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Contents

Regular papers

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

J. Organomet. Chem. 691 (2006) 3955

Trimetallic $FePd_2$ and $FePt_2$ 4-ferrocenyl-NCN pincer complexes

The synthesis and characterization of ferrocene-bridged NCN pincer complexes of structural type $Fe(\eta^5-C_5H_4-4-NCN-1-MX)_2$ (NCN = $[C_6H_2(CH_2NMe_2)_2-2,6]^-$; X = Cl, I; M = Pd, Pt) is described. Electrochemical measurements show a reversible oxidation of the ferrocene moiety and a dependency of the Fe(II)/Fe(III) potentials towards the presence of the M-halide moieties. The structure in the solid state of one (FePd₂) species (6, MX = PdI) is reported as well.



Alexander A. Korlyukov, Sergey A. Pogozhikh, Yuri E. Ovchinnikov, Konstantin A. Lyssenko, Mikhail Yu. Antipin, Aleksander G. Shipov, Oksana A. Zamyshlyaeva, Evgeniya P. Kramarova, Vadim V. Negrebetsky, Igor P. Yakovlev, Yuri I. Baukov

J. Organomet. Chem. 691 (2006) 3962

(Amidomethyl)dimethylsilanol hydrohalides: Synthesis, NMR and IR studies. Characteristic features of the electronic structure from high-resolution X-ray study and quantum chemical calculation (C,O)-chelate silanol hydrohalides RC(O)-NHCH₂SiMe₂OH \cdot HHal, their precursors, chlorides RC(O)NHCH₂SiMe₂Cl and disiloxanes [RC(O)NHCH₂SiMe₂]₂O were obtained by several routes. The original scheme of hydrolysis of the above chlorides was discussed in detail. The electron structure of silanol hydrohalides have been investigated using high-resolution X-ray study and quantum chemical calculations.



Vadim V. Negrebetsky, Peter G. Taylor, Eugeniya P. Kramarova, Sergey Yu. Bylikin, Ivan Yu. Belavin, Alexander G. Shipov, Alan R. Bassindale, Yuri I. Baukov

J. Organomet. Chem. 691 (2006) 3976

Structures and stereochemical non-rigidity of Si-substituted *N*-(dimethylsilylmethyl)- and *N*-(methylphenylsilylmethyl)amides and -lactams

Eleven new silicon-substituted *N*-(dimethylsilylmethyl)- and *N*-(methylphenylsilylmethyl)amides and -lactams bearing a chiral carbon in the amide or lactam fragment, and containing the OSiC₃X (X = Hal, OTf) coordination fragment have been synthesized and their structures determined in solution by spectroscopic means. The activation parameters (Δ G298#, Δ H#, Δ S#) for enantiomerization and diastereomerization were determined by the dynamic NMR (DNMR) method using full line-shape analysis.





Dmitri N. Cheredilin, Fedor M. Dolgushin, Alexander A. Korlyukov, Ivan A. Godovikov, Renat Kadyrov, Elena V. Balagurova, Stanislav P. Solodovnikov, Igor T. Chizhevsky

J. Organomet. Chem. 691 (2006) 3989

Isolation and characterization of the chelate *exo-nido*-ruthenacarborane intermediates formed in the thermal *exo-nido-to-closo* conversion of [*exo-nido*-5,6,10-{Cl(Ph₃P)₂Ru}-5,6,10-(μ -H)₃-10-H-7,8-R₂-7,8-C₂B₉H₆] (R = H or Me) upon the triphenylphosphine ligand displacement with the chiral (2*S*,4*S*)-(–)-2,4bis(diphenylphosphino)pentane The phosphine–diphosphine displacement reactions of $[exo-nido-5,6,10-\{Cl(Ph_3P)_2Ru\}-5,6,10-(\mu-H)_3-10-H-7,8-R_2-7,8-C_2B_9H_6]$ (R = H or Me) with the chiral (2S,4S)-(-)-2,4-bis-(diphenylphosphino)pentane (S, S-bdpp) ligand has been found to proceed via the corresponding *exo-nido* intermediate $[exo-nido-5,6,10-\{Cl(S,S-bdpp)Ru\}-5,6,10-\mu-(H)_3-10-H-7,8-R_2-7,8-C_2B_9H_6]$ to form the chelate *closo* complexes either of 18- or 17-electron structure, depending on whether substituted or non-substituted starting *exo-nido* complexes are used.



Kuang-Hway Yih, Gene-Hsiang Lee

Gleison Antônio Casagrande,

Gelson Manzoni de Oliveira,

Ernesto Schulz Lang,

J. Organomet. Chem. 691 (2006) 3997

Syntheses, displacement behavior, hetero-atom carbene, and crystal structures of platinum complexes containing the *N*,*N*-dimethyl-thiocarbamoyl, Me₂NC=S, ligand: Structures of [Pt(PPh₃)(Cl)]₂(μ , η ²-SCNMe₂)₂, [Pt(PPh₃)-(η ²-dppa){ η ¹-C(S)NMe₂}][Cl], and [Pt(PPh₃)₂-{ η ¹-C(SEt)(NMe₂)}(η ²-S₂CO)]



2 $[RTe(etu)][RTeI_4]$ (1); $[RTe(tu)][RTeI_4]$ (2)

Sebastião S. Lemos, Viviane A.S. Falcomerand $[p-PhO(C_6H_4)TechJ. Organomet. Chem. 691 (2006) 4006(2). In both compound
(2). In both compound
(2). In both compound$

New cation-dependent supramolecular arrangements of $[RTeI_4]^-$ tectons: Synthesis and X-ray structural characterization of the mixed valence complex salts $[p-CH_3O(C_6H_4)-Te(etu)][p-CH_3O(C_6H_4)TeI_4]$ (etu = ethylene-thiourea) and $[p-PhO(C_6H_4)Te(tu)][p-PhO-(C_6H_4)TeI_4]$ (tu = thiourea)

Chao-Yu Wang, Yi-Hong Liu, Shei-Ming Peng, Shiuh-Tzung Liu

J. Organomet. Chem. 691 (2006) 4012

Rhodium(I) complexes containing a bulky pyridinyl N-heterocyclic carbene ligand: Preparation and reactivity $(p-CH_3OC_6H_4Te)_2$ and $(p-PhOC_6H_4Te)_2$ react with I_2 and thiourea/ethylenethiourea to give $[p-CH_3O(C_6H_4)Te(etu)][p-CH_3O(C_6H_4)TeI_4]$ and $[p-PhO(C_6H_4)Te(tu)][p-PhO(C_6H_4)TeI_4]$ (2). In both compounds the tectonic character of $[RTeI_4]^-$ is confirmed by the assembling of polymeric chains of dimeric anions linked through $I\cdots I$ secondary bonds. The strong cation–anion interaction of 2 allows its further representation as a mixed valence molecular species.

Coordination behavior of Rh(I) complexes

with bulky pyridine N-heterocyclic carbene

ligand have been investigated.



Jie-Wen Ying, Tong Ren

J. Organomet. Chem. 691 (2006) 4021

Diruthenium compounds of thiol capped oligo(phenyleneethynyl) ligand: Synthesis and characterization Reported herein are the synthesis, electrochemical and structural characterization of Ru₂(DMBA)₄(OPE*n*-S-TMSE)₂ compounds.



Li Liu, Wai-Yeung Wong, Jian-Xin Shi, Kok-Wai Cheah, Tik-Ho Lee, Louis M. Leung

J. Organomet. Chem. 691 (2006) 4028

Synthesis, spectroscopy, structures and photophysics of metal alkynyl complexes and polymers containing functionalized carbazole spacers The preparation, optical spectroscopy, structural and photophysical properties of several metal di-ynes and poly-ynes of group 10–12 transition elements spaced by some 9-arylcarbazole moieties are described. The effects of heavy metal ions in harvesting organic triplet emissions and the influence of 9-substituted carbazole chromophore on the phosphorescence spectra of these organometallic materials are studied in detail.



Robert A. Stockland Jr., Adam J. Lipman, John A. Bawiec III, Peter E. Morrison, Ilia A. Guzei, Peter M. Findeis, John F. Tamblin

J. Organomet. Chem. 691 (2006) 4042

Remarkable tolerance of ethynyl steroids to air and water in microwave-assisted hydrophosphinylation: Reaction scope and limitations The microwave-assisted hydrophosphinylation of propargyl alcohols has been investigated using group 9 catalysts under solvent-free conditions as well as with pure water, ethyl lactate, or THF as the solvent.



Raffaello Lazzaroni, Silvia Rocchiccioli, Anna Iuliano, Laura Cipolla

J. Organomet. Chem. 691 (2006) 4054

Substrate-directed asymmetric induction in the rhodium catalyzed hydroformylation of Callyl-sugars: The influence of the glycosidemoiety on the selectivity of the reaction α - and β -C-allylgalactopyranosides, α -C-allylazaglucopyranoside and α -C-allylfruttofuranoside were hydroformylated at low temperatures affording a mixture of linear and branched aldehydes in regioisomeric and diastereoisomeric ratios depending on the glicoside structure. The influence of the different structural features of the sugar moiety on the regio- and diastereoselectivity of the hydroformylation reaction was evaluated.



Contents

Nguyen-Nguyen Pham-Tran, Ngoc-Hoa Tran Huy, Pham-Cam Nam, Louis Ricard, Minh Tho Nguyen

J. Organomet. Chem. 691 (2006) 4058

1-Boryl-3,4-dimethylphosphole trimer: Synthesis, crystal structure and quantum chemical calculations

A novel six-membered trimer of 1-boryl-3,4dimethylphosphole was prepared by reaction of 3,4-dimethylphospholyl anion with monobromoborane-methylsulfide complex $(CH_3)_2S \cdot BH_2Br$ at -60 °C.



Michael M. Möhlen, Clifton E.F. Rickard, Warren R. Roper, George R. Whittell, L. James Wright

J. Organomet. Chem. 691 (2006) 4065

Syntheses, reactions, and structures of osmium(II) distannyl complexes, L_nOs -SnMe₂SnR₃ (R = Me, Ph), from reaction between L_nOs -SnClMe₂ and either LiSnMe₃ or KSnPh₃

A simple route to distannyl complexes of osmium, L_nOs–SnR₂SnR₃, involves reaction between complexes with a chloro-substituted stannyl ligand and salts containing tri-organo tin anions. In the ¹¹⁹Sn NMR spectra of these stable osmium(II) distannyl complexes both the α -Sn and β -Sn atoms show well-resolved one-bond ¹¹⁹Sn–¹¹⁹Sn and ¹¹⁹Sn–¹¹⁷Sn coupling. Methyl groups on the α -Sn atoms are readily replaced by halides through reaction with either SnMe₂Cl₂ or I₂ without cleavage of the Sn–Sn bonds. $L_nOs-SnMe_2Cl \xrightarrow{KSnPh_3} L_nOs-SnMe_2SnPh_3 \xrightarrow{l_2} L_nOs-SnMelSnPh_3$

 $(\mathsf{L}_n\mathsf{Os}=\mathsf{Os}(\kappa^2\mathsf{-}\mathsf{S}_2\mathsf{CNMe}_2)(\mathsf{CO})(\mathsf{PPh}_3)_2 \text{ or } \mathsf{OsCl}(\mathsf{CO})_2(\mathsf{PPh}_3)_2)$

Dmitri Panov, Ants Tuulmets, Binh T. Nguyen

J. Organomet. Chem. 691 (2006) 4076

Impact of reaction products on the Grignard reaction with silanes and ketones

The alkoxide-type reaction products complex tightly with Grignard reagents and enhance in this way their nucleophilicity, thus accelerating the reaction. However, alkoxides branched at α -C atom exert an unfavorable steric hindrance to reaction resulting in a decrease in the reaction rate.



Piotr Buchalski, Andrzej Kozioł, Stanisław Pasynkiewicz, Antoni Pietrzykowski, Kinga Suwińska, Monika Zdziemborska

J. Organomet. Chem. 691 (2006) 4080

Synthesis and structural characterisation of novel nickelaindenyl and nickelafluorenyl compounds: Differences in the bonding modes of nickelacyclic rings New binuclear nickelacyclic compounds (η^5 -pentamethylcyclopentadienyl)(η^3 -(1-(η^5 -pentamethylcyclopentadienyl))-1-nickelafluorenyl)nickel and (η^5 -pentamethylcyclopentadienyl))(η^3 -(1-(η^5 -pentamethylcyclopentadienyl)))-2-phenyl-3-ethyl-1-nickelaindenyl)nickel were synthesised and characterised by high resolution mass spectrometry, magnetic moment determination and X-ray single crystal analysis. The bonding mode of the central nickel atom to the nickelacycles was not η^5 like in the previously described analogues of nickelocene but half way between η^3 and η^5 .



V. Ischenko, R. Harshe, R. Riedel, J. Woltersdorf

J. Organomet. Chem. 691 (2006) 4086

Cross-linking of functionalised siloxanes with alumatrane: Reaction mechanisms and kinetics

Cross-linking of functionalised polysiloxanes with hydrolyzed alumatrane species has been studied both experimentally and theoretically. The reaction of the Si–O–Si-polymer backbone with the hydroxy groups of the hydrolyzed alumatrane turned out to have very low activation energy (+2 kJ/mol), presenting an alternative reaction mechanism along with the ordinary condensation of the hydroxy groups and playing a key role for the controlled modification of the rheological properties of polysiloxanes.



Josefina Díez, M. Pilar Gamasa, José Gimeno, Elena Lastra, Amparo Villar

J. Organomet. Chem. 691 (2006) 4092

From alkenylphosphane aminoallenylidene ruthenium(II) complexes to highly unsaturated ruthenaphosphabicycloheptene complexes Novel unsaturated allenylidene and aminoallenylidene alkenylphosphane ruthenium(II) complexes are reported. A highly unsaturated ruthenaphosphabicycloheptene system, bearing an exocyclic butadienyl group, is synthesized by the diastereoselective intramolecular [2+2] cycloaddition between the allyl C=C and C_{α} =C_{β} bonds of the allenylidene precursor.



Mi S. Lim, Ji Young Baeg, Soon W. Lee

J. Organomet. Chem. 691 (2006) 4100

Reactivity of $[Cp^*Rh(\eta^6-C_6H_3NH_2-2,6-i-Pr_2)]$ -(OTf)₂ toward phosphines and alkynes

The cationic aniline complex $[Cp^*Rh(\eta^{6}-2,6-(Me_2CH)_2C_6H_3NH_2)](OTf)_2$ underwent substitution with phosphines or phosphites and mediated cycloaddition reactions of several alkynes in refluxing ethanol: the [2 + 2] dimerization for Ph–C=C–Ph and the [2 + 2 + 1] trimerization for Ph–C=C–H and CH₃C₆H₄–C=C–H.



Hongping Ren, Xi Zhao, Shansheng Xu, Haibin Song, Baiquan Wang

J. Organomet. Chem. 691 (2006) 4109

Synthesis and structures of cyclopentadienyl *N*-heterocyclic carbene copper(I) complexes

A series of cyclopentadienyl *N*-heterocyclic carbene copper complexes CpCu(NHC) were synthesized and structurally characterized. The effect of the substituents at the nitrogen atom of the NHC ligands on the structures and thermally stability was discussed.



Contents

Jérémie D.A. Pelletier,

Yohan D.M. Champouret, Jesus Cadarso, Lucy Clowes, Marcos Gañete, Kuldip Singh, Vakesan Thanarajasingham, Gregory A. Solan

J. Organomet. Chem. 691 (2006) 4114

Electronically variable imino-phenanthrolinylcobalt complexes; synthesis, structures and ethylene oligomerisation studies A series of arylimino-phenanthrolinecobalt(II) chloride complexes have been synthesised in which the 4-position of the 2, 6-diisopropyl-substituted aryl group has been systematically modified to include electron donating and electron withdrawing substituents; the performance of the complexes as precatalysts for ethylene oligomerisation has been probed.



M. Fernanda N.N. Carvalho, Ana S.D. Ferreira, Rudolf Herrmann

J. Organomet. Chem. 691 (2006) 4124

Conversion of pentynol to pentanone catalysed by Pd(II) metal centres

Coordinative activation of pentynols by *trans*- $[PdCl_2L_2]$ (L = canforimine) or PdCl_2 leads to the formation of heterocyclic ketal species that sequentially afford 5-hydroxy-2-pentanone.



Amit K. Jain, Vinita Sharma, Rakesh Bohra, A.A. Sukumar, V.S. Raju, John E. Drake, Michael B. Hursthouse, Mark E. Light

J. Organomet. Chem. 691 (2006) 4128

Synthesis and characterization of methylbismuth(III) complexes containing dithio ligands: 2. Crystal and molecular structure of [MeBiCl(S_2 CNEt₂)] and transformation of some [MeBi(S_2 CNR2')2] to Bi_2S_3 Methylbismuth(III) complexes containing dithio ligands of the types [MeBiCl(S₂CNR₂)] and [MeBi(S2CNR2')2] have been synthesized and characterized. Crystal structure of [Me-BiCl(S₂CNEt₂)] indicates the presence of unique Bi \cdots Cl \cdots Bi secondary bonds resulting in a distorted square pyramidal environment around the central bismuth(III) atom. TGA, XRD and SEM studies indicate low temperature transformation of some [Me-Bi(S2CNR2')2] to pure Bi₂S₃.



Sergio Stoccoro, Antonio Zucca, Giacomo Luigi Petretto, Maria Agostina Cinellu, Giovanni Minghetti, Mario Manassero

J. Organomet. Chem. 691 (2006) 4135

Dinuclear platinum(II) complexes with bridging twofold deprotonated 2,2':6', 2"-terpyridine. New molecules with a 3,5diplatinated-pyridyl inner core: $[Pt_2(terpy 2H)(Me)_2(L)_2]$, $[Pt_2(terpy-2H)(X)_2(L)_2]$ and $[Pt_2(terpy-2H)(H)_2(L)_2]$ (L = neutral ligand; X = halide) – Crystal and molecular structure of $[Pt_2(terpy-2H)(Cl)_2(PPh_3)_2]$ A series of dinuclear platinum(II) derivatives where a π -conjugated organic ligand spans the metal ions is described. Coordination around each of the platinum atoms is fulfilled by a neutral two-electron ligand and by an anion which can be an alkyl, a halide or even a hydride.



Notes

Nicholas J. Beach, Jesse M. Walker, Hilary A. Jenkins, Gregory J. Spivak

J. Organomet. Chem. 691 (2006) 4147

Ruthenium vinylidene and carbyne complexes containing a multifunctional tridentate ligand with a PNN donor set The synthesis and reactivity of a series of ruthenium vinylidene and carbyne complexes containing the multifunctional ligand *N*-(2diphenylphosphinobenzylidene)-2-(2-pyridyl)ethylamine (abbreviated PNN) are described.



Alexander M. Kirillov, Matti Haukka, M. Fátima C. Guedes da Silva, João J.R. Fraústo da Silva, Armando J.L. Pombeiro

J. Organomet. Chem. 691 (2006) 4153

A picolinate- N_2 complex of rhenium, the first dinitrogen complex bearing a carboxylate or a *N*,*O*-ligand

A dinitrogen Re(I) complex with a picolinate ligand has been prepared, providing the first example of a genuine N \equiv N complex comprising a carboxylate or a *N*,*O*-coligand, the carboxylate arm of picolinate having a net electron-donor character similar to that of chloride, stabilizing the *trans* Re–N₂ bond.





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