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Contents

Special Issue: Bio-organometallic Chemistry

Communication

Gabriela Guillena, Cornelis A. Kruithof, Miguel A. Casado, Maarten R. Egmond, Gerard van Koten

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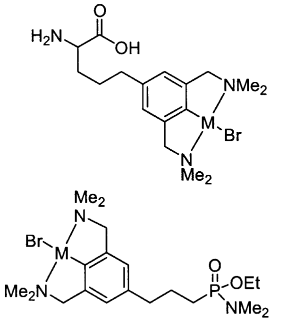
The Suzuki cross-coupling reaction: a powerful tool for the attachment of organometallic 'NCN'-pincer units to biological scaffolds

Arylplatinum(II) and arylpalladium(II) complexes have been covalently attached to the α-carbon of an α-amino acid as well as the terminal position (γ-position) of an alkyl phosphonate using Suzuki cross-coupling reactions. The free organometallic amino acid derivatives can be incorporated at various positions in the chains of polypeptides. The γ-NCN-pincer metallated phosphonate is highly interesting because phosphonates are commonly used as selective inhibitors of enzymes such as lipases.

Metallated α-amino acids and phosphonates



Regular Papers

Lubomír Pospíšil, Magdaléna Hromadová, Jan Fiedler, Christian Amatore, Jean-Noël Verpeaux

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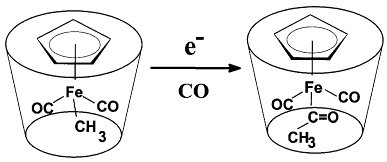
Redox activation of dicarbonyl(η^5-cyclopentadienyl)methyl iron within the cavity of β-cyclodextrin: carbon monoxide insertion in iron–methyl bond

The organometallic complex $CpFe(CO)_2$-CH_3 is included in a β-cyclodextrin cavity. The electron transfer activation of the coordination sphere leads to insertion of CO in the carbon–metal bond. The reaction inside the cavity suppresses undesirable side-reactions and retains the reacting CO at the reaction site, which simplifies the complicated overall reaction mechanism of the bond-insertion.



Magdaléna Hromadová, Michèle Salmain, Romana Sokolová, Lubomír Pospíšil, Gérard Jaouen

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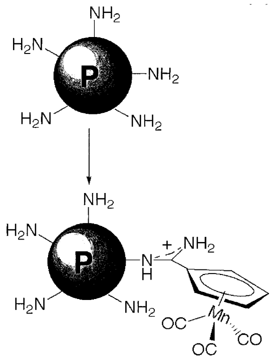
Novel redox label for proteins.
Electron transfer properties of (η^5-cyclopentadienyl) tricarbonyl manganese bound to bovine serum albumin

(η^5-Cyclopentadienyl) tricarbonyl manganese derivatives of bovine serum albumin with coupling ratios ranging from 7 to 20 were prepared. AC voltammetric detection of the reduction of cymantrene bound to BSA protein was successfully set up in aqueous solution and a detection limit of 2×10^{-7} M BSA was achieved.



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Pierre Morel, Paul Schaffer,
John F. Valliant

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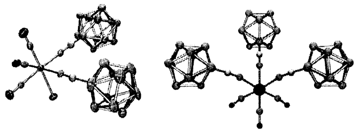
The synthesis and X-ray crystallographic structure determination of 3-isocyano-1,2-dicarba-*closo*-dodecaborane-Re(I) complexes

3-Isonitrilecarborane (**1**, L) reacts with the $[Re(CO)_3]^+$ core to form compounds of the general formulae $Re(CO)_3L_2Br$, $[Re(CO)_3L_3]^+$ and $[Re(CO)_3L_2L']$, where L′ denotes a ligand bearing a nido-carborane substituent.



Toshiyuki Moriuchi, Kazuhiro Yoshida,
Toshikazu Hirao

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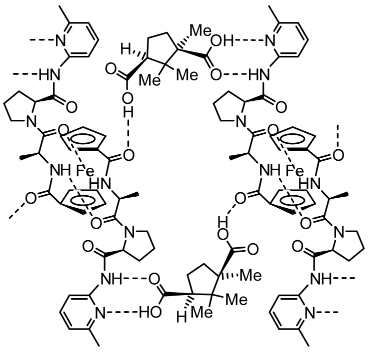
Hydrogen-bonding-directed molecular assembly of ferrocene bearing dipeptide chains (-L-Ala-L-Pro-NHPyMe) as an organometallic crystal architecture

The ferrocene bearing the dipeptide chains, -L-Ala-L-Pro-NHPyMe, which was characterized by two intramolecular interchain hydrogen bondings between CO (Ala) and NH (another Ala) of each dipeptide chain to induce the chirality organized structure, was demonstrated to form a 1:2 complex with (1*R*,3*S*)-camphoric acid through the intermolecular hydrogen bondings, forming the double-helical-like hydrogen-bonded molecular arrangement in the crystal structure.



Claire S. Allardyce, Paul J. Dyson,
David J. Ellis, Paul A. Salter,
Rosario Scopelliti

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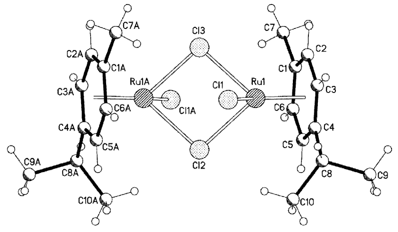
Synthesis and characterisation of some water soluble ruthenium(II)–arene complexes and an investigation of their antibiotic and antiviral properties

The water soluble ruthenium-*p*-cymene complexes $[Ru(\eta^6\text{-}p\text{-cymene})X_2]_2$ (X = Cl, Br, I or NCS), $[Ru(\eta^6\text{-}p\text{-cymene})X_2(pta)]$ (X = Cl, Br, I, or NCS; pta = 1,3,5-triaza-7-phosphatricyclo[3.3.1.1]decane) and the tetraruthenium cluster $[H_4Ru_4(\eta^6\text{-}p\text{-benzene})_4]^{2+}$ have been prepared and their antimicrobial properties evaluated.



Elina Virtanen, Juha Koivukorpi,
Jari Tamminen, Pia Mänttäri,
Erkki Kolehmainen

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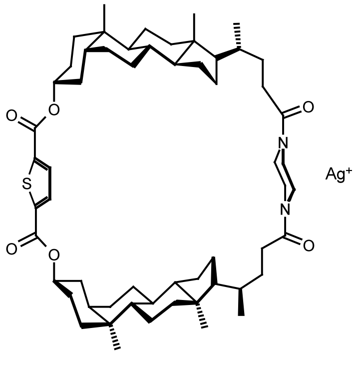
^{1}H-, ^{13}C-, and ^{15}N-NMR and ESI-TOF$^+$ MS studies of a supramolecular complex of silver(I) and a cholaphane

Synthesis, spectral characterisation, and an ability of a cholaphane to recognise Ag(I) ion over alkali metal ions is presented. The possible medical applications are also discussed.



E. Rosenberg, F. Spada, K. Sugden, B. Martin, Luciano Milone, Roberto Gobetto, Alessandra Viale, Jan Fiedler

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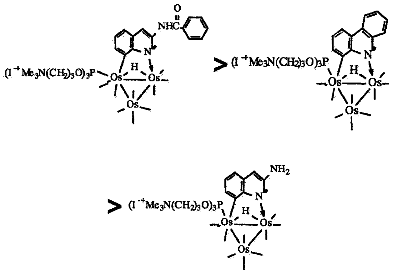
Synthesis, characterization and DNA binding affinities of water-soluble benzoheterocycle triosmium clusters

A novel class of water soluble benzoheterocycle triosmium clusters has been synthesized. Their binding to plasmid DNA is dependent on the apparent intercalating ability of the heterocyclic ligand and on the charge of the phosphine used to make the clusters water soluble.



Nathalie Fischer-Durand, Anne Vessières, Jan-Martin Heldt, Franck le Bideau, Gérard Jaouen

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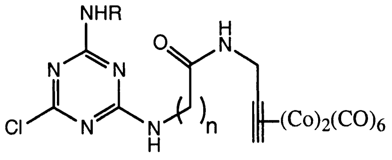
Evaluation of the carbonyl metallo immunoassay (CMIA) for the determination of traces of the herbicide atrazine

The potential of the non-isotopic immunoassay CMIA which uses metal carbonyl complexes as tracers and FT-IR spectroscopy as the detection method has been evaluated in the environmental field for the herbicide atrazine. Three dicobalt hexacarbonyl complexes of atrazine (**7**–**9**) have been prepared. The best results were obtained with **9** which leads to reproducible CMIA assay.



(**7-9**; n =1 or 5, R = Et or iPr)

R. Schibli, M. Netter, L. Scapozza, M. Birringer, P. Schelling, C. Dumas, J. Schoch, P.A. Schubiger

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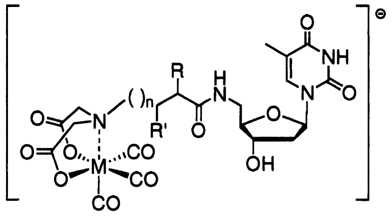
First organometallic inhibitors for human thymidine kinase: synthesis and in vitro evaluation of rhenium(I)- and technetium(I)-tricarbonyl complexes of thymidine

The first series of technetium and rhenium-tricarbonyl complexes of 5′-amino-thymidine have been synthesized for potential use in radiopharmacy. The organometallic complexes exhibit exclusively competitive inhibition of human cytosolic thymidine kinase in vitro. Towards herpes simplex virus type 1 thymidine kinase no biological activity was observed.



M = ^{99m}Tc, Re

Valentin S. Soukharev, Alexander D. Ryabov, Elisabeth Csöregi

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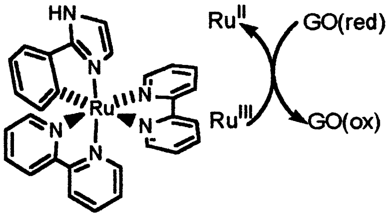
Synthesis, properties, and biosensor applications of cycloruthenated 2-phenylimidazoles

Cyclometalated ruthenium(II) complexes [Ru(phim)(4,4′-Me_2bpy)$(MeCN)_2$]PF_6 and [Ru(phim)$(LL)_2$]PF_6 (LL = bpy, phen, 4,4′-Me_2bpy), obtained by the C–H bond abstraction from 2-phenylimidazole (phim) by [Ru(η^6-C_6H_6)(μ-Cl)$Cl]_2$, are oxidized by the Compound II of horseradish peroxidase into the corresponding Ru^{III} species with the rate constants of $(2–9) \times 10^7$ M^{-1} s^{-1}. The rate constants for the oxidation of the reduced active site of glucose oxidase by Ru^{III} are in the range $(5–8) \times 10^6$ M^{-1} s^{-1}.



J. Razumiene, A. Vilkanauskyte, V. Gureviciene, V. Laurinavicius, Nataliya V. Roznyatovskaya, Yulia V. Ageeva, Marina D. Reshetova, Alexander D. Ryabov

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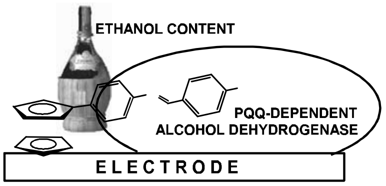
New bioorganometallic ferrocene derivatives as efficient mediators for glucose and ethanol biosensors based on PQQ-dependent dehydrogenases

The carbon electrode modified with 'bioorganometallic' ferrocene derivatives such as 2-ferrocenyl-4-nitrophenol or *N*-(4-hydroxybenzylidene)-4-ferrocenylaniline and the pyrroloquinoline quinone (PQQ) dependent glucose (GDH) and alcohol (ADH) dehydrogenases (HBFA) are used for detecting D-glucose and ethanol in various samples. The alcohol biosensor is used for measuring ethanol in wine, whereas the D-glucose biosensor reports on its sweetness.



Konrad Kowalski, Janusz Zakrzewski

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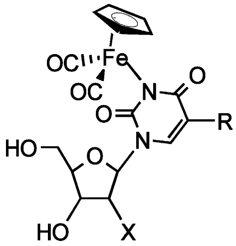
(η^5-C_5H_5)Fe$(CO)_2$-complexes of uridine and thymidine

The photochemical reaction of (η^5-C_5H_5)Fe$(CO)_2$I (FpI)/diisopropylamine with 2′,3′,5′-tri-*O*-acetyluridine, 3′,5′-di-*O*-acetylthymidine and 5′-*O*-(4,4′-dimethoxytrityl)thymidine afforded corresponding Fp-complexes of *N*(3)-deprotonated, protected nucleosides. Attempted removal of acetyl groups (K_2CO_3 or NH_3 in MeOH–H_2O) gave unseparable mixtures of 3-Fp-uridine or 3-Fp-thymidine with uridine or thymidine. On the other hand, removal of the 4,4′-dimethoxytrityl group proceeded smoothly in 80% CH_3COOH, yielding pure 3-Fp-thymidine.



R = H, Me
X = OH, H

Bogna Rudolf, Maria Makowska, Anna Domagala, Agnieszka Rybarczyk-Pirek, Janusz Zakrzewski

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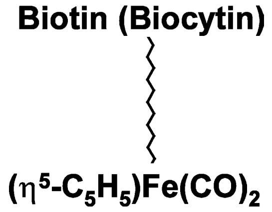
Metallo-carbonyl conjugates of biotin and biocytin

Metallo-carbonyl conjugates of biotin and biocytin bearing the (η^5-C_5H_5)Fe$(CO)_2$ moiety were prepared via the amide coupling or reaction with organometallic isothiocyanates. The HABA-Avidin test revealed high affinities of these conjugates to avidin.



Christopher E. Anson, Colin S. Creaser, Andrej V. Malkov, Ljubica Mojovic, G. Richard Stephenson

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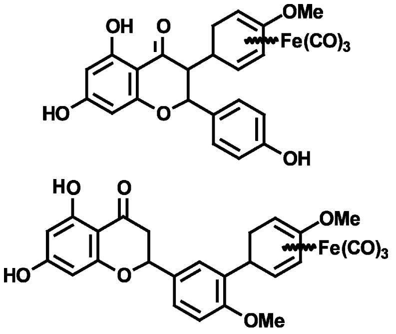
Flavonoid derivatives as organometallic bioprobes

The synthesis of organoiron derivatives of biologically active flavonoids uses lithium enolates and metallated derivatives of substituted aromatic rings as nucleophiles in combination with tricarbonyl(η^5-cyclohexadienyl)iron(1+) electrophiles. Enolates generated from protected flavanones have also been used, and a one-pot in situ protection, nucleophile addition, deprotection sequence is reported.



Anabel Elduque, Daniel Carmona, Luis A. Oro, Miriam Eisenstein, Richard H. Fish

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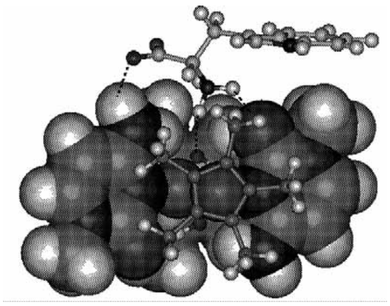
Bioorganometallic chemistry
Part 15. A novel molecular recognition process of host, *trans*-[Cp*Rh(η^1(N3)-1-methylcytosine)(μ-OH)]$_2$(OTf)$_2$, with L-aromatic amino acid guests: selective hydrogen bonding to the μ-OH groups and the 1-methylcytosine ligands

^{1}H-NMR and computer docking experiments have elucidated a unique molecular recognition process of host, *trans*-[Cp*Rh(η^1(N3)-1-methylcytosine)(μ-OH)]$_2$-(OTf)$_2$ (**1**), with L-aromatic amino acids, which is predicated on a selective hydrogen bonding regime of the NH_3^+ of the amino acid to one of the Rh–μ-OH groups, as well as to a C=O group of one of the 1-methycytosine ligands, while the COO$^-$ H-bonds to an NH_2 of the other 1-methycytosine ligand.



Hajnalka Jankovics, László Nagy, Zoltán Kele, Claudio Pettinari, Paolo D'Agati, Caterina Mansueto, Claudia Pellerito, Lorenzo Pellerito

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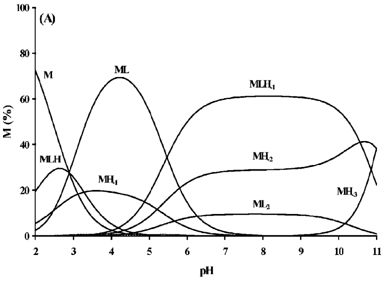
Coordination properties of the ACE inhibitor captopril towards $Me_2Sn(IV)^{2+}$ in aqueous solution, and biological aspects of some dialkyltin(IV) derivatives of this ligand

In solution of $Me_2Sn(IV)^{2+}$ and captopril monomeric complexes are formed. The neutral complex ML, similarly to the complex Me_2Sn(cap) crystallized in the same pH range, adopts a tbp structure with $-S^-$ and $-COO^-$ coordination. Me_2Sn(cap) has no toxic activity towards the embryos of *Ciona intestinalis*.



Note

F. Le Bideau, J. Hénique, P. Pigeon, J.-M. Joerger, S. Top, G. Jaouen

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A short route to cyclopentadienyltricarbonylrhenium substituted derivatives

Several fulvenes were transformed at mesitylene reflux in the presence of $Re_2(CO)_{10}$ in $CpRe(CO)_3$ substituted derivatives in good yields.