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Regular papers

Ch.G. Hartinger, A.A. Nazarov, M. Galanski, M. Reithofer, B.K. Keppler

J. Organomet. Chem. 690 (2005) 3301

Glucose ferrocenyl-oxazolines: Coordination behavior toward $[\text{Pd}(\eta^3\text{-allyl})\text{Cl}]_2$ studied by ESI-MS

The synthesis of new glucose-oxazolinyl-ferrocenes is reported. The coordination behavior of two representative ligands to-ward $[Pd(\eta^3-C_3H_5)Cl]_2$ was studied by electrospray ionization mass spectrometry.



George R. Clark, Guo-Liang Lu, Clifton E.F. Rickard, Warren R. Roper, L. James Wright

J. Organomet. Chem. 690 (2005) 3309

Metallacyclic complexes with *ortho*-silylated triphenylphosphine ligands, $L_nOs(\kappa^2(Si,P)-SiMe_2C_6H_4PPh_2)$, derived from thermal reactions of the coordinatively unsaturated trimethylsilyl, methyl complex, $Os(SiMe_3)-(Me)(CO)(PPh_3)_2$

Coordinatively unsaturated Os(SiMe₃)(Me)-(CO)(PPh₃)₂ undergoes a facile thermal reaction to give the *ortho*-silylated as well as *ortho*-metallated complex, Os($\kappa^2(Si,P)$ -SiMe₂C₆H₄PPh₂)($\kappa^2(C,P)$ C₆H₄PPh₂)(CO)-(PPh₃), with retention of the Os–Si bond. This reaction may proceed through the intermediacy of a silylene complex.



Fausto Calderazzo, Ulli Englert, Guido Pampaloni, Manuel Volpe

J. Organomet. Chem. 690 (2005) 3321

Redox reactions with $bis(\eta^6$ -arene) derivatives of early transition metals

Redox reactions with $M(\eta^6\text{-arene})_2$ derivatives (M = Ti, Cr, Mo, arene = MeC_6H_5 ; M = V, Nb, arene = 1,3,5-Me₃C₆H₃) have been investigated. Oxidation of the arene derivatives of early transition elements (Ti, V, Nb) proceeds inviably with loss of the coordianted arene ligands. Formation of $[M(\eta^6\text{-MeC}_6H_5)_2]^+$ cations has been observed for chromium and molybdenum.



Elena I. Klimova, Tatiana Klimova Berestneva, Simon Hernández Ortega, Daniel Méndez Iturbide, Alfonso García Marquez, Marcos Martínez García

J. Organomet. Chem. 690 (2005) 3333

Diferrocenylcyclopropenyl cations. Synthesis, structures, and some chemical properties

Contents

Synthesis of diferrocenylcyclopropenyl tetrafluoroborates with hetero-substituents in the three-membered ring, viz., ethoxy, trityloxy, ferrocenyl(phenyl)methoxy, *N*,*N*-diethylamino, piperidino, and morpholino, is described. The spatial structure of diferrocenyl(morpholino)cyclo-propenyl tetrafluoroborate was established based on the data from X-ray diffraction analysis. Under the action of potassium *tert*-butoxide, all the diferrocenylcyclopropenyl tetrafluoroborates undergo three-membered ring-opening with formation of the corresponding 2,3-diferrocenylacrylic acid derivatives.





Wade J. Mace, Lyndsay Main, Brian K. Nicholson

J. Organomet. Chem. 690 (2005) 3340

Reversible pyranyl complex formation and the mechanism of rearrangement to $(\eta^{5}-6-$ oxocycloheptadienyl)Mn(CO)₃ complexes in the reaction of β -cyclomanganated 1,5-diarylpenta-1,4-dien-3-ones and alkynes; the crystal structure of [2,4-diphenyl-6-(2-phenylethenyl)pyranyl- η^{5}]tricarbonylmanganese

[1-Phenyl-2-[(*E*)-3-phenylprop-2-en-1-oyl-3d- κO]ethenyl- κC^1]tetracarbonylmanganese reacts with phenylacetylene to form the *endo*-7-Ph isomer of [6-oxo-2,4,7-triphenyl-7d-cyclohepta-1,4-dienyl-1,2,3,4,5- η]tricarbonylmanganese, implicating a cyclopropyl carbonyl-addition intermediate or a cyclopropyl acyl-substitution transition state in the key rearrangement step from the initially formed pyranyl complex. Also reported are some new (oxocycloheptadienyl)Mn-(CO)₃ and (pyranyl)Mn(CO)₃ complexes from other alkynes and cyclomanganated dienones.



Warren Tully, Lyndsay Main, Brian K. Nicholson

J. Organomet. Chem. 690 (2005) 3348

N- vs *O*-Coordination in cyclomanganation of 1,5-diaryl-3-(2-pyridyl)pentane-1,5-diones and 3-(2-pyridyl)chalcones; cyclomanganation at saturated carbon and the crystal structure of [1,5-diphenyl- κC^2 -3-(2-pyridyl- κN)pentan-2-yl- κC^2 -1,5-dione- $\kappa O^1 \kappa O^5$]tetracarbonylmangan esetricarbonylmanganese 1,5-Diphenyl-3-(2-pyridyl)pentane-1,5-dione with 2.5 moles of PhCH₂Mn(CO)₅ gives mostly a dimanganation product whose Xray crystal structure reveals rare manganation at a saturated carbon (**6a**). 1,5-Dithienyl analogues of **6a** are also reported, as well as cyclomanganation products from two β -(2pyridyl)chalcones.



Oscar Mendoza, Helge Müller-Bunz, Matthias Tacke

J. Organomet. Chem. 690 (2005) 3357

Cocondensation reactions of nitrogen- containing heterocycles with lithium atoms at 77 $\rm K$

Lithium atoms were cocondensed with aromatic nitrogen-containing heterocycles in the presence of THF. The reaction led to a variety of products depending on the heterocyclic compound used. C–H activation, dimerisation of reactants and dimerised hexadienes were the main products found.



Yessenia Ocasio-Delgado, Jonathan de Jesús-Segarra, José E. Cortés-Figueroa

J. Organomet. Chem. 690 (2005) 3366

A biphasic displacement of [60]fullerene from *fac*-(dihapto-[60]fullerene)(dihapto-1, 10-phenanthroline) tricarbonyl molybdenum (0) The ligand/[60]fullerene exchange reactions on fac-(η^2 -C₆₀)(η^2 -phen)Mo(CO)₃ are biphasic where the first segment of the biphasic plot corresponds to formation of fac-(η^1 -L)(η^2 -phen)Mo(CO)₃ and the second segment corresponds to decomposition of fac-(η^1 -L)(η^2 -phen)Mo(CO)₃. Results from this investigation support some degree of solvent–Mo bond formation in the transition state leading to formation of fac-(solvent)(η^2 -phen)Mo(CO)₃. The Mo–C₆₀ bond is estimated to be in the vicinity of 110 kJ/ mol.



Edward J. Crust, Ian J. Munslow, Peter Scott

J. Organomet. Chem. 690 (2005) 3373

Diazaallyls of group 4 metals based on *trans*-1,2-diaminocyclohexane

Bis(aminopyridinato) and bis(aminothiazolinato) ligands based on 1,2-diaminocyclohexane give complexes of zirconium in which the N_4M unit is distorted from planarity by the presence of the chiral backbone. For the smaller metal Ti, X-ray crystallography shows that the constrained architecture leads to coordination of three N atoms only.

Mona Bogza, Thomas Oeser, Janet Blümel

J. Organomet. Chem. 690 (2005) 3383

Synthesis, structure, immobilization and solid-state NMR of new dppp- and tripod-type chelate linkers

The chelating phosphines (EtO)Si-(CH₂PPh₂)₃, (EtO)₂Si(CH₂PPh₂)₂, and Si-(CH₂PPh₂)₄, and two metal complexes, (EtO)₂Si(CH₂PPh₂)₂PdCl₂ and (EtO)Si(CH₂-PPh₂)₃W(CO)₃, have been synthesized in high yields. The ethoxysilane linkers, as well as a Pd complex thereof have been characterized by X-ray structures. All compounds have been successfully immobilized on silica, as proven by ³¹P solid-state NMR of the dry materials and of the suspensions.



Kevin R. Flower, Laura G. Leal, Robin G. Pritchard

J. Organomet. Chem. 690 (2005) 3390

The synthesis and crystallographic characterisation of the complexes [RuX-(CO)(η^2 -C,N- $C_6H_5C(H)NC_6H_4$ -4Me)(P-Ph₃)₂]·CHCl₃ (X = Cl, Br, I, F): Evidence for competing Ru–X···Cl–CHCl₂ and Ru–X···HCCl₃ interactions in the solid state

The compounds $[RuX(CO)(\eta^2-C,N-C_6H_5-C(H)=NC_6H_4-4Me)(PPh_3)_2] \cdot CHCl_3$ (X = Cl, Br, I) have been prepared and crystallographically characterised. The Ru–X bond engages in hydrogen or halogen bonding to a chloroform of crystallisation.

 $\begin{array}{c} \operatorname{Ru} & \xrightarrow{} X & \cdots \\ \operatorname{or} \\ \operatorname{Ru} & \xrightarrow{} X & \cdots \\ \operatorname{Cl} & \xrightarrow{} \operatorname{CHCl}_2 \end{array}$

Elizaveta P. Shestakova, Yuri S. Varshavsky, Aleksei B. Nikolskii

J. Organomet. Chem. 690 (2005) 3397

Reactivity of cationic methyl rhodium(III) complexes *cis*-[Rh(β -diket)(PPh₃)₂(CH₃)(CH₃-CN)][BPh₄] toward ligands of different character: pyridine, carbon monoxide, and triphenylphosphine Cationic methyl complexes of rhodium(III), cis-[Rh(β -diket)(PPh₃)₂(CH₃)(CH₃CN)][B-Ph₄], react readily with ligands of different nature (pyridine, carbon monoxide, triphenylphosphine). On the action of carbon monoxide, they yield pentacoordinate acetyl complexes.



Guiyun Zhong, Qingfu Liu, Xueqing Song, George Eng, Qinglan Xie

J. Organomet. Chem. 690 (2005) 3405

Studies of the reaction of dimethyltin dichloride with mercaptoacetic acid in the presence of amines and crystal structure of $[(n-Pr)_3NH][Me_2Sn(\mu^2-SCH_2COO)CI]$

A series of new five-coordinated ionic organotin(IV) complexes with general formula [Q][Me₂Sn(μ^2 -SCH₂COO)CI] have been synthesized and characterized by elemental analyses, IR and ¹H NMR spectroscopies. The crystal structure of [(*n*-Pr)₃NH][Me₂Sn(μ^2 -SCH₂COO)CI] was determined by X-ray crystallography.

Christopher S. Griffith, George A. Koutsantonis, Brian W. Skelton, Allan H. White

J. Organomet. Chem. 690 (2005) 3410

Transformation of C_2 units on a bimetallic tetranuclear cluster. Reactivity of $[Ru_3-Mo(\mu_3-\eta^1-CC)(\mu-CO)_3(CO)_2(\eta-C_5H_4R)_3(\eta-C_5H_5)]$ (R = H, Me) The reactivity of $[Ru_3Mo(\mu_4-\eta^2-CC)(\mu-CO)_3(CO)_2(\eta-C_5H_4R)_3(\eta-C_5H_5)]$ (R = H; Me) have been investigated, initially to elucidate the nature of the starting material, and, latterly, to define the reactivity of an interesting ethane-1,2-bis(ylidyne) species. While the mixed RuMo clusters were unreactive towards simple electrophiles and carbonyl substitution by phosphine ligands they did react with atmospheric oxygen or carbon monoxide to give substantially different products.

Michael S. Datt, Jerald J. Nair, Stefanus Otto

J. Organomet. Chem. 690 (2005) 3422

Synthesis and characterisation of two novel Rh(I) carbene complexes: Crystal structure of $[Rh(acac)(CO)(L_1)]$

Two [Rh(acac)(CO)(L)] (L = carbene) complexes were prepared and evaluated as catalyst precursors in the hydroformylation of 1-hexene. In the presence of an added phosphine or phosphite ligand no added benefit is derived from the presence of the carbene ligand as compared to using [Rh-(acac)(CO)₂] as catalyst precursor. ³¹P NMR spectroscopy indicates liberation of the carbene under these conditions.



M.Z. Kassaee, S. Arshadi, M. Acedy, E. Vessally

J. Organomet. Chem. 690 (2005) 3427

Singlet-triplet energy separations in divalent five-membered cyclic conjugated C_5H_3X , C_4H_3SiX , C_4H_3GeX , C_4H_3SnX , and C_4H_3PbX (X = H, F, Cl, and Br)

Ab initio and DFT calculations on 2X- and/ or 3X-cyclopenta-2,4-dien-ylidenes, and their group 14 analogous (silylenes, germylenes, stanylenes and plumbylenes; M = Si, Ge, Sn, and Pb, respectively), show linear relationships between singlet-triplet energy gaps with: (a) the size of the divalent element (M), (b) the C–M–C angle, and (c) the $\Delta G_{(LUMO-HOMO)}$ of the singlet states involved (for X = H, F, Cl, Br).



Michael W. Stoddart, John H. Brownie, Michael C. Baird, Hartmut L. Schmider

J. Organomet. Chem. 690 (2005) 3440

On the coordination chemistry of corannulene, the smallest "buckybowl"

An extensive series of attempts to synthesize the compounds (η^6 -corannulene)M(CO)₃ (M = Cr, Mo, W), utilizing virtually every standard and non-standard procedure known for the synthesis of compounds of the type (η^6 -arene)M(CO)₃, have all failed miserably. DFT calculations suggest that the η^6 -corannulene–Cr bond of (η^6 -corannulene)Cr(CO)₃ is only marginally weaker than the correspond arene–metal bond in the very stable (η^6 -benzene)Cr(CO)₃, and it seems that the reasons for synthetic failures are kinetic in nature.



Shinichi Saito, Kouhei Takeuchi, Takaya Mise, Yasuo Wakatsuki

J. Organomet. Chem. 690 (2005) 3451

Ruthenium-catalyzed cycloisomerization of 1,1,2,2-tetramethyl-1,2-divinyldisilane: Selective formation of a five-membered silacycle

We carried out the isomerization of 1,1,2,2tetramethyl-1,2-divinyldisilane in the presence of various ruthenium–diphosphine complexes and observed the highly selective formation of a five-membered silacycle in the presence of a ruthenium–dppv complex. The mechanism of this reaction was also discussed.



Irina Odinets, Tamás Kégl, Elena Sharova, Oleg Artyushin, Evgenii Goryunov, Galina Molchanova, Konstantin Lyssenko, Tatyana Mastryukova, Gerd-Volker Röschenthaler, György Keglevich, László Kollár

J. Organomet. Chem. 690 (2005) 3456

Novel α -fluorinated cyclic phosphite and phosphinite ligands and their Rh-complexes as suitable catalysts in hydroformylation

Benzoanellated cyclic phosphite (1) and phosphinite (5) ligands with fluorine containing substituents were synthesized and converted to Rh^{III}(L)(Cp^{*})Cl₂ complexes (4 and **6**, respectively, where L = 1 and 5). In two cases their stereostructures were evaluated. The enantiomers of complex **6a** were separated by spontaneous resolution. The complexes (4 and 6) were tested in the hydroformylation of styrene. In situ systems formed from Rh^I(CO)₂(acac) precursor and the above P-ligands were also investigated and were found to be more efficient than the preformed ones.



Padavattan Govindaswamy,

Chittaranjan Sinha, Mohan Rao Kollipara J. Organomet. Chem. 690 (2005) 3465

Syntheses and characterization of η^5 cyclopentadienyl and η^5 -indenyl ruthenium-(II) complexes of arylazoimidazoles: The molecular structure of the complex $[(\eta^5-C_5H_5)Ru(PPh_3)(C_6H_5-N=N-C_3H_3N_2)]^+$ The reaction of $[Cp'Ru(PPh_3)_2Cl]$ $(Cp' = C_5H_5, C_9H_7)$ with arylazoimidazole (RaaiR') ligands in the presence of ammonium hexafluorophosphate generates greenish-brown and brown colored mononuclear cationic complexes $[Cp'Ru(PPh_3)(RaaiR')]^+$. The representative complex **2** has been established by X-ray diffraction study.

Zachary S. Sales, Roger Nassar, J. Jacob Morris, Kenneth W. Henderson

J. Organomet. Chem. 690 (2005) 3474

Stereoselective synthesis of enones from the reaction of aldehydes with sterically hindered dimethylaluminum enolates

Aluminum enolates may be prepared from the reaction of Me_3Al with sterically hindered aromatic ketones. The resulting metal enolates undergo aldol addition reactions with aldehydes at elevated temperatures, and the resulting aldolates rapidly eliminate to form stable enone products.

Yan-Jun Zhu, Jin-Xiang Chen, Wen-Hua Zhang, Zhi-Gang Ren, Yong Zhang, Jian-Ping Lang, Seik-Weng Ng

J. Organomet. Chem. 690 (2005) 3479

Syntheses, crystal structures and luminescent properties of two novel lanthanide/4-pya complexes: $[Ln(4-pya)_3(H_2O)_2]_2$ (Ln = Eu, La; 4-pya = *trans*-4-pyridylacrylate)

Two new lanthanide/4-pya complexes [Ln(4pya)₃(H₂O)₂]₂ (1: Ln = Eu; **2**: Ln = La) were isolated either from reactions of Ln₂O₃ and *trans*-4-pyridylacrylic acid (4-Hpya) or from reactions of LnCl₃ · 6H₂O with 4-Hpya/ aqueous ammonia in EtOH/H₂O or in MeOH/H₂O. The structures of both compounds were characterized by X-ray crystallography and their luminescent properties in solid state were studied.

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