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Carmen Leiva, H. Christine Lo, Richard H. Fish

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Aqueous organometallic chemistry. 3. Catalytic hydride transfer reactions with ketones and aldehydes using $[Cp*Rh(bpy)-(H_2O)](OTf)_2$ as the precatalyst and sodium formate as the hydride source: Kinetic and activation parameters, and the significance of steric and electronic effects Precatalyst, $[Cp^*Rh(bpy)(H_2O)](OTf)_2$ (1), with sodium formate provided the hydride complex, $[Cp^*Rh(bpy)(H)]^+$ (2), *in situ*, at pH 7.0, which was then evaluated in an aqueous, catalytic hydride transfer process with substrates that encompass 2-pentanone (3), cyclohexanone (4), acetophenone (5), propionaldehyde (6), benzaldehyde (7), and *p*-methoxybenzaldehyde (8). The relative rate scale at 23 °C: $8 > 7 \approx 6 > 5 >$ 4 > 3.



İrfan Acar, Halit Kantekin, Zekeriya Bıyıklıoğlu

J. Organomet. Chem. 695 (2010) 151

The synthesis, using microwave irradiation and characterization of novel, metal-free and metallophthalocyanines The synthesis of novel metal-free (4) and metallophthalocyanines (5, 6, 7 and 8) were prepared by cyclotetramerization of a novel 4-[2-(1-naphthyloxy)ethoxy]phthalonitrile (3). New substitute phthalocyanines showed the enhanced solubility in organic solvents. The new compounds were characterized by a combination of IR, ¹H NMR, ¹³C NMR, UV–Vis and MS spectral data.



Indira Torres-Sandoval, Simon K. Brayshaw, Paul R. Raithby, María J. Rosales-Hoz

J. Organomet. Chem. 695 (2010) 156

Reaction of the diyne complex $[Os_3(\mu-CO)(CO)_9{\mu_3-\eta^2-Me_3SiCCC\equivCSiMe_3}]$ with phosphines and phosphites: Characterization of monophosphine substituted clusters $[Os_3(\mu-CO)(CO)_8(PR_3){\mu_3-\eta^2-Me_3-}$ SiCCC \equiv CSiMe_3] (PR_3 = PPh_3, P(OEt)_3, PEt_3, PHPh_2 and Ph_2PCH_2PPh_2) The reaction of $[Os_3(\mu-CO)(CO)_9\{\mu_3-\eta^2-Me_3SiC\equivCC\equivCSiMe_3\}]$ with phosphorus donor ligands affords carbonyl mono-substitution products $[Os_3(\mu-CO)(CO)_8(L)\{\mu_3-\eta^2-Me_3SiC_2C_2SiMe_3\}]$ where the cluster geometry adopted can be related to the steric bulk of the phosphorus donor ligand.



Contents

A. García-Fernández, M.P. Gamasa, E. Lastra

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Alkyne activation by half-sandwich ruthenium(II) complexes bearing the water-soluble phosphane 1,3,5-triaza-7phosphaadamantane (PTA) Novel alkynyl [Ru($C \equiv CR$){ $\kappa^3(N,N,N)$ -Tp}-(PPh₃)(PTA)] and allenylidene [Ru{ $\kappa^3(N,N,N)$ -Tp}(PPh₃)(PTA)($C \equiv C \equiv CR_2$)][X] complexes have been isolated and characterized. Electrophilic attack led chemoselectively to the alkylation of the PTA ligand and no electrophilic attacks to the β -carbon of the alkynyl or to the allenylidene complexes have been detected.



Nick C. Johnstone, Elham S. Aazam, Peter B. Hitchcock, J. Robin Fulton

J. Organomet. Chem. 695 (2010) 170

Synthesis of aluminium complexes bearing a piperazine-based ligand system

Aluminium complexes bearing the *N*,*N*-chelating ligand 1,4-bis(2-hydroxy-3,5-di*tert*-butyl)piperazine have been synthesised. Both monometallic and bimetallic aluminium alkyl complexes have been generated, with the bimetallic species more stable in solution. A series of monometallic aluminium alkoxide complexes has also been synthesised.



Le Xin Song, Peng Xu, Zheng Dang

J. Organomet. Chem. 695 (2010) 177

Thermal release behavior of Fe⁺, CpFe⁺ and (Cp)₂Fe⁺ ions from the molecular aggregate of β -cyclodextrin with ferrocene

The special molecular structure of β -CD has served to prevent the sublimation of Fc, and its decomposition mode upon inclusion was drastically changed. This study provides a paradigm that the complexed Fc decomposes through the release of Fe⁺, CpFe⁺ and (Cp)₂Fe⁺ ions.



Raghubir Singh, Jugal Kishore Puri, Varinder Kaur Chahal, Raj Pal Sharma, Paloth Venugopalan

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Synthesis and reactivity of novel 3-isothiocyanatopropylsilatrane derived from aminopropylsilatrane: X-ray crystal structure and theoretical studies A novel silatrane 3-isothiocyanatopropylsilatrane has been synthesized and characterized by elemental analysis, spectroscopic methods and X-ray crystallography. The structure was correlated with theoretical studies such as semiempirical (AM1, PM3, PM3MM and MNDO), Density Functional Theory (B3LYP) and Hartree–Fock at $3-21+G^*$ and $6-31G^*(d)$ levels. The reactivity of compound was also studied with some Lewis acids and bases.



Zilu Chen, Jing Miao, Zhong Zhang, Fupei Liang, Qiang Wu

J. Organomet. Chem. 695 (2010) 189

Transition metal salts dependent intramolecular cyclization of a diimine The intramolecular cyclization of a new diimine of 1,4-bis(N-tosylethylamino)-2,3-diphenyl-1,4-diaza-1,3-butadiene presents a much dependence on the transition metal salts used. The presence of Ni(II) and Mn(II) salts induced the formation of a substituted imidazole with one imidazole ring, while the presence of $Cu(CH_3COO)_2$ ·H₂O led to the formation of a bicyclic derivative.



Satoshi Sakaguchi, Miaki Kawakami, Justin O'Neill, Kyung Soo Yoo, Kyung Woon Jung

J. Organomet. Chem. 695 (2010) 195

Tridentate, anionic tethered N-heterocyclic carbene of Pd(II) complexes

Efficient synthetic routes to two kinds of azolium salts, such as azolium iodide and chloride, having both N-anionic functional group and N-alkyl group have been developed. Thus, several anionic amidate/NHC–Pd complexes was successfully synthesized.



Eleazar Lumbreras Jr., Elizabeth M. Sisler, Quinetta D. Shelby

J. Organomet. Chem. 695 (2010) 201

Synthesis, X-ray crystal structure, and reactivity of $Pd_2(\mu$ -dotpm)₂ (dotpm = bis-(di-*ortho*-tolylphosphino)methane)

Alkylation of PdCl₂(dotpm) with *n*-butyllithium produces $Pd_2(\mu$ -dotpm)₂. The Pd– Pd bond distance in $Pd_2(\mu$ -dotpm)₂ is 2.8560(6) Å. Each palladium atom has a nearly linear geometry, and the methyl groups of the dotpm ligands shield the open coordination sites on both metal centers. $Pd_2(\mu$ -dotpm)₂ undergoes oxidative addition of dichloromethane to form $Pd_2Cl_2(\mu$ -CH₂)(μ -dotpm)₂.



Krishna K. Pandey, Agustí Lledós

J. Organomet. Chem. 695 (2010) 206

Linear versus bent bonding in metal-phosphinidene complexes: Theoretical studies of the electrophilic phosphinidene complexes $[(Cp)(CO)_2M \equiv PMe)]^+$, $[(Cp)(CO)_3M \equiv PMe)]^+$ (M = Cr, Mo, W) Theoretical calculations have been performed for the linear and bent phosphinidene complexes. The major differences between the linear and bent phosphinidene complexes are found in the degree of π -bonding. Linear complexes show a true M–P π bond and a deviated π bond due to slight bent M–P–C bond angles whereas bent complexes show a true M–P π bond and a lone-pair on phosphorus.



Hongyan Wang, Quan Du, Yaoming Xie, R. Bruce King, Henry F. Schaefer III

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The hapticity of cyclooctatetraene in its first row mononuclear transition metal carbonyl complexes: Several examples of octahapto coordination

The cyclooctatetraene metal carbonyls $C_8H_8M(CO)_n$ (M = Ti, V, Cr, Mn, Fe, Co, Ni; n = 4, 3, 2, 1) have been investigated by density functional theory. The lowest energy structures $(\eta^8 - C_8 H_8) Ti(CO)_n$ (n = 3, 2, 1)1), $(\eta^8 - C_8 H_8) M(CO)_n$ (M = V, Cr; n = 2, 1), and $(\eta^8 - C_8 H_8) Mn(CO)$ all are predicted to have octahapto η^8 -C₈H₈ rings. Other $C_8H_8M(CO)_3$ derivatives are predicted to have hexahapto, 1,2,3,4-tetrahapto, 1,2,5,6tetrahapto, or dihapto C₈H₈ rings.



Kota Thirumala Prasad, Bruno Therrien, Kollipara Mohan Rao

J. Organomet. Chem. 695 (2010) 226

Mono and dinuclear complexes of halfsandwich platinum group metals (Ru, Rh and Ir) bearing a flexible pyridyl-thiazole multidentate donor ligand

Reactions of η^5 - and η^6 -cyclichydrocarbons of platinum group metal complexes with flexible pyridyl-thiazole multidentate donor ligand 4,4'-bis(2-pyridyl-4-thiazole) (L) resulted in the formation of mono and dinuclear complexes.



Fatou Ba, Francoise Robin-Le Guen, Nolwenn Cabon, Pascal Le Poul, Stéphane Golhen, Nicolas Le Poul, Bertrand Caro

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Ferrocenyl and pyridyl methylenepyrans as potential precursors of organometallic electron-rich extended bipyrans: Synthesis, characterization and crystal structure

Guoliang Li, Oian-Shu Li, Yaoming Xie, R. Bruce King, Henry F. Schaefer III

J. Organomet. Chem. 695 (2010) 244

Formation of a four-electron donor carbonyl group in the decarbonylation of the unsaturated H₂C₂Fe₂(CO)₆ tetrahedrane as an alternative to an iron-iron triple bond

Ferrocenyl and pyridyl methylenepyrans were obtained from a Wittig reaction between a pyran phosphorane and ferrocenyl or pyridylaldehvdes. The nucleophilic nature of the exocyclic C-C bond allowed the formylation of these compounds by a Vilsmeier type reaction. All new products were characterized by IR spectroscopy, ¹H and ¹³C NMR spectroscopy, Mass spectroscopy and (or) elemental analysis. Electrochemistry of representative compounds 2, 10 and 13 was undertaken. In addition, a crystal structure of the ferrocenyl pyranylidene acetaldehyde 5 was described and the pyrylium character of this compound specified.

Density functional theory predicts an Fe_2C_2 tetrahedrane structure for $H_2C_2Fe_2(CO)_6$ with a formal Fe=Fe double bond very similar to the experimental structure for t-Bu₂C₂Fe₂(CO)₆. Decarbonylation of H₂C₂- $Fe_2(CO)_6$ is predicted to give an $H_2C_2Fe_2$ - $(CO)_5$ isomer retaining the Fe₂C₂ tetrahedrane structure with an Fe=Fe double bond but with a four-electron donor bridging carbonyl group.





Gilles Gasser, Jonathan D. Carr, Simon J. Coles, Stephen J. Green, Michael B. Hursthouse, Sean M. Cafferkey, Helen Stoeckli-Evans, James H.R. Tucker

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Synthesis and complexation properties of novel triazoyl-based ferrocenyl ligands

The full characterisation and binding properties of two new ferrocene-containing ligands, which have been designed to form $[2 \times 2]$ grids upon complexation with metal ions, is described.

Fel OI ONS

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

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Step by step palladium mediated syntheses of new 2-(pyridin-2-yl)-6-R-nicotinic acids and esters

C(3) functionalization of 6-alkyl-substituted-2,2'-bipyridines was achieved through "rollover cyclopalladation" followed by carbonylation. The reaction produced novel and rare 2-(2-pyridin-2-yl)-6alkyl-nicotinic acids or esters which contain the core of the nicotinic acid and therefore are of biological and pharmaceutical interest.



Luba Kaganovsky, Dmitri Gelman, Karola Rueck-Braun

J. Organomet. Chem. 695 (2010) 260

Trans-chelating ligands in palladium-catalyzed carbonylative coupling and methoxycarbonylation of aryl halides The manuscript describes the use of a *trans*-chelated palladium complex derived from 1,8-bis-(4-(diphenylphosphino)phe-nyl)anthracene (1) and *p*-TolPdI(TMEDA) as a precatalyst in carbonylative Suzuki coupling and methoxycarbonylation of aryl iodides and bromides. The catalyst is active in 0.01–1 mol% loading and demonstrates highly selective transformations. The selectivity is attributed to the unique structural features of the *trans*-chelating ligands.



Fatma Eroğlu, Didem Kâhya, Ender Erdik

J. Organomet. Chem. 695 (2010) 267

Sulfonyl transfer mechanism in C–S coupling of phenylmagnesium bromide with phenyl arenesulfonates The kinetics of C–S coupling of phenylmagnesium bromide with phenyl arenesulfonates has been studied in THF:toluene (7:10) at 90 °C. Kinetic data and Hammett relationship are consistent with an asynchronous S_N a mechanism in which rate determining thiophilic attack of carbanion takes place much ahead of phenoxy group departure.

PhMgBr + χ So₂OPh $\xrightarrow{\text{THF: toluene}}$ χ So₂Ph + PhOMgBr Y: H, 4-Me, 3-Me, 4-t-Bu, 4-MeO

Contents

Petr Štěpnička, Ivana Císařová, Aleš Růžička

J. Organomet. Chem. 695 (2010) 271

Preparation and structural characterization of simple and donor-substituted triorganostannyl 1'-(diphenylphosphino)-1-ferrocenecarboxylates and their P-chalcogenide derivatives A series of triorganotin carboxylates [Fe-(η^{5} -C₅H₄P(E)Ph₂)(η^{5} -C₅H₄CO₂SnR₃)] (SnR₃/ E = SnMe₃/void^{*}, SnMe₃/O^{*}, SnMe₃/S; SnPh₃/void, SnMe₂(L^{NC})/void^{*}, SnMe₂(L^{NC})/ O^{*}, and SnMe₂(L^{NC})/S^{*}) have been prepared and characterized by spectroscopic methods. Crystal structures of five representatives (denoted with an asterisk) have been determined by X-ray crystallography, revealing a decisive influence of the substitution pattern at tin (L^{NC} vs. simple substituents) and the nature of the phosphorus group (P vs. P=O/P=S) on the solidstate structures.



Marcel Kahnes, Julia Richthof, Helmar Görls, Daniel Escudero, Leticia González, Matthias Westerhausen

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Mechanistic studies on the alcoholysis and aminolysis of $[(MeZn)_2\{\mu\text{-}N(H)tBu\}\{\mu\text{-}N-(CH_2Py)_2\}]$

Treatment of $[(MeZn)2\{\mu-N(H)tBu\}\{\mu-N-(CH2Py)2\}]$ with methanol or t-butylamine leads to the exchange of the μ -N(H)tBu moiety. Extensive DFT calculations on the mechanism predict intermediates with Zn[μ -(X···H···Y)]Zn (X = O, N; Y = N) functionalities which could be detected by ¹H NMR spectroscopy.



Shigekazu Ito, Shuhei Kusano, Noboru Morita, Koichi Mikami, Masaaki Yoshifuji

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Ligand effect of bulky 2,2-dialkyl-1-phosphaethenes on Au-catalyzed cycloisomerization of 1,6-enynes and lactonization of pent-4-ynoic acids Mononuclear phosphaalkene–chlorogold(I) complexes [Mes*P=CRR'][AuCl] (R, R' = Me, CH₂Ph; Mes* = 2,4,6-'Bu₃C₆H₂) catalyzed cyclizations of 1,6-enynes and pent-4-ynoic acids affording vinylcyclopentenes and methylenelactones, respectively, in the absence of co-catalyst.



Jin Zhou, Xiaoyan Li, Hongjian Sun

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An efficient and recyclable water-soluble cyclopalladated complex for aqueous Suzuki reactions under aerial conditions

A new water-soluble cyclopalladated complex was proved to be an efficiently recyclable catalyst precursor for Suzuki reactions in neat water under aerial conditions without additives.



Notes

V.P. Dyadchenko, N.M. Belov, D.A. Lemenovskii, M.Yu. Antipin, K.A. Lyssenko, A.E. Bruce, M.R.M. Bruce

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Synthesis, crystal and molecular structure of gold(I) thiophenolate with 4'-ferroce-nyl[1,1']biphenylisocyanides

The syntheses of ferrocenylbiphenylisocyanide gold(I) thiophenolato complexes are described. The preparative route starts from ferrocenylphenylbromide and proceeds in six steps. The synthetic pathways were developed as a first step toward preparing metallomesogens based on ferrocenyl-polyphenylenes coordinated to gold(I) thiophenolates.



Dennis Troegel, Frank Möller, Reinhold Tacke

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(2-Halogeno-5-pyridyl)dimethyl(oxiran-2ylmethyl)silanes: New potential building blocks for the synthesis of silicon-containing drugs The (2-halogeno-5-pyridyl)dimethyl(oxiran-2-ylmethyl)-silanes **1a** and **1b** were prepared in two-step syntheses, starting from allylchlorodimethylsilane. Compounds **1a** and **1b** were characterized by elemental analyses and NMR studies. With the synthesis of compounds **1a** and **1b**, new potential building blocks for the synthesis of silicon-containing drugs have been made accessible.





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