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Contents

Special Issue: Second International Symposium on Bio-Organometallic Chemistry – Dedicated to Professor Richard H. Fish on the occasion of his 65th birthday

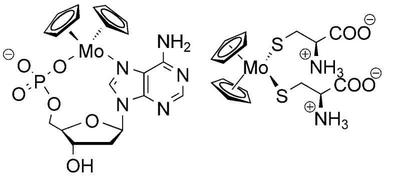
Review

Jenny B. Waern, Margaret M. Harding

J. Organomet. Chem. 689 (2004) 4655

Bioorganometallic chemistry of molybdocene dichloride

This review summarizes the bioorganometallic chemistry of molybdocene dichloride which has attracted significant interest as a potential antitumor metallocene. Key results reported in the last decade include detailed studies of the hydrolysis chemistry, interactions with nucleic acids and proteins, novel catalytic properties that may be relevant for cleavage of biomolecules, and structure–activity and mechanistic studies.



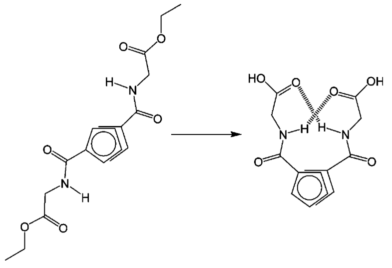
Regular papers

Francis E. Appoh, Todd C. Sutherland, Heinz-Bernhard Kraatz

J. Organomet. Chem. 689 (2004) 4669

Changes in the hydrogen bonding pattern in ferrocene peptides

Control over the conformation and H-bonding in bis-substituted ferrocene glycine conjugates is achieved.

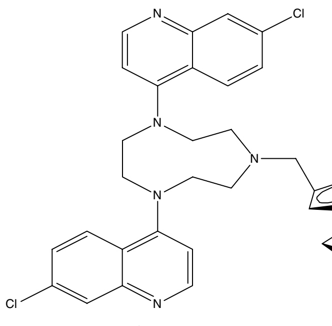


Christophe Biot, Jean Dessolin, Isabelle Ricard, Daniel Dive

J. Organomet. Chem. 689 (2004) 4678

Easily synthesized antimalarial ferrocene triazacyclononane quinoline conjugates

Starting from triazacyclononane, easily accessible ferrocenic quinoline derivatives were synthesized. Their antiplasmodial properties were investigated against chloroquine sensitive (HB3) and chloroquine resistant (Dd2) *Plasmodium falciparum*. Compound **4** showed potent antimalarial activity in vitro against the chloroquine-resistant strain Dd2 and therefore revealed to be the most promising lead from the present work for new organometallic antimalarial agents.



4 [IC_{50}=62 nM, (Dd2)]

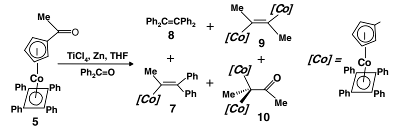
Elsevier B.V.
doi:10.1016/S0022-328X(04)00874-5

Yannick Ortin, John Grealis, Conor Scully, Helge Müller-Bunz, Anthony R. Manning, Michael J. McGlinchey

J. Organomet. Chem. 689 (2004) 4683

McMurry reactions of (η^5-acetylcyclopentadienyl) cobalt-(η^4-tetraphenylcyclobutadiene) with benzophenone: ketone couplings and a pinacol/pinacolone rearrangement

The reaction of (η^4-C_4Ph_4) Co[η^5-C_5H_4–C(=O)Me], **5**, with benzophenone under McMurry conditions ($TiCl_4$/Zn/THF) gives the coupled product (η^4-C_4Ph_4)Co[η^5-C_5H_4–C(Me)=CPh_2], **7**, together with the dicobalt species: *trans*-(η^4-C_4Ph_4)Co[(η^5-C_5H_4–C(Me)=C(Me)-η^5-C_5H_4–)]Co(η^4-C_4Ph_4), **9**, and the pinacolone Me[(η^4-C_4Ph_4)Co(η^5-C_5H_4)]$_2$C–C(=O)Me, **10**. In the latter case, preferential migration of an (η^4-C_4Ph_4)Co[(η^5-C_5H_4)] moiety rather than a methyl group is rationalized in terms of a favored transition state involving a metal-stabilized cation.

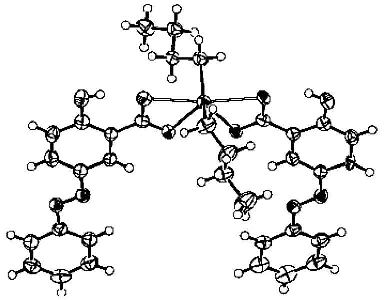


Tushar S. Basu Baul, Wandondor Rynjah, Rudolph Willem, Monique Biesemans, Ingrid Verbruggen, Michal Holèapek, Dick de Vos, Anthony Linden

J. Organomet. Chem. 689 (2004) 4691

Dibutyltin(IV) complexes of the 5-[(*E*)-2-(Aryl)-1-diazenyl]-2-hydroxybenzoic acid ligand: an investigation of structures by X-ray diffraction, solution and solid state tin NMR, electrospray ionisation MS and assessment of in vitro cytotoxicity

A series of dibutylbis{5-[(*E*)-2-(aryl)-1-diazenyl]-2-hydroxybenzoato}tin(IV) complexes have been prepared, characterized by NMR (^{1}H, ^{13}C, ^{119}Sn), and ESI mass spectrometry in solution, and the crystal structures of several examples are presented. The trapezoidal bipyramid structures of the complexes are preserved in solution, as revealed by the ^{117}Sn CP-MAS and ^{119}Sn solution NMR data.

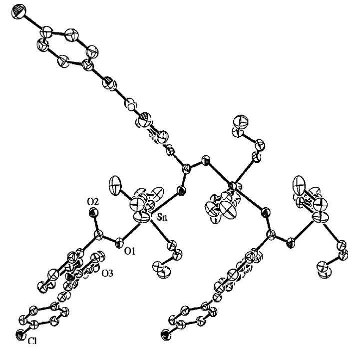


Tushar S. Basu Baul, Keisham Surjit Singh, Xueqing Song, Alejandra Zapata, George Eng, Antonin Lycka, Anthony Linden

J. Organomet. Chem. 689 (2004) 4702

Synthesis and characterization of tributyltin(IV) complexes of 2-[(*E*)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]benzoic acid and 4-[((*E*)-1-{2-hydroxy-5-[(*E*)-2-(2-carboxyphenyl)-1-diazenyl]phenyl}methylidene)amino]aryls – crystal structures of polymeric ($Bu_3Sn[O_2CC_6H_4${N=N(C_6H_3-4-OH-5-CHO)}-*o*])$_n$ and ($Bu_3Sn[O_2CC_6H_4${N=N(C_6H_3-4-OH(C(H)=NC_6H_4Cl-4))}-*o*])$_n$ – toxicity studies on the second instar of *Aedes aegypti* mosquito larvae

The tri-*n*-butyltin(IV) complexes of 2-[(*E*)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]benzoic acid and 4-[((*E*)-1-{2-hydroxy-5-[(*E*)-2-(2-carboxyphenyl)-1-diazenyl]phenyl}methylidene)amino]aryls (aryls = 4-CH_3, 4-Br, 4-Cl, 4-OCH_3) have been synthesized and characterized by ^{1}H, ^{13}C, ^{119}Sn NMR, IR and ^{119m}Sn Mössbauer spectroscopic techniques in combination with elemental analysis. The crystal structures of two compounds revealed a *trans*-R_3SnO_2 trigonal bipyramidal coordination geometry with equatorial butyl groups and carboxylate O atoms occupying axial positions, one being from each of two aryl ligands. The results of a toxicity study of a tributyltin compound on the second larval instar of *Aedes aegypti* mosquito larvae are reported.

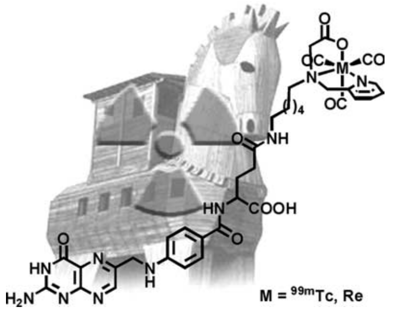


Cristina Müller, Cécile Dumas, Ute Hoffmann, P. August Schubiger, Roger Schibli

J. Organomet. Chem. 689 (2004) 4712

Organometallic ^{99m}Tc-technetium(I)- and Re-rhenium(I)-folate derivatives for potential use in nuclear medicine

Site specific modified folate and pteroate derivatives have been synthesized for potential use as a “Trojan horse” in diagnostic and therapeutic nuclear medicine. The derivatives were labeled with $[M(OH_2)_3(CO)_3]^+$ (M = ^{99m}Tc, Re) and tested in vitro. The organometallic complexes exhibited high and specific binding to the targeted folate receptor.

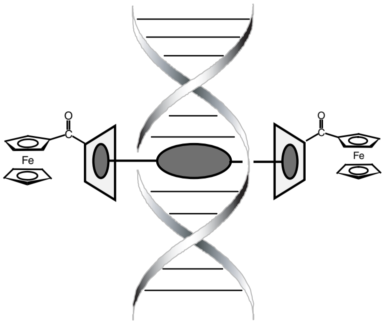


Shinobu Sato, Takahiko Nojima,
Shigeori Takenaka

J. Organomet. Chem. 689 (2004) 4722

Electrochemical gene detection based on supramolecular complex formation by ferrocenyl-β-cyclodextrin and adamantyl-naphthalene diimide bound to double stranded DNA

Newly synthesized adamantylnaphthalene diimide **1** can bind to double stranded DNA (dsDNA) by the threading intercalation mode and its complex was stabilized by capping of the adamantyl moieties of **1** projecting over the major and minor grooves of dsDNA with ferrocenyl-β-cyclodextrin. This supramolecular complex could be applied to the electrochemical gene detection coupled with a DNA probe-immobilized electrode.

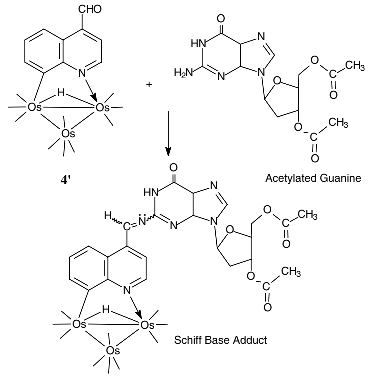


Edward Rosenberg, Fabrizio Spada,
Kent Sugden, Brooke Martin,
Roberto Gobetto, Luciano Milone,
Alessandra Viale

J. Organomet. Chem. 689 (2004) 4729

Selective covalent binding of a positively charged water-soluble benzoheterocycle triosmium cluster to single- and double-stranded DNA

The water-soluble triosmium cluster [$Os_3(CO)_9(\mu\text{-}\eta^2\text{-}(4\text{-}CHO)C_9H_5N)(\mu\text{-}H)(P(OCH_2CH_2N(CH_3)_3I)_3)$] (**4**) was tested for its reactivity with plasmid DNA and with a 22-oligomer (sequence 5′-AGT TGT GGT GAC TTT CCC AGG C-3′). Evidence for selective covalent binding with the TGT triad is presented and these results are consistent with the observation of the formation of an adduct between [$Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}(4\text{-}CHO)C_9H_5N)(\mu\text{-}H)$] (**4′**) and acetylated guanine in methanol.

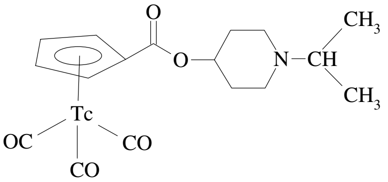


M. Saidi, S. Seifert, M. Kretzschmar,
R. Bergmann, H. Pietzsch

J. Organomet. Chem. 689 (2004) 4739

Cyclopentadienyl tricarbonyl complexes of ^{99m}Tc for the in vivo imaging of the serotonin 5-HT_{1A} receptor in the brain

The chemical identity of cytectrene complexes was determined by ES-MS and comparison of their chromatographic data with those of kit formulated tricarbonyl ^{99m}Tc(I) complexes. The ^{99m}Tc tricarbonyl cyclopentadienyl complexes combine high brain uptake with a remarkable affinity towards 5-HT_{1A} and α_1 adrenergic receptors.



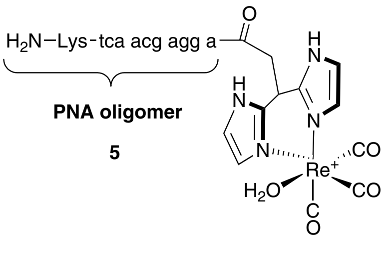
Cytectrene II

Ramin Hamzavi, Thomas Happ,
Katharina Weitershaus, Nils Metzler-Nolte

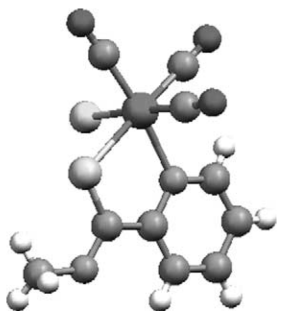
J. Organomet. Chem. 689 (2004) 4745

The use of 3,3-bis(2-imidazolyl) propionic acid (bip-OH) as a new chelating ligand for $Re(CO)_3$ and Ru complexes: Formation of organometallic PNA oligomers with (bip)$Re(CO)_3$ and their interaction with complementary DNA

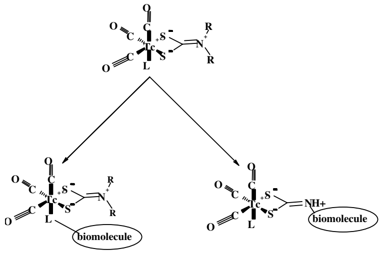
The synthesis and full characterization of complexes Re(bip-O)$(CO)_3$ **2** and [Ru$(bpy)_2$(bip-OH)]$^{2+}$ **3** is reported (bip-OH = 3,3-bis(2-imidazolyl) propionic acid **1**). Conjugates of **2** with peptide nucleic acid (PNA) oligomers are reported and for the first time, a melting temperature of an organometallic PNA conjugate **5** with complementary DNA is reported.



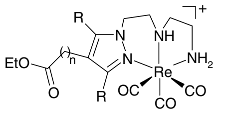
Syntheses of a bidentate ligand L = *N*-methyl-2-pyridinecarbothioamide and its tricarbonylchlororhenium(I) complex, [*fac*-$Re\text{-}(CO)_3LCl$], are described. The molecular structures of both complex and ligand have been establish ed by means of X-ray single crystal diffraction and by FT-IR spectroscopy. Lipophilicity of both appeared to be moderate as determined from the partition coefficients in the *iso*-octanol–water systems.



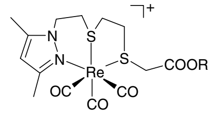
"2+1" Dithiocarbamate–isocyanide chelating systems were used for linking $M(CO)_3^+$ (M = ^{99m}Tc, Re) fragment to biomolecules. Conjugation was performed by post-labeling procedure via monodentate isocyanide ligands and by prelabeling procedure via bidentate dithiocarbamate ligands. The $^{99m}Tc(CO)_3^+$ complexes were identified using corresponding rhenium analogs as references.



Novel bifunctional N_3 and NS_2 ligand donor sets based on pyrazole have been prepared and found to form stable complexes of the type *fac*-$[Re(CO)_3(\kappa^3\text{-}L)]^+$. In these complexes the pyrazolyl anchors acts as a tridentate ligand without any interference of the carboxylate and/or ester functional groups, which stay available for coupling to biologically relevant molecules.

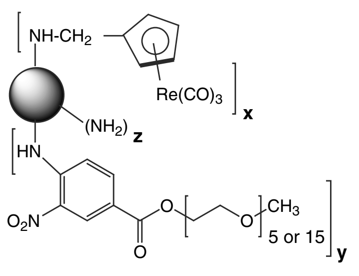


1, n = 0, R = H
2, n = 1, R = Me



4, R = Et
5, R = H

The first poly(amidoamine) (PAMAM) dendrimers tethered with both (η^5-cyclopentadienyl) rhenium tricarbonyl (CpRe-$(CO)_3$)units and polyethylene glycol (PEG) chains were prepared and characterized by combining NMR and FT-IR spectroscopy. These water-soluble metallodendrimers represent new infrared probes designed to be used in amplified format for carbonyl metallo immunoassay (CMIA).



$\mathbf{x + y + z} = $ 64 for PAMAM-G4, 32 for PAMAM-G3

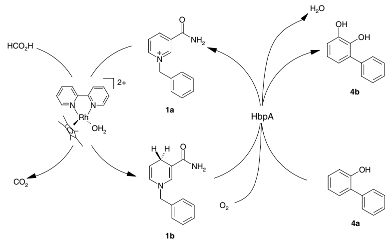
$\mathbf{13 \leqslant x \leqslant 29\ ,\ 4 \leqslant y \leqslant\ 21}$

Jochen Lutz, Frank Hollmann, The Vinh Ho, Adrian Schnyder, Richard H. Fish, Andreas Schmid

J. Organomet. Chem. 689 (2004) 4783

Bioorganometallic chemistry: biocatalytic oxidation reactions with biomimetic NAD^+/NADH co-factors and $[Cp^*Rh(bpy)H]^+$ for selective organic synthesis

Tandem co-factor regeneration, using $[Cp^*Rh(bpy)(H_2O)](Cl)_2$ and formate with **1a** (bromide counter ion) to provide **1b**, with a flavin containing and NAD^+ dependent, monooxygenase enzyme, 2-hydroxybiphenyl 3-monooxygenase (HbpA), for selective hydroxylation of 2-hydroxybiphenyl, **4a**, to its catechol derivative, 2,3-dhydroxybiphenyl, **4b**, was studied. Some difficult aspects of this tandem catalysis scheme were observed, for example, $[Cp^*Rh(bpy)(H_2O)](Cl)_2$ inhibition of HbpA activity, which was mitigated by supporting HbpA on a polymer matrix.

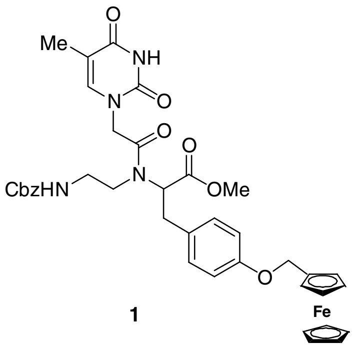


Clara Baldoli, Luigi Falciola, Emanuela Licandro, Stefano Maiorana, Patrizia Mussini, Prasanna Ramani, Clara Rigamonti, Giovanna Zinzalla

J. Organomet. Chem. 689 (2004) 4791

A new ferrocene conjugate of a tyrosine PNA monomer: synthesis and electrochemical properties

A new chiral ferrocene-labelled tyrosine PNA monomer **1** has been synthesised in good yield in racemic and enantiomerically pure forms. It is suitable for insertion in various positions of PNA oligomers. In view of possible applications to nucleic acid detection, a preliminary voltammetric investigation on the electrochemical activity of monomer **1** has been carried out in DMF.



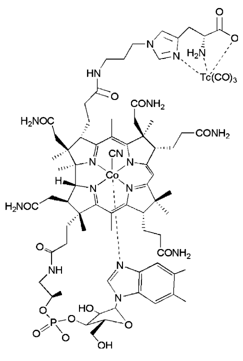
1

Dave R. van Staveren, Robert Waibel, Stefan Mundwiler, P. August Schubiger, Roger Alberto

J. Organomet. Chem. 689 (2004) 4803

Conjugates of vitamin B12 with N_ε-functionalized histidine for labeling with $[^{99m}Tc(OH_2)_3(CO)_3]^+$: synthesis and biodistribution studies in tumor bearing mice

Four different cyanocobalamin (vitamin B12) conjugates of histidine are synthesized and subsequently labeled by the reaction with $[^{99m}Tc(OH_2)_3(CO)_3]^+$. The biodistribution and tumor uptake of the labeled conjugates are determined in mice with B16-F10 melanoma tumors.

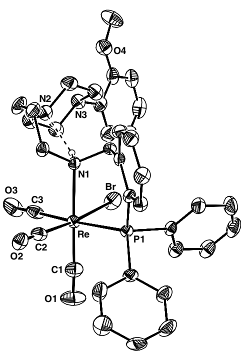


Elisa Palma, João D.G. Correia, Ângela Domingos, Isabel Santos, Roger Alberto, Hartmut Spies

J. Organomet. Chem. 689 (2004) 4811

Rhenium and technetium tricarbonyl complexes anchored by $5\text{-}HT_{1A}$ receptor-binding ligands containing P,O/N donor atom sets

Re and ^{99m}Tc tricarbonyl complexes containing $5\text{-}HT_{1A}$ receptor-binding ligands of the type $[M(CO)_3X(\kappa^2\text{-}L)]$ were prepared and characterized. The in vitro binding affinity/selectivity for the $5HT_{1A}$ receptor subtype of the rhenium complexes decreases when the spacer length between the chelating unit and receptor-binding domain increases, and/or the amide group in the chelator was replaced by an amine.

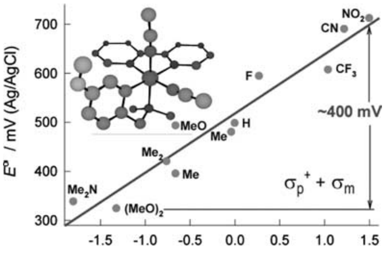


Ronan Le Lagadec, Laura Rubio, Larissa Alexandrova, Rubén A. Toscano, Ekaterina V. Ivanova, Rolandas Meškys, Valdas Laurinavičius, Michel Pfeffer, Alexander D. Ryabov

J. Organomet. Chem. 689 (2004) 4820

Cyclometalated *N,N*-dimethylbenzylamine ruthenium(II) complexes $[Ru(C_6HR^1R^2R^3\text{-}o\text{-}CH_2NMe_2)(bpy)(RCN)_2]PF_6$ for bioapplications: synthesis, characterization, crystal structures, redox properties, and reactivity toward PQQ-dependent glucose dehydrogenase

Easily made cycloruthenated complexes $[Ru(C_6HR^1R^2R^3\text{-}o\text{-}CH_2NMe_2)(bpy)(RCN)_2]PF_6$ (R = Me and CMe_3) derived from *N,N*-dimethylbenzylamines contain two labile *cis*-nitrile ligands and therefore they are convenient precursors for further modification. Electronic properties of the complexes are sensitive to substituents in the aromatic ring of cyclometalated ligand and the redox potentials vary in a 400 mV range. A significant bioelectrochemical potential of the complexes has been demonstrated by showing that they reoxidize readily the reduced active site of PQQ-dependent enzyme glucose dehydrogenase.

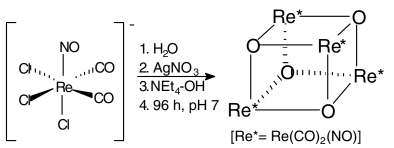


D. Rattat, A. Verbruggen, H. Berke, R. Alberto

J. Organomet. Chem. 689 (2004) 4833

Exploring the nitrosyl-approach: "$Re(CO)_2(NO)$"- and "$Tc(CO)_2(NO)$"-complexes provide new pathways for bioorganometallic chemistry

A method is described for the conversion of a "$M(CO)_3$-moiety" (M = Re, Tc) into a dicarbonyl-nitrosyl moiety "$M(CO)_2NO$". The syntheses of important precursor complexes and intermediates, their behavior in water and possible applications for this new kind of Re- and Tc-chemistry are shown, taking $[ReCl_3(CO)_2(NO)]^-$, $[Re(\mu_3\text{-}O)(CO)_2(NO)]_4$ and $[^{99m}Tc(DTPA)(CO)_2(NO)]$ as examples.

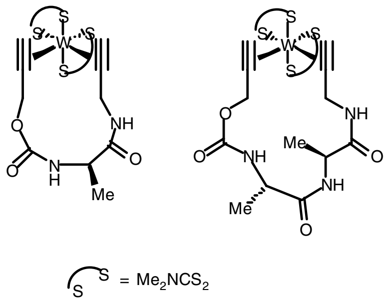


Timothy P. Curran, Richard S.H. Yoon, Brian R. Volk

J. Organomet. Chem. 689 (2004) 4837

N-terminus to C-terminus metallacyclicpeptides employing tungsten–alkyne coordination

Metallacyclicpeptides were prepared by linking the N- and C-termini of dialkynylpeptides to tungsten. In solution the resulting metallacyclicpeptides exist as a mixture of different isomeric forms.

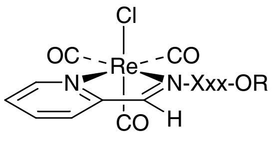


Richard S. Herrick, Iwona Wrona, Naomi McMicken, Glenn Jones, Christopher J. Ziegler, Janet Shaw

J. Organomet. Chem. 689 (2004) 4848

Preparation and characterization of rhenium(I) compounds with amino ester derivatized diimine ligands. Investigations of luminescence. Crystal structures of $Re(CO)_3Cl$(pyca-β-Ala-OEt) and $Re(CO)_3Cl$(pyca-L-Asp(OMe)-OMe)

Rhenium (I) tricarbonyl compounds with an amino ester conjugate ligand have been prepared. Esters of β-alanine, alanine, valine, GABA, aspartic acid and methionine condense with pyridine-2-carboxaldehyde in the presence of $Re(CO)_5Cl$ forming the diimine compounds. The β-alanine derivative is luminescent at 298 K. Crystal structures of the β-alanine and aspartic acid derivatives are presented.

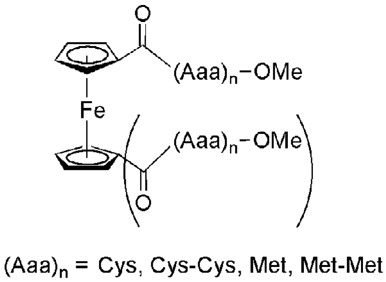


Xavier de Hatten, Thomas Weyhermüller, Nils Metzler-Nolte

J. Organomet. Chem. 689 (2004) 4856

Ferrocenoyl peptides with sulfur-containing side chains: synthesis, solid state and solution structures

The synthesis and full characterization of more than a dozen ferrocene derivatives with pendant cysteine and methionine amino acid side chains is reported. Their structures were investigated in solution by NMR, IR and CD spectroscopy. Three compounds were also characterized by X-ray crystallography and interesting differences between solution and solid state structures were revealed.



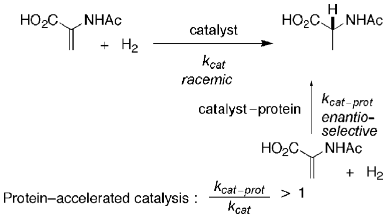
Notes

Jérôme Collot, Nicolas Humbert, Myriem Skander, Gérard Klein, Thomas R. Ward

J. Organomet. Chem. 689 (2004) 4868

Artificial metalloenzymes for enantioselective catalysis: the phenomenon of protein accelerated catalysis

We report on the phenomenon of protein-accelerated catalysis in the field of artificial metalloenzymes based on the non-covalent incorporation of biotinylated rhodium–diphosphine complexes in (strept)avidin as host proteins.



Benot Ferber, Siden Top, Gérard Jaouen

J. Organomet. Chem. 689 (2004) 4872

Introduction of a planar chirality onto steroid substrates: synthesis of (*S*) and (*R*)-2′-formylcymantrenyl-17α-ethynylestradiols using (*S*) and (*R*)-1-formyl-2-iodo-cymantrenes

Synthesis of (*S*) and (*R*)-2′-formylcymantrenyl-17α-ethynylestradiol synthesized using the Sonogashira cross-coupling reaction between optically pure (*S*) and (*R*) 1-formyl-2-iodo cymantrene and ethynylestradiol. (*S*) and (*R*) 1-formyl-2-iodo cymantrene were obtained from the same precursor: (2*R*,4*R*)-4-(methoxymethyl)-2-cymantrenyl-1,3-dioxane.