Ahmet Gül

J. Organomet. Chem. 692 (2007) 940

Peripherally tetra-palladated phthalocyanines

Phthalocyanines (M = Co, Zn or 2H) with four ({4-[(Z or E)-phenylazo]-1-naphthyl}oxy) substituents on the periphery have been synthesized to enlarge the absorbing range of the dyestuffs. Cyclopalladation of the azobenzene groups lead to network-type oligomeric products by formation of binuclear palladium (II) complexes and they have been further converted into monomeric species by treatment with acetylacetonate. The electronic spectra clearly indicate the absorptions resulting from phenylazo and naphthyl groups along with the Q and B bands of the phthalocyanines. The consequence of the palladation is a relatively intense broad absorption due to LMCT with maxima around 520 nm.



Svetlana V. Amosova, Alexander V. Martynov, Natalia A. Mahaeva, Olga V. Belozerova, Maxim V. Penzik, Alexander I. Albanov, Oleg G. Yarosh, Mikhail G. Voronkov

J. Organomet. Chem. 692 (2007) 946

Unsaturated five-membered selenium-silicon containing heterocycles based on the reactions of selenium di- and tetrahalides with diorganyl diethynyl silanes Reactions of selenium dihalides with diorganyl diethynyl silanes (1) in CHCl₃ at room temperature afford fulvene-type unsaturated fivemembered heterocycles 2, 3, mainly, as Z-isomers. Reactions of selenium tetrahalides with silanes 1 in similar conditions lead to 1-selena-3-silacyclopentenes-4 4, 5 together with 2, 3. The structures of the heterocycles 2–5 were confirmed by multinuclear NMR (¹H, ¹³C, ²⁹Si, ⁷⁷Se) and MS–GC. Long-range, through five bonds, spin-spin interaction of *exo-* and *endo-*cyclic olefinic protons was revealed in *Z*-isomers of 2, 3.





I.A. Tikhonova, K.I. Tugashov, F.M. Dolgushin, A.A. Yakovenko, P.V. Petrovskii, G.G. Furin, A.P. Zaraisky, V.B. Shur

J. Organomet. Chem. 692 (2007) 953

Coordination chemistry of anticrowns: Complexation of cyclic trimeric perfluoro-*o*phenylenemercury with nitro compounds The ability of the mercury anticrown $(o-C_6F_4Hg)_3$ (1) to bind nitro compounds is reported. In the case of nitromethane, nitrobenzene and 5-nitroacenaphthene, 1:1 complexes are formed, differing, however, in their structures. With 1-nitropyrene, 1:1 and 3:1 complexes were isolated. The synthesized adducts are the first examples of complexes of nitro compounds with an anticrown.



J. Organomet. Chem. 692 (2007) 963

Reactions of the rhenium fragment $(\eta^5-C_5Me_5)Re(CO)_2$ with chlorinated ethylenes: Coordination and C–Cl bond activation Photochemical reactions of Cp^{*}Re(CO)₂N₂ with tetrachloroethylene and trichloroethylene yield the coordination complexes Cp^{*}Re-(CO)₂(η^2 -C₂Cl₄) (1) and Cp^{*}Re(CO)₂(η^2 -C₂HCl₃) (2), respectively. Complex 1 reacts thermally in polar organic solvents to produce the C–Cl bond activation product *cis*-Cp^{*}Re(CO)₂(C₂Cl₃)Cl (3).

a of $Cp^*Re(CO)_2N_2$ and trichloroethylene complexes Cp^*Re nd $Cp^*Re(CO)_2(n^2-$



Hg

(1)

William H. Watson, Srikanth Kandala, Michael G. Richmond

J. Organomet. Chem. 692 (2007) 968

Ligand chelation, P–C bond cleavage, and phenyl-group transfer in the reaction between RCCo₃(CO)₉ and 1,8-bis(diphenylphosphino)naphthalene (dppn): Syntheses and X-ray diffraction structures of PhCCo₃(CO)₄(μ -CO)₃-(dppn) and PhCCo₃(CO)₈[η^1 -PPh(OH)C₁₀H₆-P(O)Ph₂]

J.W. Faller, Philip P. Fontaine

J. Organomet. Chem. 692 (2007) 976

Epimerization, diastereoselectivity and hemilability in dicationic chiral ruthenium complexes with bidentate (P^S) bisphosphine monosulfide ligands The tricobalt cluster PhCCo₃(CO)₉ (1) reacts with 1,8-bis(diphenylphosphino)naphthalene (dppn) to give PhCCo₃(CO)₈[PPh₂(1-C₁₀H₇)] (2) and PhCCo₃(CO)₄(μ -CO)₃(dppn) (3). Similar reactions using the methylidyne-capped cluster HCCo₃(CO)₉ (4) afford the corresponding products HCCo₃(CO)₈[PPh₂(1-C₁₀H₇)] (5) and HCCo₃(CO)₄(μ -CO)₃(dppn) (6), in addition to the phenyl-capped cluster PhCCo₃(CO)₈[η^1 -PPh(OH)C₁₀H₆P(O)Ph₂] (7). The chelation of the dppn ligand to a single cobalt atom in 3 and the formal transfer of a phenyl group from the dppn ligand to the methylidyne moiety in cluster 4 to ultimately produce 7 have been established by X-ray crystallography.

cluster 3 cluster 7

Binding of heterobidentate P^S ligands allow the possibility of producing metal-centered chirality as well as the planar chirality present in the parent complex $Ru(\eta^6:\eta^1NMe_2C_6H_4-C_6H_4PCy_2)Cl_2$. Observed diastereomeric ratios for the kinetic and thermodynamic products vary dramatically depending upon ring size in the chelate formed by the P^S ligand.





M. Angeles Alvarez, Yvonne Anaya, M. Esther García, Miguel A. Ruiz

J. Organomet. Chem. 692 (2007) 983

Chemistry of highly electrophilic binuclear cations. 6. Synthesis of the alkyne-bridged complexes $[Mo_2(\eta^5-C_5H_5)_2\{\mu-\eta^2:\eta^2-HC_2(p-tol)\}(CO)_2(\mu-L_2)][B\{3,5-C_6H_3(CF_3)_2\}_4]_2$ and their isocyanide derivatives $(L_2 = Ph_2PCH_2-PPh_2, Me_2PCH_2PMe_2)$

One-electron oxidation of the alkyne-bridged radical cations $[Mo_2Cp_2{\mu-\eta^2:\eta^2-HC_2(p-tol)}(CO)_2(\mu-A_2PCH_2PA_2)]$ (A = Ph, Me) gives the 32-electron cations $[Mo_2Cp_2{\mu-\eta^2:\eta^2} HC_2(p-tol)](CO)_2(\mu-A_2PCH_2PA_2)]^{2+}$ which display two isomers differing in the relative position (*cis* or *trans*) of the alkyne and diphosphine bridges. Displacement of CO by CN'Bu (L) occurs readily in the latter to give only *cis* derivatives.



Haibo Yu, Ling Shao, Jianxin Fang

J. Organomet. Chem. 692 (2007) 991

Synthesis and biological activity research of novel ferrocenyl-containing thiazole imine derivatives

A series of novel N-substituted benzylidene-4ferrocenyl-5-(1*H*-1,2,4-triazol-1-yl)-1,3-thiazol-2-amine derivatives were synthesized by condensation of substituted-benzaldehydes with 2-amino-4-ferrocenyl-5-(1*H*-1,2,4-triazol-1-yl)-1,3-thiazole. The bioassay results of the title compounds showed that some title compounds exhibited some degree of plant growth regulatory and antifungal activities.



Piotr Bałczewski, Aldona Szadowiak, Agnieszka Bodzioch, Tomasz Białas, Wanda M. Wieczorek, Małgorzata Szyrej

J. Organomet. Chem. 692 (2007) 997

The difference in reactivity of (–)-mono and dimenthyl vs. diethyl alkylphosphonates in the α -lithiation reaction: Carbanionic synthesis of unknown (–)-dimenthyl 1-iodoalkylphosphonates and their first use in the radical iodine atom transfer addition (I-ATRA) and cyclisation (I-ATRC) reactions

(-)-Mono and dimenthyl alkylphosphonates as well as (-)-dimenthyl phosphites revealed much lower reactivity in metalation and radical reactions (I-ATRA and I-ATRC) than their diethyl analogs due to a steric hindrance around reactive centers. New protocols for metalation reactions of these classes of compounds have been elaborated.



Han Dong Yin, Fa Hui Li, Lin Wei Li, Gang Li

J. Organomet. Chem. 692 (2007) 1010

Self-assembly of triorganotin(IV) or diorganotin(IV) moieties and 2-methylpyrazine-5acid: Syntheses, characterizations and crystal structures of monomeric, polymeric or tetranuclear macrocyclic compounds A series of diorganotin(IV) and triorganotin(IV) compounds with 2-methylpyrazine-5acid have been synthesized. All compounds were characterized by elemental, IR, and NMR spectra analyses. The crystal structure of compounds 1, 8–11 were determined by Xray single crystal diffraction.



Joji Ohshita, Shinji Kangai, Yosuke Tada, Hiroto Yoshida, Koichi Sakamaki, Atsutaka Kunai, Yoshihito Kunugi

J. Organomet. Chem. 692 (2007) 1020

Synthesis of diarylenenaphthylene- and diaryleneanthrylene-containing organosilicon polymers and their applications to organic EL devices

Stille coupling of bis(stannylphenyl- and stannylthienyl)silane with dibromonaphthalene and bis(bromothienyl)anthracene gave the corresponding polymers. Of those, the diphenyleneanthrylene-containing polymer was found to be usable as a good hole-transporting material in a double-layered EL device.



Suparna Baksi, Rama Acharyya, Swati Dutta, Alexander J. Blake, Michael G.B. Drew, Samaresh Bhattacharya

J. Organomet. Chem. 692 (2007) 1025

Interaction of 2-(arylazo)phenols with rhodium. Usual coordination vs. C–H and C–C activation

Reaction of $[Rh(PPh_3)_3Cl]$ with 2-(2'-hydroxyphenylazo)phenol in refluxing benzene in the presence of triethylamine afforded complex **9** in which the ligand shows the usual O,N,O mode of coordination. Similar reaction with 2-(2'-carboxyphenylazo)-4-methylphenol yielded complexes **10** and **11**, where the ligand underwent C–C and C–H activation, respectively.

Hong Li, Kun Wei, Chenxia Du, Yu Zhu, Chen Xu, Yangjie Wu

J. Organomet. Chem. 692 (2007) 1033

Synthesis, characterization and crystal structures of a new 2-ferrocenylnaphthoxazole and its mercurated derivatives A new ferrocenylnaphthoxazole $[(\eta^5-C_5H_3)-Fe\{(\eta^5-C_5H_4)-C(O)=N(C_{10}H_6)\}]$ (1) and its mercurated derivatives $[HgCl\{(\eta^5-C_5H_5)Fe-[(\eta^5-C_5H_3)C(O)=N(C_{10}H_6)]\}]$ (2) and $[HgCl-\{(\eta^5-C_5H_4)Fe[(\eta^5-C_5H_4)C(O)=N(C_{10}H_6)]\}]$ (3) were synthesized. The crystal structure of 1 was stabilized by the intermolecular $\pi-\pi$ stacking interaction between the Cp ring and naphthoxazole ring. In the crystal of 2, there exist bridged Cl–Hg bonds, $\pi-\pi$ stacking interactions, which facilitate construction of this complex into a 3D supramolecular structure.



Abraham F. Jalbout, Ali Jameel Hameed, Bartosz Trzaskowski

J. Organomet. Chem. 692 (2007) 1039

Study of the structural and electronic properties of 1-(4, 5 and 6-selenenyl derivatives-3-formyl-phenyl) pyrrolidinofullerenes We have examined a series of 1-(4, 5 and 6-selenenyl derivatives-3-formyl-phenyl) pyrrolidinofullerenes molecules C_{60} - C_2H_4N -[3-(CHO)- C_6H_3SeX] theoretically using DFT theory at the B3LYP/3-21G* level of the theory. The substituents include: X = CN, CH₂CH(NH₂)CO₂H and CH₂CH₂CH(NH₂)CO₂H. We have selected these substituents to be in *ortho, meta* and *para* positions with relation to formyl group in order to show the effect of such structural change on the electronic properties of the molecules. The theoretical IR spectra, physical, chemical and thermodynamics properties of the molecules studied are obtained and discussed.



Doris Domin, David Benito-Garagorri, Kurt Mereiter, Christian Hametner, Johannes Fröhlich, Karl Kirchner

J. Organomet. Chem. 692 (2007) 1048

Synthesis and characterization of new chiral palladium β -diimine complexes

The synthesis and characterization of a range of chiral β -diimine ligands and their complexes with palladium(II) has been investigated. The introduction of chirality can be easily achieved through a combination of both achiral and chiral building blocks.



Krishna K. Pandey

J. Organomet. Chem. 692 (2007) 1058

Energy analysis of metal-metal bonding in [RM-MR] (M = Zn, Cd, Hg; R = CH₃, SiH₃, GeH₃, C₅H₅, C₅Me₅)

The trend of the M–M bond dissociation energy in [RM–MR] for the substituents R shows for metals the order GeH₃ < SiH₃ < CH₃ < C₅Me₅ < C₅H₅. Electrostatic forces between the metals are always attractive and they are strong (-75.8 to -110.5 kcal/mol).



Lucie Routaboul, Sandrine Vincendeau, Cédric-Olivier Turrin, Anne-Marie Caminade, Jean-Pierre Majoral, Jean-Claude Daran, Eric Manoury

J. Organomet. Chem. 692 (2007) 1064

New phosphorus dendrimers with chiral ferrocenyl phosphine-thioether ligands on the periphery for asymmetric catalysis

The synthesis of new dendrimers with chiral ferrocenyl phosphine-thioether ligands on the periphery (up to the fourth generation) and their use in asymmetric allylic substitution is reported.



Tamer Andrea, Eyal Barnea, Mark Botoshansky, Moshe Kapon, Elisheva Genizi, Zeev Goldschmidt, Moris S. Eisen

J. Organomet. Chem. 692 (2007) 1074

Synthesis and characterization of new thorium and uranium phenolate complexes

The synthesis and characterization of new organoactinide complexes using amino bis-(phenolate) and salicylaldiminato ligands is reported. The crystal structure similarity between thorium and uranium complexes indicates that the 5f electrons are not involved in the bonding. The bridging effect among the ancillary ligand is presented.



Contents

Elinor C. Spencer, Mahimaidoss Baby Mariyatra, Judith A.K. Howard, Alan M. Kenwright, Krishnaswamy Panchanatheswaran

J. Organomet. Chem. 692 (2007) 1081

The synthesis and structural characterisation of the mercury (II) halide complexes of the phosphorus ylide carbethoxymethylenetriphenylphosphorane The reaction of the phosphorus ylide, carbethoxymethylenetriphenylphosphorane, Ph₃-PCHCOOEt, with a mercury (II) halide yields a dimeric complex of the form [(Ph₃PCH-COOEt)(HgX₂)]₂ where X is either bromine, chlorine or iodine. These structures have been characterised fully using spectroscopic techniques and single-crystal X-ray diffraction.



Thiruvengadam Munisamy, Stephen L. Gipson

J. Organomet. Chem. 692 (2007) 1087

The effect of 19-electron formation constants on the electrochemistry and electron transfer induced substitution reactions of cyclopentadienylmetal halide complexes The electrochemical reduction of $CpFe(CO)_2I$ proceeds via an ECE mechanism, while that for $Cp'Mo(CO)_3I$ is dominated by the DISP pathway. Reductively induced substitution reactions of the two complexes give completely different products. These differences are explained in terms of a difference in the formation constants of 19-electron intermediates.



Christophe Michon, Jean-Pierre Djukic, Michel Pfeffer, Nathalie Gruber-Kyritsakas, André de Cian

J. Organomet. Chem. 692 (2007) 1092

Synthesis of cyclomanganated complexes derived from 2,5-diphenyl-1,3,4-oxadiazole and their reactivity with respect to 1,1diphenyldiazomethane: Evidence for a fluxional trihaptobenzylic coordination mode The thermolytic coupling of 1,1-diphenyldiazomethane with mono-manganated 2,5-diphenyl-1,3,4-oxadiazole afforded substantial amounts of a new fluxional trihaptobenzylic complex.



Mauricio Fuentealba, Loïc Toupet, Carolina Manzur, David Carrillo, Isabelle Ledoux-Rak, Jean-René Hamon

J. Organomet. Chem. 692 (2007) 1099

The pentamethyl cationic $[Cp^*Fe(\eta^6-C_6H_5)]^+$ fragment was used as electron acceptor in combination, through a hydrazone bridge, with mesityl and ferrocenyl donors to form push–pull chromophores exhibiting low-lying intramolecular charge transfer transition and enhanced second-order NLO properties (µβ), as measured by EFISH technique at 1.907 µm.



J.W. Faller, Philip P. Fontaine

J. Organomet. Chem. 692 (2007) 1110

Chiral memory effects in catalytic hydrogenations with dynamically chiral ligands The interconversion rate for conformations of dynamically chiral 2,2'-NMe₂C₆H₄C₆H₄PCy₂ decreases upon coordination. Individual diastereomers of planar chiral arene-tethered complex [Ru($\eta^6:\eta^1$ - NMe₂C₆H₄C₆H₄P-Cy₂)((1*S*,2*S*)-DPEN)](SbF₆)₂ (2) do not epimerize readily. *S*_{Ar},*S*,*S*-2 is more enantioselective than *R*_{Ar},*S*,*S*-2 in the catalytic hydrogenation of acetophenone. Therefore, the ligand retains a memory of its configuration even though the arene is no longer η^6 .



Hong-Ting Sheng, Hui Zhou, Hua-Dong Guo, Hong-Mei Sun, Ying-Ming Yao, Jun-Feng Wang, Yong Zhang, Qi Shen

J. Organomet. Chem. 692 (2007) 1118

Synthesis and molecular structure of the cationic samarium phenoxide complex $[(ArO)_2Sm(DME)_2][BPh_4] \cdot THF$ and its catalytic activity for the polymerization of ε -caprolactone

The first cationic samarium phenoxide complex, $[(ArO)_2Sm(DME)_2][BPh_4] \cdot THF$ (ArO = 2,6-di-tert-butyl-4-metyl-phenoxide), can be used as a single-component catalyst for the ring-opening polymerizations of ε -caprolactone with much higher activity than that of the parent neutral complex (ArO)_3Sm(THF)_2.

Ming-Zhong Cai, Gui-Qin Chen, Wen-Yan Hao, Dong Wang

J. Organomet. Chem. 692 (2007) 1125

A facile stereoselective synthesis of 1,3-dienyl sulfones via Stille coupling reactions of (E)- α -stannylvinyl sulfones with alkenyl iodides

Palladium-catalyzed hydrostannylation of acetylenic sulfones in benzene at room temperature gives stereoselectively (E)- α -stannylvinyl sulfones in good yields. (E)- α -Stannylvinyl sulfones are new difunctional group reagents which undergo Stille coupling reactions with alkenyl iodides to afford stereoselectively 1,3-dienyl sulfones in high yields.



Wen-Yi Lee, Hsiang-Hua Hsieh, Chun-Chin Hsieh, Hon Man Lee, Gene-Hsiang Lee, Jui-Hsien Huang, Tsun-Cheng Wu, Shiow-Huey Chuang

J. Organomet. Chem. 692 (2007) 1131

Four- and five-coordinate magnesium compounds containing ketiminate ligands. Synthesis and characterization of L_2Mg , $L_2Mg(LH)$, and $L_2Mg(Py)$, where L = MeC(O)CHC(NAr)Me A series of magnesium complexes containing ketiminate ligands were synthesized. The fourcoordinate magnesium compound [Me-C(O)CHC(NAr)Me]₂Mg (1) acts as a Lewis acid, accepting one equiv. of Lewis base such as [MeC(O)CHC(NHAr)Me] and pyridine to form five-coordinate magnesium compounds. The magnesium compounds act as initiators at 70 °C to polymerize ε -caprolactone and the polydispersity index (PDI) of these poly- ε -caprolactones is in the range 1.57–3.18.



Evans O. Changamu, Holger B. Friedrich

J. Organomet. Chem. 692 (2007) 1138

A study of β -hydride abstraction from alkanediyl homobimetallic complexes [{Cp(CO)₂Fe}₂{ μ -(C_nH_{2n})}] (n = 4–10, Cp = η^5 -C₅H₅) The complexes $[Cp(CO)_2Fe_2\mu-(CH_2)_n]$ (n = 5-10, $Cp = \eta^5-C_5H_5$) undergo both single and double hydride abstraction to give the monocationic complexes, $[Cp(CO)_2Fe_2\mu-(C_nH_{2n-1})]$ -PF₆, and the dicationic complexes, $[Cp(CO)_2$ -Fe₂ $\mu-(C_nH_{2n-2})](PF_6)_2$ upon reaction with Ph₃CPF₆. The complex where n = 4 gives only the monocationic complex $[{Cp(CO)_2Fe}_2\mu-(C_4H_7)]PF_6$.



D. Jaganyi, N. Xaba, A. Mzinyati, C. Grimmer

J. Organomet. Chem. 692 (2007) 1150

Kinetics and mechanism of hydroboration reactions of $HBBr_2 \cdot SMe_2$ and $HBCl_2 \cdot SMe_2$ – Application of ¹¹B NMR spectroscopy

A detailed kinetic and mechanistic study of $HBBr_2 \cdot SMe_2$ and $HBCl_2 \cdot SMe_2$ with 1-octene and 1-hexyne has been undertaken, including the role of the Lewis base (Me₂S) on the hydroboration of these haloboranes. The kinetic data were obtained by exploiting the applicability of ¹¹B NMR spectroscopy as a tool for hydroboration kinetics.



Riadh El Abed, Faouzi Aloui, Jean-Pierre Genêt, Béchir Ben Hassine, Angela Marinetti

J. Organomet. Chem. 692 (2007) 1156

Synthesis and resolution of 2-(diphenylphosphino)heptahelicene (Heptahelicen-2-yl)diphenylphosphine oxide has been obtained *via* photocyclization of a stilbene derivative. After reduction of the phosphine oxide, resolution of the monodentate helical phosphine has been performed by means of the *ortho*-metallated (R)-1-(naphthyl)ethylamine palladium complex.

PPh₂

Derek A. Wann, Sarah L. Hinchley, Heather E. Robertson, Matthew D. Francis, John F. Nixon, David W.H. Rankin

J. Organomet. Chem. 692 (2007) 1161

The molecular structure of $[In(P_3C_2Bu_2^\prime)]$ using gas-phase electron diffraction and *ab initio* and DFT calculations

The structure of $[In(P_3C_2Bu_2^\prime)]$ has been determined both experimentally by electron diffraction and theoretically, with recommendations made about the use of pseudopotentials for calculations on this class of compounds.



Naima Chaouche, Juan Forniés, Consuelo Fortuño, Abdelaziz Kribii, Antonio Martín

J. Organomet. Chem. 692 (2007) 1168

An organometallic tetranuclear cluster with phosphine and phosphido ligands in nonclassical bonding modes: X-ray structural characterization The elimination of the NCMe ligands in [(C₆F₅)₂Pt(μ -PPh₂)₂M(NCCH₃)₂] results in the formation of the tetranuclear cluster 1 through the PPh₂/C₆F₅ reductive coupling. The structure of 1 indicates that one of the palladium centres is connected to the rest of the centres through two M–M bonds and two weaker η^2 -C₆H₅ and η^2 -P–C interactions.



Erratum		1173



Full text of this journal is available, on-line from ScienceDirect. Visit www.sciencedirect.com for more information.