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# Contents

## Communication

## Bartłomiej Janowski, Krzysztof Pielichowski

J. Organomet. Chem. 693 (2008) 905

Microwave-assisted synthesis of cyclopentyl-trisilanol ({\it c-C\_5H\_9})\_7Si\_7O\_9(OH)\_3

Microwave-assisted synthesis of cyclopentyltrisilanol by the hydrolytic condensation of the cyclopentyltrichlorosilane in aqueous acetone has been successfully performed. The reaction under microwave irradiation is considerably shorter in time in comparison to the traditional procedure and may be utilized for preparation of Si-containing building blocks for nanocomposite materials.



## **Regular Papers**

## Duanchao Yan, Michael Bolte, Norbert Auner

J. Organomet. Chem. 693 (2008) 908

Synthesis, structure, and photoluminescence of organosilicon based compounds containing stilbene, butadiene or styrene subunits

A series of novel organosilicon based compounds (such as **2**, **3**, **6**–**8**) was synthesized by basic organic and organometallic reaction routes. The compounds were fully characterized and their photoluminescence spectra were recorded. Owing to their optoelectronic properties these compounds might be useful precursors for the design of new materials, such as sensitive sensors, optical switches and luminescent polymers.



## Lin Liu, Xiaodong Li, Xin Xing, Changcheng Zhou, Haifeng Hu

J. Organomet. Chem. 693 (2008) 917

A modified polymethylsilane as the precursor for ceramic matrix composites

This is the  $^{29}$ Si MAS NMR of the cured PMS and cured A-PMS. Cured A-PMS is made of highly crosslinked structure SiC<sub>4</sub>, while cured PMS is made of Si–Si structure. This indicating that SbCl<sub>3</sub> promoted the transformation of Si–Si to Si–C.



# Ole Winkelmann, Christian Näther, Ulrich Lüning

J. Organomet. Chem. 693 (2008) 923

Bimacrocyclic NHC transition metal complexes

Seven bimacrocyclic metal complexes bearing a concave NHC ligand have been prepared and characterized. The structures of silver complex 2, copper complex 3 and palladium complex 4 were elucidated by X-ray analysis. Silver complex 2 and copper complex 3 were tested as catalysts for the cyclopropanation of styrene and indene with EDA (ethyl diazoacetate).



$$\begin{split} \mathsf{M} &= \mathsf{Ag}(\mathsf{I}), \, \mathsf{Cu}(\mathsf{I}), \\ \mathsf{Pd}(\mathsf{II}), \, \mathsf{Rh}(\mathsf{I}), \, \mathsf{Ir}(\mathsf{I}) \end{split}$$

#### Rico Packheiser, Petra Ecorchard, Bernhard Walfort, Heinrich Lang

J. Organomet. Chem. 693 (2008) 933

Heterotrimetallic and heterotetrametallic transition metal complexes

The synthesis of  $(\eta^5-C_5H_5)L_2Ru-C\equiv C$ -bipy  $(L_2 = 2 \text{ PPh}_3, \text{ dppf}; \text{ bipy} = 2,2'-\text{bipyridine}_{5-yl}; \text{ dppf} = 1,1'-\text{bis}(\text{diphenylphosphino})-ferrocene) and Fc-C\equiv C-NCN-Pt-C\equiv C-R$  (R = bipy, C<sub>5</sub>H<sub>4</sub>N; NCN = [1,4-C<sub>6</sub>H<sub>2</sub>(CH<sub>2</sub>-NMe<sub>2</sub>)<sub>2</sub>-2,6]<sup>-</sup>) and their reaction behavior towards different organometallics to give heterobi-, -tri- and -tetrametallic transition metal complexes is described. The solid-state structure of four samples is discussed.



#### Tao Liu, Hong-Xing Zhang, Bao-Hui Xia

J. Organomet. Chem. 693 (2008) 947

Theoretical studies on structures and spectroscopic properties of bis-cyclometalated iridium complexes  $[Ir(ppy)_2X_2]^-$ 

The structures and spectroscopic properties of a series of mixed bis-cyclometalated iridium(III) complexes [Ir(ppy)<sub>2</sub>X<sub>2</sub>]<sup>-</sup> (X = CN, 1; X = NCS, 2; X = NCO, 3; ppy = 2-phenylpyridl) were investigated by DFT and ab initio methods. The calculated results showed that the transition character of the absorption and emission can be changed by adjusting the  $\pi$  electron-accepting abilities of the X ligands and the phosphorescent color can be tuned by altering the X ligands.



X= CN (1); X = NCS, (2); X = NCO (3)

# Jens Beckmann, Jens Bolsinger, Johann Spandl

J. Organomet. Chem. 693 (2008) 957

The structural diversity of Te–I interactions within tetraorganoditelluroxane diiodides and related compounds

The supramolecular structures of the tetraorganoditelluroxane diiodides  $(R_2Te)_2OI_2$  (3, R = p-MeOC<sub>6</sub>H<sub>4</sub> (Figure); **5**, R = Me) and the related compounds (*p*-MeOC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>TeI<sub>2</sub> · 12I<sub>2</sub> (**1a**) and 2 (Me<sub>2</sub>Te)<sub>2</sub>O(I)OH · H<sub>2</sub>O (7) are dominated by inter- or intramolecular secondary Te···I interactions (blue broken bonds).



## Contents

# David L. Davies, Omar Al-Duaij, John Fawcett, Kuldip Singh

J. Organomet. Chem. 693 (2008) 965

Cyclometallated imine complexes with oxygenfunctionalised side-chains: Effect of the nature of the functional group, chain length and charge on coordination of the oxygen Cyclopalladated imines containing oxygenfunctionalised side-arms were synthesised and fully characterised. The length of the tether, nature of the functional group (R = H, Me) and the nature of the other ligands X,Y and charge on the complex all affect whether the oxygen atom is coordinated or not.



### Do Young Kim, Yujian You, Gregory S. Girolami

J. Organomet. Chem. 693 (2008) 981

Synthesis and crystal structures of two (cyclopentadienyl)titanium(III) hydroborate complexes, [Cp\*TiCl(BH<sub>4</sub>)]<sub>2</sub> and Cp<sub>2</sub>Ti(B<sub>3</sub>H<sub>8</sub>)

Treatment of Cp<sup>\*</sup>TiCl<sub>3</sub> and Cp<sub>2</sub>TiCl<sub>2</sub> with NaB<sub>3</sub>H<sub>8</sub> affords the compounds [Cp<sup>\*</sup>TiCl-(BH<sub>4</sub>)]<sub>2</sub> and Cp<sub>2</sub>Ti(B<sub>3</sub>H<sub>8</sub>), respectively. The former compound arises by means of a new reaction, the metal-induced fragmentation of the B<sub>3</sub>H<sub>8</sub> anion. Dimeric [Cp<sup>\*</sup>TiCl(BH<sub>4</sub>)]<sub>2</sub> has bridging chloride ligands and tridentate BH<sub>4</sub> groups. The Ti–Ti distance of 3.452(1) Å indicates that there is no metal–metal bond. In Cp<sub>2</sub>Ti(B<sub>3</sub>H<sub>8</sub>), the Ti–B distances are 0.04 Å longer than those in niobium analog, Cp<sub>2</sub>Nb(B<sub>3</sub>H<sub>8</sub>), probably because it has one fewer skeletal bonding electron.



### Marisol Reyes-Lezama, Herbert Höpfl, Noé Zúñiga-Villarreal

J. Organomet. Chem. 693 (2008) 987

One pot synthesis of dimanganese carbonyl complexes containing sulfur and phosphorus donor ligands using tricarbonylpentadienylmanganese

The reaction of tricarbonylpentadienylmanganese with aryl mercaptans in the presence of

#### phosphines or phosphites afforded dinuclear complexes $[Mn_2(CO)_4(\mu-CO)(\mu-SR)_2(PR'_3)_2];$ R = Ph for $PR'_3 = PPh_3$ , $PMe_3$ , $P(OMe)_3$ , $P(OEt)_3$ , $PMePh_2$ and R = m-, p- $NH_2C_6H_4S$ -, for $PR'_3 = PPh_3$ in one pot synthesis. Two reaction routes were proposed for the formation of the dinuclear complexes depending on the relative basicity of the sulfur vs. phosphine ligands. Characterization of the complexes was effected in solution and, for [Mn<sub>2</sub>(CO)<sub>4</sub>(µ-CO)(µ-SPh)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] and [Mn<sub>2</sub>(CO)<sub>4</sub>(µ-CO)(µ-SPh)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>], by X-ray crystallographic analysis.



## Maura Pellei, Simone Alidori, Franco Benetollo, Giancarlo Gioia Lobbia, Marilena Mancini, Gaia Emanuela Gioia Lobbia, Carlo Santini

J. Organomet. Chem. 693 (2008) 996

Di- and tri-organotin(IV) complexes of the new bis(1-methyl-1*H*-imidazol-2-ylthio)acetate ligand and the decarboxylated analogues

The new ligand sodium bis(1-methyl-1*H*-imidazol-2-ylthio)acetate, Na[(*S*-tim)<sub>2</sub>CHCO<sub>2</sub>], has been prepared and the related di- and triorganotin(IV) derivatives have been synthesized from reaction between SnR<sub>n</sub>Cl<sub>4-n</sub> acceptors and Na[(*S*-tim)<sub>2</sub>CHCO<sub>2</sub>]. Complexes of the type {[ $\kappa^1 O$ -(*S*-tim)<sub>2</sub>CHCO<sub>2</sub>]SnR<sub>3</sub>} and related decarboxylated species {[ $\kappa^2 N$ ,*N*-(*S*-tim)<sub>2</sub>CHCO<sub>2</sub>]SnR<sub>2</sub>Cl<sub>2</sub>} have been obtained and fully characterized. The adducts {[ $\kappa^1 O$ -(*S*-tim)<sub>2</sub>CHCO<sub>2</sub>]Sn(H<sub>2</sub>O)(C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>} and {[(*S*-tim)<sub>2</sub>CHCO<sub>2</sub>]SnCl(H<sub>2</sub>O)(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>} were characterized by X-ray crystal structure determination.



## Alexander D. Dilman, Vitalij V. Levin, Alexander A. Korlyukov, Pavel A. Belyakov, Marina I. Struchkova, Mikhail Yu. Antipin, Vladimir A. Tartakovsky

J. Organomet. Chem. 693 (2008) 1005

Complexation of tris(pentafluorophenyl)silanes with neutral Lewis bases Monodentate and bidentate complexes of tris(pentafluorophenyl)silanes with Lewis bases have been prepared and studied by X-ray diffraction analysis.



## Guoqun Liu, Yaomin Zhao, Duxia Cao

J. Organomet. Chem. 693 (2008) 1020

Argon matrix effect on the geometry and infrared spectrum of  $H_2C=MH_2$  (M = Ti, Zr, Hf): A theoretical study

An argon matrix effect on the geometry and infrared spectrum of the  $H_2C=TiH_2$  complex is simulated within the framework of IEF-PCM. The simulation indicates a significant variation of the molecular structure (planar  $\rightarrow$  pyramidal) and a remarkable enhancement of the agostic interaction.



### Elke Jaime, Alexander N. Kneifel, Matthias Westerhausen, James Weston

J. Organomet. Chem. 693 (2008) 1027

Mechanistic studies on the hydrolysis of a dimeric alkylzinc bis(2-pyridylmethyl)amide

The hydrolysis of a dimeric alkylzinc amides surprisingly leads to exchange of the amido ligand by a hydroxo group. Based on the  $pK_a$ values, one would instead expect the formation of an alkane. DFT investigations of the reaction pathways clearly demonstrate the importance of N–H–O bridges during the formation of transition structures.



## Halit Kantekin, Gülsev Dilber, Zekeriya Bıyıklıoğlu

J. Organomet. Chem. 693 (2008) 1038

A new polymeric phthalocyanine containing 16-membered tetrathia macrocyclic moieties by microwave irradiation: Synthesis and characterization

Tetranitrile monomer (**3**) was synthesized by nucleophilic aromatic substitution of 1,5,9,13tetrathiacyclohexadecane-3,11-diol (**1**) onto 4nitrophthalonitrile (**2**). The metal-free phthalocyanine polymer (**4**) was prepared by the reaction of a tetranitrile monomer with 4-({11-[3-cyano-4-(cyanomethyl)phenoxy]-1,5,9, 13-tetrathiacyclohexadecan-3-yl}oxy)phthalonitrile in 2-(dimethylamino)ethanol. Ni(II), Co(II), Cu(I)-phthalocyanine polymers were prepared by the reaction of the tetranitrile compound with the chlorides of Ni(II), Co(II) and Cu(I) in DMAE. Zn(II)-phthalocyanine polymer was prepared by the reaction of the tetranitrile compound with the acetates of Zn(II) in DMAE. The new compounds were characterized by a combination of IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, UV–Vis, elemental analysis and MS spectral data.



## Floriana Vitale, Rosa Vitaliano, Chiara Battocchio, Ilaria Fratoddi, Emanuela Piscopiello, Leander Tapfer, Maria Vittoria Russo

J. Organomet. Chem. 693 (2008) 1043

Synthesis and characterization of gold nanoparticles stabilized by palladium(II) phosphine thiol

Innovative functionalization of gold nanoparticles with an organometallic thiolate  $[CH_3COSPd(PBu_3)_2(C \equiv CC_6H_5)]$  has been obtained by linkage between Pd(II) and Au nanoparticles through a simple single S bridge. The proposed new hybrid is expected to show interesting optoelectronic properties.

by the chemical reaction depicted below. Spectroscopic techniques in combination with

microanalytical data confirm the formation of 1:2 and 1:4 (Sn:Naindtc) type complexes de-

pending on the molar ratio of the sodium salt

of indolinedithiocarbamate employed. A sym-

metrical bidentate coordination of the in-

dolinedithiocarbamate has been observed. An octahedral arrangement around the Sn atom is evident from <sup>119</sup>Sn NMR data. The *in vitro* cytotoxicity of butyl and phenyl analogues has



## Sadaf Khan, Shahab A.A. Nami, K.S. Siddiqi

J. Organomet. Chem. 693 (2008) 1049

Mononuclear indolyldithiocarbamates of SnCl<sub>4</sub> and R<sub>2</sub>SnCl<sub>2</sub>: Spectroscopic, thermal characterizations and cytotoxicity assays *in vitro* 

Mononuclear indoline dithiocarbamates of  $SnCl_4$  and  $R_2SnCl_2$  have been synthesized

## Denis A. Kissounko, Maxim V. Zabalov, Neil M. Boag, Yurii F. Oprunenko, Dmitri A. Lemenovskii

J. Organomet. Chem. 693 (2008) 1058

Evaluating the kinetic indenyl effect of a  $\pi$ -thiaphentalenyl ancillary ligand

been studied against the standard human tumor cell lines and the compounds resulted to be biologically active. The magnitude of the "kinetic indenyl effect" for the π-thiapentalenyl ligand, isoelectronic heteroanalogue of the indenyl ligand, has been evaluated by experimental kinetic and computational DFT methods. Results obtained are correlated with the corresponding carbocyclic

analogues.





k<sub>Cp analogue</sub> < k<sub>3</sub> << k<sub>Ind analogue</sub>

# Afaf R. Genady, Tarek A. Fayed, Detlef Gabel

J. Organomet. Chem. 693 (2008) 1065

Synthesis, characterization, and spectrophotometric studies of novel fluorescent *arachno* decaborane and nonaborane clusters containing aza-distyrylbenzene derivatives Distyrylbenzene analogues containing *arachno*-borane clusters have been synthesized. The resulting compounds undergo *trans-cis* photoisomerization upon excitation.



## Kefeng Wang, Katrin Wedeking, Weiwei Zuo, Dongheng Zhang, Wen-Hua Sun

J. Organomet. Chem. 693 (2008) 1073

Iron(II) and cobalt(II) complexes bearing N-((pyridin-2-yl)methylene)-quinolin-8-amine derivatives: Synthesis and application to ethylene oligomerization

A series of tridentate N^N^N iron(II) and cobalt(II) complexes containing *N*-((pyridin-2-yl)methylene)-quinolin-8-amine derivatives were synthesized and characterized by elemental and spectroscopic analyses. On treatment with modified methylaluminoxane, these metal complexes exhibited good catalytic activities up to  $2.8 \times 10^6$  g mol<sup>-1</sup>(Fe) h<sup>-1</sup> for ethylene oligomerization, and butenes were the major products with nice selectivity for  $\alpha$ -C<sub>4</sub>. The steric and electronic effects on catalytic activities of metal complexes were carefully investigated as well as the influence of various reaction parameters.



## Ingo Schranz, Luke Grocholl, Christopher J. Carrow, Lothar Stahl, Richard J. Staples

J. Organomet. Chem. 693 (2008) 1081

Heterocarbenoids of germanium and tin and their polyhedral oxidation products: The case for thermodynamic product control in Group 14 chalcogenides The oxidation of the heterocarbenoids  $[E'(\mu N'Bu)_2E'({}^{t}BuN)_2]M$ , M = Ge, Sn; E' = P, SiMe with chalcogens (E) furnished the dimeric chalcogenides { $[E'(\mu - N'Bu)_2E'({}^{t}BuN)_2]$ -ME}<sub>2</sub>, whose degree of aggregation is controlled by thermodynamics. The case is made that most currently known Group 14 chalcogenides, even those labeled "kinetically stabilized", are really thermodynamic products.





# J.G. Małecki, R. Kruszynski, M. Jaworska, P. Lodowski, Z. Mazurak

## J. Organomet. Chem. 693 (2008) 1096

Synthesis, spectroscopic and electronic characterizations of two half sandwich ruthenium(II) complexes with 2-(2'-hydroxyphenyl)-benzoxazole and 4-picolinic acid ligands

The [(C<sub>6</sub>H<sub>6</sub>)RuCl(HPB)] and [(C<sub>6</sub>H<sub>6</sub>)RuCl<sub>2</sub>-(C<sub>3</sub>H<sub>4</sub>NCOOH)] complexes have been prepared and studied by IR, UV–Vis spectroscopy and X-ray crystallography. The complexes was prepared in reaction of [(C<sub>6</sub>H<sub>6</sub>)RuCl<sub>2</sub>]<sub>2</sub> with 2-(2'-hydroxyphenyl)benzoxazole or 4-picolinic acid in methanol. The electronic spectra of the obtained compounds have been calculated using the TDDFT method. The luminescence property of the half sandwich complex [(C<sub>6</sub>H<sub>6</sub>)RuCl-(HPB)] was studied by the DFT method and the mechanism was suggested.



## Hikaru Meguro, Take-aki Koizumi, Takakazu Yamamoto, Takaki Kanbara

J. Organomet. Chem. 693 (2008) 1109

Synthesis, structure, and quaternization and complexation reactions of  $\kappa^3$ SCS pincer palladium complexes having 3,5-pyridinediyl unit

The cyclopalladation of 3,5-bis(diphenylphosphinothioyl)pyridine afforded new  $\kappa^3$ S,C,Spincer palladium complexes with a  $\sigma$ -bond between Pd and 4C of the centered 3,5-pyridinediyl unit. By utilizing the quaternization and complexation ability of the pyridine imine nitrogen (N<sub>py</sub>) atom, various new pincer-type complexes, including hetero-binuclear complexes, have been synthesized.



## Contents

## Farkhanda Shaheen, Amin Badshah, Marcel Gielen, Christine Gieck, Mariyam Jamil, Dick de Vos

J. Organomet. Chem. 693 (2008) 1117

Synthesis, characterization, in vitro cytotoxicity and anti-inflammatory activity of palladium(II) complexes with tertiary phosphines and heterocyclic thiolates: Crystal structure of  $[PdC_{28}H_{19}N_8PS_2]$ 

Four-coordinated mononuclear palladium(II) complexes  $[Pd(L)_nCl(ROR_2P)]$ , 1–9, with chelating heterocyclic thiolates and tertiary phosphines (L = Pym2SH (pyrimidine-2-thiolate), Pur6SH

#### László Jánosi, Tamás Kégl, László Kollár

J. Organomet. Chem. 693 (2008) 1127

Platinum–alkyl– $B(C_6F_5)_3$  (or  $BF_3$ ) '*in situ*' systems as tin(II) halide-free enantioselective hydroformylation catalysts

(purine-6-thiolate), Py2SH (pyridine-2-thiolate), R<sub>3</sub>P = PPh<sub>3</sub>, P(o-tolyl)<sub>3</sub>, PPh<sub>2</sub>Cl), n = 1, 2) have been synthesized by the direct reaction of [PdCl<sub>2</sub>(ROR<sub>2</sub>P)<sub>2</sub>] with polyfunctional heterocyclic thiolates and fully characterized. The X-ray diffraction study of non-ionic compound **5** showed that the thiolate acts as unidentate and that the chelating (N,S) ligand adopts a slightly distorted square planar geometry around the palladium atom.

In vitro the anti-inflammatory inhibitions of compounds 1-9 was 10-15% greater than that of the standard drug Declofenac.

Compounds 1 and 4 showed mostly a moderate to low cytotoxicity against seven human tumor cell lines whereas compound 3 was somewhat more active.

The dialkyl/diaryl-platinum complexes  $(Pt(CH_3)_2(P-P); PtPh_2(P-P) and Pt(2-Thioph)_2(P-P), where P-P stands for 2,4-bis-(diphenylphosphino)pentane) proved to be active hydroformylation catalysts in the presence of a boron additive <math>(B(C_6F_5)_3, PPh_3 \text{ or } BF_3)$ . The alkyl/aryl ligand abstraction by the boron additives has been proved by NMR studies and DFT/PCM calculations.





#### Ana Bellomo, David Gonzalez, Hèlio A. Stefani

J. Organomet. Chem. 693 (2008) 1136

Synthesis of unnatural cyclitols via a combined enzymatic-palladium catalysis approach

The Suzuki–Miyaura cross-coupling reaction of a hydroxylated vinyl bromide obtained by a chemoenzymatic approach with a diverse range of potassium organotrifluoroborates has been accomplished catalyzed by  $Pd(PPh_3)_4$  in satisfactory yields. A variety of functional groups are tolerated in the nucleophilic partner.



#### Abraham F. Jalbout

J. Organomet. Chem. 693 (2008) 1143

 $Li@C_{60}$  complexes with amino acids: A theoretical analysis

In this work, we explore the ability of the  $Li@C_{60}$  fullerene to interact with amino acids at the DFT-BLYP/DND level of theory. The calculations suggest that the most favorable interactions of the fullerene is with arginine, leucine, and tryptophan which is related to the backbone structure of the corresponding amino acids.



### Note

## Lien-Hoa Tran, Lars Eriksson, Licheng Sun, Björn Åkermark

J. Organomet. Chem. 693 (2008) 1150

A new square planar mononuclear Mn<sup>III</sup> complex for catalytic epoxidation of stilbene

Using **2** as catalyst, both (*Z*)- and (*E*)-stilbene may be converted to the epoxide in good yield. The mayor products were formed from *cis*addition of the oxygen but some of the isomeric epoxide was also formed in each case.

PhIO (5 equiv) MeCN 11 h



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