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# Contents

#### Communications

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#### Sara Sobhani, Elham Safaei, Mozaffar Asadi, Fariba Jalili

J. Organomet. Chem. 693 (2008) 3313

An eco-friendly procedure for the efficient synthesis of dialkyl  $\alpha$ -aminophosphonates in aqueous media

A new, convenient and high yielding procedure for the preparation of diethyl  $\alpha$ -aminophosphonates in water by one-pot reaction of aldehydes, amines, tri/dialkyl phosphites in the presence of a low catalytic amount of [Cu(3,4-tmtppa)]-(MeSO<sub>4</sub>)<sub>4</sub> (0.16 mol%) as a highly stable and re-usable catalyst is described.

 $\begin{array}{c} R_{1}^{1} & P(OR^{3})_{3} \\ H^{2} + or \\ Q \\ H^{2}(OR^{3})_{2} \\ H^{2}(OR^{3})_{2} \\ H^{2}(OR^{3})_{2} \\ R^{2} = ayl, alkyl, alkyl, heteroary \\ R^{2} = ayl, alkyl, alkyl, heteroary \\ R^{2} = ayl, alkyl, alkyl, heteroary \\ R^{2} = ayl, alkyl, alkyl, alkyl, alkyl, alkyl, heteroary \\ R^{2} = ayl, alkyl, alkyl$ 

#### Ilya Bezkishko, Vasily Miluykov, Alexander Kataev, Igor Litvinov, Dmitry Krivolapov, Oleg Sinyashin, Evamarie Hey-Hawkins

J. Organomet. Chem. 693 (2008) 3318

An unusual reaction of cyclopropenylphosphonium bromide with sodium polyphosphides – A novel approach to sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide 1,2,3-Triphenylcyclopropenylphosphonium bromide reacts with sodium polyphosphides to give sodium 3,4,5-triphenyl-1,2-diphosphacyclopentadienide in high yield.



#### Sergey E. Lyubimov, Andrey A. Tyutyunov, Pavel A. Vologzhanin, Anton S. Safronov, Pavel V. Petrovskii, Valery N. Kalinin, Konstantin N. Gavrilov, Vadim A. Davankov

J. Organomet. Chem. 693 (2008) 3321

Carborane-derived diphosphites: New ligands for Pd-catalyzed allylic amination

A series of chiral diphosphite ligands bearing sterically congested carborane fragments have been prepared and applied in the Pd-catalyzed allylic amination of 1,3diphenylallyl acetate with pyrrolidine and di-*n*-propylamine (up to 83% ee).



### **Regular Papers**

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#### Luciano Canovese, Fabiano Visentin, Carlo Levi, Claudio Santo

J. Organomet. Chem. 693 (2008) 3324

Transmetalation reactions. The role of the stabilizing olefin in determining the overall reaction rate

A systematic study concerning the transmetalation reaction between the palladium butadienyl complexes [PdCl((ZC=CZ)<sub>2</sub>-Me)(L-L')] (Z = COOMe; L-L' = MeN-SPh (1A), N-SPh (1B), DPPQ-Me (1C), BiPy (1D), DPPE (1E)) and tributyl-phenylethynyl-stannane in the presence of some stabilizing olefins (ma, fn, nq, dmfu, and tmetc) was undertaken. The nature of the stabilizing olefin heavily affects the reaction rates which also depend on the donor capability and steric characteristics of the ligands.



J. Organomet. Chem. 693 (2008) 3331

An efficient synthesis of 12-vertex *closo*-rhodacarboranes  $[3-(\eta^5-C_5Me_5)-1-R^1-2-R^2-3,1,2-closo-RhC_2B_9H_9]$  (R<sup>1</sup>, R<sup>2</sup> = H, Alk) via two-step reactions of [K][7-R<sup>1</sup>-8-R<sup>2</sup>-7,8-*nido*-C\_2B\_9H\_{10}] mono-anions with [Rh<sub>2</sub>( $\eta^5-C_5Me_5$ )<sub>2</sub>Cl<sub>4</sub>]: structural characterization of the first purely *closo*-type metallacarborane with sterically demanding C,C'-dibenzylsubstituted carborane ligand

#### Yi Zhang, Tareq Irshaidat, Haixia Wang, Kris V. Waynant, Haobin Wang, James W. Herndon

J. Organomet. Chem. 693 (2008) 3337

Coupling of Fischer carbene complexes with conjugated enediynes featuring radical traps: Novel structure and reactivity features of chromium complexed arene diradical species

#### Svetlana V. Amosova, Maxim V. Penzik, Alexander V. Martynov, Nataliya A. Makhaeva, Nina O. Yarosh, Mikhail G. Voronkov

J. Organomet. Chem. 693 (2008) 3346

Unsaturated five-membered seleniumgermanium containing heterocycles based on the reactions of selenium di- and tetrahalides with diorganyl diethynyl germanes

Regio- and stereoselective reactions of selenium dihalides with diorganyl diethynyl germanes in CHCl<sub>3</sub> afford in yields up to quantitative the first representatives of a new class of selenium–germanium containing heterocycles - 3,6-dihalogen-4,4-diorganyl-1,4-selenagermafulvenes. The reaction An efficient two-step reaction of the salts [K][7-R<sup>1</sup>-8-R<sup>2</sup>-7,8-*nido*-R<sub>2</sub>C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] with [Rh<sub>2</sub>(η<sup>5</sup>-Cp<sup>\*</sup>)<sub>2</sub>Cl<sub>4</sub>] affords *closo* complexes [3-(η<sup>5</sup>-Cp<sup>\*</sup>)-1-R<sup>1</sup>-2-R<sup>2</sup>-3,1,2-*closo*-RhC<sub>2</sub>B<sub>9</sub>-H<sub>9</sub>], of which one is the first 12-vertex *closo*-type metallacarborane species bearing sterically demanding C,C'-dibenzyl-substituted carborane ligand; the first step ionic intermediates,  $[(η^5-Cp^*)Rh-(\mu-Cl)_3Rh(η^5-Cp^*)][7,8-R_2-7,8-$ *nido* $-C_2B<sub>9</sub>H<sub>10</sub>], were isolated and the crystal structure of one representative (R<sup>1</sup> = R<sup>2</sup> = PhCH<sub>2</sub>) has been determined by an X-ray diffraction study.$ 

The reaction of Fischer carbene complexes with conjugated enediynes that feature a pendant alkene group has been examined. The reaction proceeds through carbenealkyne coupling to generate an enyneketene intermediate, which undergoes Moore cyclization followed by 6-endo radical cyclization to afford fused polycyclic arenes. The intermediate diradical species were evaluated computationally in both the singlet and triplet configurations.

of selenium tetrachloride under the same conditions leads to the first representatives of a new class of selenium-germanium containing cyclopentene heterocycles - 2dichloromethyl-2,4-dichloro-3,3-diorganyl-1-selena-3-germacyclopenetenes-4 as well as to the unknown 3,6,6-trichloro-4,4-dialkyl-1,4-selenagermafulvenes formed as a result of a spontaneous dehydrochlorination of the cyclopentene heterocycles. In a case of SeBr<sub>4</sub> the process of dehydrobromination is dominating. The structures of the heterocycles were proved by multinuclear (<sup>1</sup>H, <sup>13</sup>C, <sup>77</sup>Se) spectroscopy and mass-spectrometry. In the <sup>1</sup>H NMR spectra of Z-isomers of 1,4selenagermafulvenes a long-range spin-spin interaction between exo- and endocyclic olefinic protons through five bonds is revealed lacking in the E-isomers.







R1, R2 = H. Me. PhCHa

1 CeHe-EtOF

(80-91%)

2a-d C<sub>6</sub>H<sub>6</sub>-EtOH (5 days)

#### Evans O. Changamu, Holger B. Friedrich

J. Organomet. Chem. 693 (2008) 3351

Synthesis, characterization and reactions of the transition metal halogenoalkyl carbocation complexes  $[Cp(CO)_2M{\eta^2-CH_2CH(CH_2)_nX}]PF_6$  (*n* = 1–8, 10, M = Fe; *n* = 3, 4 M = Ru; X = Br, I) The halogenoalkyl complexes  $[Cp(CO)_2M\{(CH_2)_nX\}]$ (n = 3 - 10,12. M = Fe; n = 5, 6, M = Ru, X = Br, I) react with  $Ph_3CPF_6$  to give the corresponding carbocation complexes  $[Cp(CO)_2M{\eta^2} (CH_2CH(CH_2)_{n-2}X)]PF_6$  in high yields. The reactions of some of the cationic complexes with NaI. PPh<sub>3</sub> and Et<sub>3</sub>N lead to halogenoolefin displacement, formation of the unstable phosphonium adducts [Cp(CO)<sub>2-</sub>  $Fe{CH_2CH(PPh_3)(CH_2)_{n-2}X}]PF_6$  and allylic deprotonation, respectively.



#### D. Pérez, P. Sharma, N. Rosas, A. Cabrera, J.L. Arias, F. del Rio-Portilla, J. Vazquez, R. Gutierrez, A. Toscano

J. Organomet. Chem. 693 (2008) 3357

Tris-(1,2-*N*,*N*-dimethylaminomethylferrocenyl)stibine and its heterotrimetallic complex New tertiary chloro-bis-(1,2-ferrocenyl)stibine (1) and tris-(1,2-ferrocenyl)stibine ligand (2) containing CH<sub>2</sub>NMe<sub>2</sub> pendenant arm at the ortho-position have been synthesized. This new stibine(2) was then complexed with  $PtCl_4^{2-}$  to obtain hetero trimetallic cis-PtCl<sub>2</sub>L<sub>2</sub> (3) complex, where this stibine acts as a bidentate ligand. The molecular structures of these compounds were determined. It is to be noted that tris(1,2aminomethylferrocenyl)stibine representing the first example of a structurally characterized ferrocenyl pnictogen where three 1,2 disubstituted ferrocenyl rings are attached to the central atom and phosphorus analogue of these stibine is missing in the literature. Stibine (1) shows a hypervalent Sb-N interaction while stibine (2) does not show this interaction in solid state.



#### Xu-Qiong Xiao, Guo-Xin Jin

J. Organomet. Chem. 693 (2008) 3363

Functionalized N-heterocyclic carbene iridium complexes: Synthesis, structure and addition polymerization of norbornene Functionalized N-Heterocyclic carbene iridium complexes have been synthesized and characterized structurally. The iridium carbene complexes **4** and **6** show moderate catalytic activities for polymerization of norbornene in the presence of methylaluminoxane (MAO) as co-catalyst.



### Andreas A. Danopoulos, Pamela Cole, Steven P. Downing, David Pugh

J. Organomet. Chem. 693 (2008) 3369

Copper and palladium complexes with *N*-heterocyclic carbene ligands functionalised with carboxylate groups

Copper (I) and Pd(II) complexes with carboxylate-functionalised *N*-heterocyclic carbene ligands give rise to organometallic polymers and new chelating complexes, respectively.



#### Ken-ichi Fujita, Yoshinori Takahashi, Hirohide Nakaguma, Taro Hamada, Ryohei Yamaguchi

J. Organomet. Chem. 693 (2008) 3375

Activation of C–H and H–H bonds by dinuclear iridium complexes. Oxidative addition to highly active unsaturated 32e<sup>–</sup> diiridium species Highly active unsaturated 32e<sup>-</sup> diiridium species were generated by the deprotonation of dihydrido-bridged diiridium complexes. Oxidative addition of C–H bond in aromatic molecules and H–H bonds of hydrogen to such active species occurred under ambient conditions. Mechanistic aspects of the activation reactions are also demonstrated.



#### Ganesan Prabusankar, Bernard Jousseaume, Thierry Toupance, Hassan Allouchi

J. Organomet. Chem. 693 (2008) 3383

A discrete unsymmetrically substituted dihydrodioxadistannetane with both  $\eta^1$  and intramolecular  $\eta^2\mu_2$  sulfonate bondings

The tetrasulfonato 1,3-dihydro-1,3-dioxa-2,4-diaryl-2,4-distannetane 4 is the smallest discrete tin sulfonate cluster with absence of intermolecular interactions. It also exhibits unusual  $\eta^1$  and intramolecular  $\eta^2\mu_2$  bonding modes for the sulfonate groups.



#### Lifeng Tan, Sheng Zhang, Xiaohua Liu, Yuandao Chen, Xuewen Liu

J. Organomet. Chem. 693 (2008) 3387

Experimental and density functional theory (DFT) studies on the DNA-binding trend and spectral properties of two new Ru(II) complexes:  $[Ru(L)_2(mip)](ClO_4)_2$  (L = 2,9-dmp and 4,7-dmp)

Photoactivated cleavage of pBR-322 DNA in the absence and presence of the complex 1 (a) or 2 (b) after 60 min irradiation at 365 nm. Lane 0, in DNA alone; lanes (1–4), at 5, 10, 20, and 40  $\mu$ M Ru(II) complexes, respectively.



#### Gemma Aragay, Josefina Pons, Jordi García-Antón, Xavier Solans, Mercè Font-Bardia, Josep Ros

J. Organomet. Chem. 693 (2008) 3396

Synthesis, characterization and X-ray crystal structure determination of cyclopalladated [Csp<sup>2</sup>,N,N']<sup>-</sup>, zwitterionic and chelated compounds in the reaction of 3,5-diphenyl-*N*-alkylaminopyrazole derived ligands with Pd(II)

In this paper is described the synthesis and characterization of three types of compounds, cyclopalladated, zwitterionic and chelated, which are obtained in a one pot but two steps reaction. X-ray crystal structures of three compounds are presented.



#### Tressia A.P. Paulose, Jeremy A. Olson, J. Wilson Quail, Stephen R. Foley

I. Organomet. Chem. 693 (2008) 3405

Non-symmetrically substituted di-N-heterocyclic carbene palladium(II) complexes: Synthesis, structure and catalytic activity

The synthesis of non-symmetric di-N-heterocyclic carbene ligands along with their silver(I) and palladium(II) complexes are described. The activity of the Pd(II) complexes in the Suzuki-Miyaura coupling reaction of bulky substrates was investigated.



#### Marta S. Saraiva, Susana Quintal, Fátima C.M. Portugal, Telma A. Lopes, Vitor Félix. Iosé M.F. Nogueira. Margarida Meireles, Michael G.B. Drew, Maria José Calhorda

J. Organomet. Chem. 693 (2008) 3411

Nitrogen donor ligands bearing N-H groups: Effect on catalytic and cytotoxic activity of molybdenum  $\eta^3\mbox{-allyldicarbonyl}$ complexes

New complexes  $[Mo(\eta^3-C_3H_5)Br(CO)_2-$ (N-N)], where N-N are several bidentate nitrogen ligands with N-H groups, were synthesized and characterized. They are active precursors for olefin epoxidation in the presence of TBHP and some of them exhibit cytotoxic activity against human carcinomic strain cells.



#### Michaël Gras, Bruno Therrien, Georg Süss-Fink, Petr Štěpnička, Anna K. Renfrew, Paul J. Dyson

J. Organomet. Chem. 693 (2008) 3419

Water-soluble arene ruthenium complexes containing pyridinethiolato ligands: Synthesis, molecular structure, redox properties and anticancer activity of the cations  $[(\eta^6 \text{-} \text{arene}) \text{Ru}(p \text{-} \text{SC}_5 \text{H}_4 \text{NH})_3]^{2+}$ 

The cationic complexes  $[(\eta^6-\text{arene})-\text{Ru}(SC_5H_4\text{NH})_3]^{2+}$  (arene =  $C_6H_6$ ,  $C_6H_5\text{Me}$ , p-<sup>i</sup>PrC<sub>6</sub>H<sub>4</sub>Me, C<sub>6</sub>Me<sub>6</sub>) are accessible from the reaction of the corresponding dinuclear precursor  $[(\eta^6 \text{-} \text{arene})_2 Ru_2(\mu_2 \text{-} Cl)_2 Cl_2]$  and 4-pyridinethiol.

Olcay Bekircan, Zekeriya Bıyıklıoğlu, Irfan Acar, Hakan Bektas, Halit Kantekin

J. Organomet. Chem. 693 (2008) 3425

Novel metallophthalocyanines bearing 3-(p-chlorophenyl)-5-p-tolyl-4H-1,2,4-triazole bulky substituents by microwave irradiation

The synthesis of metallophthalocyanines [6-9; M = Ni(II), Zn(II), Co(II) and Cu(II)]with four 1,2,4-triazole units obtained 4-{(4-chloro-2-fluorobenzyl)[3-(4from chlorophenyl)-5-(4-methylphenyl)-4H-1,2, 4-triazol-4-yl]amino}phthalonitrile (5) in the presence of dimethylaminoethanol or the corresponding anhydrous metal salts is described. The thermal stabilities of the Pc compounds were determined by thermogravimetric analysis. The new compounds were characterized by a combination of IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, UV–Vis, elemental analysis.





#### Martin Lamač, Josef Cvačka, Petr Štěpnička

J. Organomet. Chem. 693 (2008) 3430

The reaction of  $(S_p)$ -2-(diphenylphosphino)ferrocenecarboxylic acid with carbodiimide reagents: Characterisation of the acid anhydride and urea products

The reaction of  $(S_p)$ -2-(diphenylphosphino)ferrocenecarboxylic acid  $[(S_p)$ -1] with *N*,*N'*dicyclohexylcarbodiimide or *N*-ethyl-*N'*-[3-(dimethylamino)propyl]carbodiimide affords the respective urea  $(S_p)$ -2 and  $(S_p)$ -2-(diphenylphosphino)ferrocenecarboxylic anhydride  $[(S_p,S_p)$ -3], the product ratio changing with the diimide agent and in the presence of a base (DMAP = 4-(dimethylamino)pyridine).



#### Oliver Kaufhold, F. Ekkehardt Hahn, Tania Pape, Alexander Hepp

J. Organomet. Chem. 693 (2008) 3435

Ruthenium(II) and iron(II) complexes of *N*-pyridyl substituted imidazolin-2-ylidenes

The unsymmetrically substituted donorfunctionalized imidazolium salts **1a** and **1b** react with RuCl<sub>3</sub> · xH<sub>2</sub>O to give the dinuclear ruthenium(II) complexes [**3a**]-(PF<sub>6</sub>)<sub>2</sub> or [**3b**](PF<sub>6</sub>)<sub>2</sub>. Reaction of [**3a**](PF<sub>6</sub>)<sub>2</sub> with silver pyridylcarboxylate or sodium L-prolinate produces the mononuclear complex [**4**]PF<sub>6</sub> and diastereometric complexes [**5**]PF<sub>6</sub>, respectively.



#### Clovis Peppe, Rafael Pavão das Chagas, Robert Alan Burrow

J. Organomet. Chem. 693 (2008) 3441

Indium(I) bromide-promoted stereoselective preparation of cyclopropanes via sequential aldol-type coupling/elimination/Michael-induced ring closure reaction from  $\alpha, \alpha$ -dichloroacetophenone and aldehydes The indium enolate generated from indium(I) bromide and  $\alpha$ , $\alpha$ -dichloroacetophenone reacts with aldehydes to produce (*syn* + *an*-*ti*)-2-chloro-3-hydroxy-propan-1-ones which can be converted to their *trans*-prop-2-en-1-ones derivatives upon reaction with an extra equivalent of InBr. The enones undergo Michael-induced ring closure reactions with an extra equivalent of the initial enolate to afford the corresponding cyclo-propane derivatives, according to a sequenced reaction mechanism.



#### Notes

#### Blanka Kašná, Roman Jambor, Markus Schürman, Klaus Jurkschat

J. Organomet. Chem. 693 (2008) 3446

Synthesis and characterization of novel intramolecularly O,C,O-coordinated heteroleptic organostannylenes and their tungstenpentacarbonyl complexes The syntheses are reported of the novel intramolecularly coordinated organostannylenes 1 and 2, and of their transition metal complexes 3–5. The strength of the intramolecular  $O \rightarrow Sn$  coordination is controlled by the identity of R, M, and X.



- **2**; R = *t*-Bu, X = Cl, [M] = lone pair **3**; R = Me, X = Cl, [M] = W(CO)<sub>5</sub> **4**; R = *t*-Bu, X = Cl, [M] = W(CO)<sub>5</sub>
- **5**; R = Me, X = H, [M] = W(CO)<sub>5</sub>

#### Andrey I. Poddel'sky, Nikolay V. Somov, Yury A. Kurskii, Vladimir K. Cherkasov, Gleb A. Abakumov

J. Organomet. Chem. 693 (2008) 3451

Hexacoordinate triphenylantimony(V) complex with tridentate bis-(3,5-di-*tert*butyl-phenolate-2-yl)-amine ligand: Synthesis, NMR and X-ray study Novel hexacoordinate complex [bis-(3,5di-*tert*-butyl-phenolate-2-yl)-amine]triphenylantimony(V), [(AP-AP)H]SbPh<sub>3</sub> (1) have been prepared and characterized. The molecular structure of 1·acetone was studied by a single-crystal X-ray. Compound 1 was found to be air-stable both in solid and in solution. Its oxidation by PbO<sub>2</sub> leads to paramagnetic [4,6-di-*tert*-butyl-*N*-(3,5-di-*tert*-butyl-phenolate-2-yl)-o-iminobenzosemiquinolato]triphenylantimony(V), [(AP-ISQ)]SbPh<sub>3</sub> (2).



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