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Contents

Regular papers

Jaisheila Rajput, Alan T. Hutton, John R. Moss, Hong Su, Christopher Imrie

J. Organomet. Chem. 691 (2006) 4573

Ferrocenyl-nitrogen donor ligands. Synthesis and characterization of rhodium(I) complexes of ferrocenylpyridine and related ligands

The preparation of a series of complexes of the types $[RhCl(CO)_2(L)]$, [RhCl(cod)(L)] and $[Rh(cod)(L)_2]ClO_4$, where L is a ligand incorporating a ferrocenyl group and a pyridine ring, is described.



J. Organomet. Chem. 691 (2006) 4589

Theoretical investigation of the electronic structure of 1-(3,4; 3,5 and 3,6-bis-seleno-cyanato-phenyl) pyrrolidinofullerenes

We have examined 1-(3,4; 3,5 and 3,6-bis-selenocyanato-phenyl)pyrrolidinofullerenes systems theoretically using DFT theory. Full geometry optimization was performed for the systems studied at the B3LYP/3-21G* and B3LYP/6-31G* levels of theory. The optimized structures and the electronic properties of the molecules are obtained. On all levels of theory the *ortho* isomer is predicted to be the most stable.



Frédéric-Georges Fontaine, Karl A. Tupper, T. Don Tilley

J. Organomet. Chem. 691 (2006) 4595

Synthesis, characterization and reactivity of tetramethylphospholyl complexes of scandium

Reaction of $(C_4Me_4P)Li(tmeda)$ with ScCl₃-(THF)₃ gave the new compound $(\eta^5-C_4Me_4P)_2ScCl_2Li(tmeda)$ (1). A phospholyl moiety in 1 is labile, as demonstrated by reactions of 1 with LiCH(SiMe_3)_2 and Cp^{*}-Li (Cp^{*} = C_5Me_5) to afford, respectively, $(\eta^5-Me_4C_4P)Sc[CH(SiMe_3)_2]Cl_2Li(tmeda)$ and $(\eta^5-Me_4C_4P)Cp^*ScCl_2Li(tmeda)$.



Michael I. Bruce, Marcus L. Cole, Maryka Gaudio, Brian W. Skelton, Allan H. White

J. Organomet. Chem. 691 (2006) 4601

Some complexes containing carbon chains end-capped by $M(CO)_2Tp'$ [M = Mo, W; $Tp' = HB(pz)_3$, $HB(dmpz)_3$] groups

 $M \equiv CC \equiv CAu(PPh_3) (CO)_2 Tp'$ Reactions of (M = Mo 5, W 6) with $Co_3(\mu_3-CBr)(\mu-dppm)(CO)_7$ give the C₄-bridged $\{Tp(OC)_2M\}\equiv CC\equiv CC\equiv$ $\{Co_3(\mu-dppm)(CO)_7\}$ (M = Mo 7, W 8), while Mo(=CBr)(CO)₂Tp* and Co₃{µ₃-C(C=C)₂Au-(PPh₃)}(µ-dppm)(CO)₇ give {Tp^{*}(OC)₂Mo}=C(C=C)₂- $C \equiv \{Co_3(\mu-dppm)(CO)_7\}$ (9). The C₃ complexes $Tp'(OC)_2M \equiv CC \equiv CRu(dppe)Cp^*$ (Tp' = Tp, M =Mo 10, W 11; $Tp' = Tp^*$, M = Mo 12) were obtained from 2-4 and RuCl(dppe)Cp* via KF-induced metalla-desilylation reactions, while reactions between $Mo(\equiv CBr)(CO)_2Tp^*$ and $Ru\{(C\equiv C)_nAu(PPh_3)\}$ - $(dppe)Cp^*$ (n = 2, 3) afforded $\{Tp^*(OC)_2Mo\}\equiv C$ - $(C \equiv C)_n \{ Ru(dppe) Cp^* \}$ (*n* = 2 13, 3 14), respectively.

M = Mo (2), W (4) H = Mo (7), W (8)

Evans O. Changamu, Holger B. Friedrich, Martin O. Onani, Melanie Rademeyer

J. Organomet. Chem. 691 (2006) 4615

Reaction studies on some functionalized alkyl transition metal compounds and the crystal structure of $[Cp(CO)_3W\{(CH_2)_3NO_2\}]$

Reactions of $[Cp(CO)_3W\{(CH_2)_nX\}]$ (n = 3-5; X = Br, I) with nucleophiles Z^- gave $[Cp(CO)_3W\{(CH_2)_nZ\}]$, whilst those of $[Cp(CO)_2(PPhMe_2)Mo\{(CH_2)_nBr\}]$ gave substitution or cyclic carbene compounds. Reactions of the heterobimetallic compounds, $[Cp(CO)_3W\{(CH_{2})_3Mo(CO)L_y]$ { $L_y = (CO)_2$ -Cp, (CO)_2Cp * and (CO)(PMe_3)Cp}, with PPh_3 and CO were found to be totally metalloselective. Hydrolysis of $[Cp(CO)_3W(CH_2)_3C(O)-Mo(CO)(PPh_3)(PMe_3)Cp]$ gave $[Cp(CO)_3-W\{(CH_2)_3COOH\}]$, whilst thermolysis of $[Cp(CO)_2Fe(CH_2)_3Mo(CO)_2(PMe_3)Cp]$ gave cyclopropane and propene.

$$\begin{split} Cp(CO)_3W\{(CH_2)_3\}Mo(CO)L_y + Y &\longrightarrow Cp(CO)_3W\{(CH_2)_3\}C(O)MoL_yY\\ &Y=PPh_3, or CO; L_y=(CO)_2Cp, \ (CO)_2Cp^* \ or (CO)PMe_3Cp \end{split}$$

Stefanus Otto, Andreas Roodt

J. Organomet. Chem. 691 (2006) 4626

Reactivity studies of *trans*-[PtClMe(SMe₂)₂] towards anionic and neutral ligand substitution processes

The substitution behaviour of *trans*-[PtClMe(SMe₂)₂] towards anionic and neutral ligands was investigated using stopped-flow spectrophotometry. The anionic ligands substitute the Cl⁻ ligand while the neural ligands substitute a SMe₂ ligand in the first step. All reactions follow an associative mode of activation as confirmed by large negative entropies of activation.



Jun Hou, Xiaojun Peng, Zhiyou Zhou, Shigang Sun, Xing Zhao, Shang Gao

J. Organomet. Chem. 691 (2006) 4633

Tris(*N*-pyrrolidinyl)phosphine substituted diiron dithiolate related to iron-only hydrogenase active site: Synthesis, characterization and electrochemical properties A tris(*N*-pyrrolidinyl)phosphine monosubstituted complex, $[(\mu$ -pdt)Fe₂(CO)₅P(NC₄H₈)₃] was synthesized as a functional model of the hydrogen-producing capability of the iron hydrogenase active site.



Lei Zhang, Jie Sun, Huping Zhu, Qiang Xu, Nobuko Tsumori, Jiabi Chen

J. Organomet. Chem. 691 (2006) 4641

Syntheses, structures and reactivities of diindenyl-coordinated diiron bridging carbene complexes

A new type of diindenyl-coordinated diiron bridging alkoxycarbene complexes 2–4 were synthesized, and the reactions of the cationic bridging carbyne complex of 4 with nucleophiles involving carbonylmetal anions were investigated, which afforded a series of the new diindenyl-coordinated diiron bridging carbene complexes.



Stephan Enthaler, Ralf Jackstell, Bernhard Hagemann, Kathrin Junge, Giulia Erre, Matthias Beller

J. Organomet. Chem. 691 (2006) 4652

Efficient transfer hydrogenation of ketones in the presence of ruthenium *N*-heterocyclic carbene catalysts

Various ruthenium carbene complexes have been *in situ* generated and tested for transfer hydrogenation of aromatic and aliphatic ketones. Turnover frequencies up to 346 h⁻¹ were obtained for reduction of acetophenone. In addition a comparative study involving ruthenium carbene and ruthenium phosphine complexes has been performed.



Elizabeth A. Duplessis, Paul A. Jelliss, Charles C. Kirkpatrick, Shelley D. Minteer, Keith M. Wampler

J. Organomet. Chem. 691 (2006) 4660

Electrocatalytic reductive dimerization of the 2,2'-bipyridyl tungsten alkylidyne complex $[W(\equiv CC_6H_4NMe_2-4)(NCMe)(CO)_2\{\kappa^2-2,2'-(NC_5H_4)_2\}]^+$

Reductive electrodimerization of the cationic tungsten alkylidyne complex $[W(\equiv CC_6H_4N-Me_2-4)(NCMe)(CO)_2\{\kappa^2-2,2'-(NC_5H_4)_2\}]^+$ has been observed by cyclic voltammetry measurements and verified by subsequent data analysis. The coupled product is deposited on the electrode and appears to act as an electrocatalyst in subsequent potential cycles. Experimental results are supported by DFT computational analysis, which indicates a 2,2'-bipyridyl-centered LUMO and surprisingly little contribution from the MeCN ligand to the frontier HOMOs.



Jack W. Faller, Philip P. Fontaine

J. Organomet. Chem. 691 (2006) 4667

Stereodynamics and conformational equilibria in some chiral pseudo-octahedral tungsten crotyl complexes The stereodynamics of the complexes $W(CO)_2(\eta^3 \text{-crotyl})(\text{diphos})X$, where X = Cl and I were investigated with focus on the effect of the crotyl ligand on the chirality at the metal. The spontaneous resolution of the neutral complex $W(CO)_2(\eta^3 \text{-crotyl})(\text{diphos})Cl$ provides a route for obtaining optically active samples of these compounds.



William H. Watson, Bhaskar Poola, Michael G. Richmond

J. Organomet. Chem. 691 (2006) 4676

Synthesis and diphosphine ligand fluxionality in $Os_3(CO)_{10}(bmi)$: Kinetic evidence for nondissociative diphosphine isomerization and X-ray crystal structure of 1,1-Os₃-(CO)₁₀(bmi) The diphosphine ligand 2,3-bis(diphenylphosphino)-N-*p*-tolylmaleimide (bmi) reacts with the activated cluster $1,2-Os_3(CO)_{10}(MeCN)_2$ at room temperature to give the diphosphinebridged cluster $1,2-Os_3(CO)_{10}(bmi)$ (**2b**) as the major product. Heating cluster **2b** under CO produces the chelating isomer $1,1-Os_3-(CO)_{10}(bmi)$ (**2c**) in quantitative yield. The isomerization reaction exhibits first-order kinetics and proceeds via a nondissociative migration of the bmi ligand about the triosmium cluster. These new clusters have been fully characterized in solution and by X-ray diffraction analysis in case of $1,1-Os_3-(CO)_{10}(bmi)$.



Alok Goel, David Savage, Steven R. Alley, Tara Hogan, Paula N. Kelly, Sylvia M. Draper, Christopher M. Fitchett, Peter T.M. Kenny

J. Organomet. Chem. 691 (2006) 4686

The synthesis and structural characterization of *N-para*-ferrocenyl benzoyl dipeptide esters: The X-ray crystal structure of *N-{para-*(ferrocenyl)benzoyl}-L-alanine-glycine ethyl ester A series of *N-para*-ferrocenyl benzoyl dipeptide esters **2**–**5** were prepared by coupling *para*-ferrocenyl benzoic acid (1) to the dipeptide ethyl esters using the conventional 1,3-dicyclohexylcarbodiimide (DCC), 1-hydroxybenzotriazole (HOBt) protocol. The dipeptides employed in the synthesis were Ala-Gly(OEt), Ala-Ala(OEt), Ala-Leu(OEt) and Ala-Phe(OEt). The compounds were fully characterized by a range of NMR spectroscopic techniques, electrospray ionization mass spectrometry (ESI-MS) and tandem mass spectrometry (MS/MS). In addition the X-ray crystal structure of the L-alanine-glycine derivative **2** has been determined.



Alla B. Antonova, Michael I. Bruce, Paul A. Humphrey, Maryka Gaudio, Brian K. Nicholson, Nancy Scoleri, Brian W. Skelton, Allan H. White, Natasha N. Zaitseva

J. Organomet. Chem. 691 (2006) 4694

Alkynyl and poly-ynyl derivatives of carbontricobalt clusters Alkynyl-tricobalt carbonyl clusters, $Co_3(\mu_3-C_nR)(\mu-dppm)(CO)_7$ [R = Bu', Ph, C_6H_4I , $C_6H_4C\equiv CPh$, SiMe₃, Fc, Au(PPh₃)] containing three, five or seven carbons in the chain, are prepared from reactions between $Co_3(\mu_3-CBr)(\mu-dppm)(CO)_7$ and Au($C\equiv CR$)(PPh₃) or between $Co_3(\mu_3-CC\equiv CAu(PR_3))(\mu-dppm)(CO)_7$ (R = Ph, tol) and IC $\equiv CR'$ (R' = SiMe₃, Fc). The use of poly-substituted arenes or ferrocenes has enabled preparation of the complexes 1,4-{(OC)₇(μ -dppm)Co₃($\mu_3-CC\equiv C\}_2C_6H_3X-5$ (X = H, Br), 1,3,5-{(OC)₇(μ -dppm)Co₃($\mu_3-CC\equiv C)$ }₃C₆H₃ and 1,1'-{(OC)₇(μ -dppm)Co₃($\mu_3-CC\equiv C)$ }₂Cé (Fc') = Fe(η -C₅H₄-)₂].



Muthiah Senthil Kumar, Shailesh Upreti, Hanuman P. Gupta, Anil J. Elias

J. Organomet. Chem. 691 (2006) 4708

Reactions of $[\eta^5$ -carboxycyclopentadiene] $[\eta^4$ -tetraphenylcyclo butadiene] cobalt with alkyl and aryl tin oxides: Synthesis, structural studies and electrochemistry of novel monomeric and dimeric $[\eta^5$ -carboxy-cyclopentadiene] $[\eta^4$ -tetraphenylcyclobutadiene]-cobalt based stannoxanes

Cobalt based organostannoxanes have been synthesized by the reaction of $Ph_4C_4CoC_5H_4$ -COOH with $(Ph_3Sn)_2O$, $[(n-Bu)_2SnO]_n$ and $(Ph_2SnO)_n$ and their structures and electrochemistry are compared with ferrocene analogues.



Contents

Herbert Schumann, Yilmaz Aksu, Stefan Schutte, Birgit C. Wassermann, Stefan H. Mühle

J. Organomet. Chem. 691 (2006) 4717

Synthesis and characterization of new siliconcentred tin-dendrimers $Si[CH_2CH_2SnR_3]_4$. Single-crystal X-ray structure of the tetrahydrofuran adduct of tetrakis[2-(tribromostannyl)ethyl]silane First-generation silicon-centred tin dendrimers $Si(CH_2CH_2SnR_3)_4$ [R = CH₃ (3), ^{*i*}Bu (4), C=CCH₃ (5), C₆H₄CH₃-4 (6), C₆H₄OCH₃-4 (7), (CH₂)₄OCH₂CH₂OCH₃ (8), CH₂SiMe₃ (9)] were prepared by the reaction of Si(CH₂CH₂SnBr₃)₄ (2) with the appropriate Grignard reagent or LiCH₂SiMe₃ in tetra-hydrofuran.



W. Rekik, H. Naïli, T. Bataille, T. Mhiri

J. Organomet. Chem. 691 (2006) 4725

Synthesis, crystal structure, phase transition and thermal behaviour of a new dabcodiium hexaaquanickel(II) bis(sulphate), $(C_6H_{14}N_2)$ - $[Ni(H_2O)_6](SO_4)_2$ A new transition metal sulphate in the presence of dabco amine, $(C_6H_{14}N_2)[Ni(H_2O)_6]-(SO_4)_2$, was prepared and characterised. The structural arrangement is pointed out, in which dabco plays a templating role. A structural phase transition was detected at -53.7/-54.6 °C on heating-cooling runs and the thermal decomposition of the precursor, at high temperature, was discussed.



Oliver Segnitz, Manuela Winter, Roland A. Fischer

J. Organomet. Chem. 691 (2006) 4733

Novel complexes of nickel with N-heterocyclic ligands and the hemilabile [2-(dimethyl-amino)ethyl]cyclopentadienyl group

Starting out from $[Cp^NNiI]$ (1), three new $[Cp^NNi(L)]$ derivatives with polar carbazolato, maleimidato and phthalimidato ligands were synthesized by salt elimination. The presence of electron withdrawing groups R at the negatively polarized N-atom, allowing for charge delocalization, strongly contribute to the stability of amido and/or imidato complexes at the Cp^NNi fragment.



Zhifang Li, Xiaojun Cao, Guoqiao Lai, Jinhua Liu, Yong Ni, Jirong Wu, Huayu Qiu

J. Organomet. Chem. 691 (2006) 4740

Controlled introduction of allylic group to chlorosilanes

Allylation of chlorosilanes has been achieved with allylsamarium bromide in a controlled manner. Thus allylation of trichlorosilanes (RSiCl₃) can selectively afford mono-, di-, and tri-allylation products. Perchlorosilane (SiCl₄) was allylated stepwise and the corresponding silanes containing one, two, three or four allylic groups, respectively, were obtained in satisfactory yields.



Annabelle G.W. Hodson

J. Organomet. Chem. 691 (2006) 4747

Effect of substituents on the molybdenum mediated carbonylation and methoxycarbonylation of dihaloalkynes

Nucleophilic attack of $[Mo(CO)_3(phen)Y]^-$ on YCH(R)C=CCH(R)Y or YCR₂C=CCR₂Y (R = H or Me; Y = Cl, Br, I) yields carbonylation or methoxycarbonylation products containing a substituted η^3 -bonded butadienyl or hexadienyl unit. The type of halogen and degree of substitution of the alkyne control formation of this complex, $[Mo(CO)_3-(phen)Y_2]$ or η^3 -allyl $[Mo(CO)_2(\eta^3CH(R) C(CO_2Me)C(OMe)(CH_2R))(phen)Y].$

Contents



Kien-Wee Tan, Fengli Liu, Yongxin Li, Geok-Kheng Tan, Pak-Hing Leung

J. Organomet. Chem. 691 (2006) 4753

Asymmetric synthesis of a chiral arsinophosphine *via* a metal template promoted asymmetric Diels–Alder reaction between diphenylvinylphosphine and 2-furyldiphenylarsine The metal-template promoted asymmetric Diels–Alder reaction between diphenylvinylphosphine and 2-furyldiphenylarsine successfully generates a single product isomer containing the oxanorbornene skeleton which consequently gives an optically active arsinophosphine upon liberation from the metal template.



Wenjuan Zhang, Wen-Hua Sun, Biao Wu, Shu Zhang, Hongwei Ma, Yan Li, Jiutong Chen, Peng Hao

J. Organomet. Chem. 691 (2006) 4759

Synthesis of palladium complexes containing 2-methoxycarbonyl-6-iminopyridine ligand and their catalytic behaviors in reaction of ethylene and norbornene

The palladium complexes bearing 2-methoxycarbonyl-6-iminopyridines have been prepared and fully characterized by FT-IR, NMR spectra, elemental analysis and X-ray crystallography. These palladium complexes exhibited moderate catalytic activities for ethylene dimerization and/or polymerization in the presence of methylaluminoxane (MAO), and showed remarkable catalytic activity for norbornene polymerization.



M. Sarah Mohlala, Xin-Ying Liu, Neil J. Coville

J. Organomet. Chem. 691 (2006) 4768

Synthesis of multi-walled carbon nanotubes catalyzed by substituted ferrocenes

A range of substituted ferrocenes were used as catalysts for the synthesis of multi-walled carbon nanotubes and carbon fibers and the ferrocene ring substituents influenced both the CNT diameter and the carbon product formed.



Leonor Maria, Carolina Moura, António Paulo, Isabel C. Santos, Isabel Santos

J. Organomet. Chem. 691 (2006) 4773

Synthesis and structural studies of rhenium(I) tricarbonyl complexes with thione containing chelators

Thione-based ligands, containing boron or carbon as bridgehead atoms, allowed the synthesis of *fac*-[Re{ κ^3 -H(\mu-H)B(tiaz)_2(CO)₃] (1) and *fac*-[ReBr{ κ^2 -H₂C(tim^{Me})_2}(CO)₃] (2). Solid state and solution studies have shown that complex 1 presents a B-H···Re interaction, while complex 2 does not present any C-H···Re interaction.

S2 BC3 S1 C1 Br1 C2 (2)

Sanjib K. Patra, Moumita Majumdar, Jitendra K. Bera

J. Organomet. Chem. 691 (2006) 4779

Ligand assisted homolytic cleavage of the Ru– Ru single bond in $[Ru_2(CO)_4]^{2+}$ core and the chemical consequence The reaction of 2-*i*-propyl-1,8-naphthyridine (^{*i*}PrNP) with [Ru₂(CO)₄(MeCN)₆][BF₄]₂ and subsequent crystallization in [*n*-Bu₄N][OTf] provide the Ru–Ru singly bonded *cis*-[Ru₂(^{*i*}PrNP)₂(CO)₄(OTf)₂] whereas the *t*-butyl appendage in ^{*t*}BuNP leads to the oxidative cleavage of the Ru–Ru bond resulting in the *trans*-[Ru(^{*t*}BuNP)₂(MeCN)₂][BF₄]₂[NC(Me)C-(Me)N]. The dianion *anti*-[NC(Me)C(Me)N]²⁻ is the product of the two-electron reductive coupling of two acetonitrile molecules.



ORTEP diagram of the cationic unit trans-[Ru('BuNP)_2-(MeCN)_2]²⁺ in compound ${\bf 2}$ with important atoms labeled. Hydrogen atoms are omitted for the sake of clarity.

Christoph E. Strasser, Stephanie Cronje, Hubert Schmidbaur, Helgard G. Raubenheimer

J. Organomet. Chem. 691 (2006) 4788

The preparation, properties and X-ray structures of gold(I) trithiophosphite complexes

The novel gold(I) complexes of mono- and bidentate trithiophosphites presented as a result of this preparative and structural study differ significantly in their properties and (supra)molecular structures from their classical phosphite and phosphane counterparts.



Notes

Samuel Dagorne

J. Organomet. Chem. 691 (2006) 4797

Reactivity studies of a four-coordinate methyl chloro aluminium aminophenolate complex with $B(C_6F_5)_3$

The Al complex $\{6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O\}Al(Me)(Cl)$, readily available by reaction of the corresponding aminophenolate Li salt with MeAlCl₂, slowly reacts with B(C₆F₅)₃ to yield a 1/1 mixture of the Al methyl cation $\{6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O\}Al(Me)-(THF)^+$ (**2**, as MeB(C6F5)3- salt) and the Al dichloro derivative $\{6-(CH_2NMe_2)-2-CPh_3-4-Me-C_6H_2O\}AlCl_2$ (**3**). This reaction most likely proceeds via a Me⁻ abstraction/ligand exchange sequence.



Contents

Oleg V. Ozerov, Chengyun Guo, Bruce M. Foxman

J. Organomet. Chem. 691 (2006) 4802

Missing link: PCP pincer ligands containing P–N bonds and their Pd complexes

New PCP ligands in which the phosphine donor arms are connected to the central aromatic ring via NH moieties and their (PCP)PdCl complexes have been prepared. The (PCP)PdCl complexes are exceptionally robust towards oxygen and water despite the presence of P–N bonds.





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