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Special Issue: Third International Symposium on Bioorganometallic Chemistry (ISBOMC'06)

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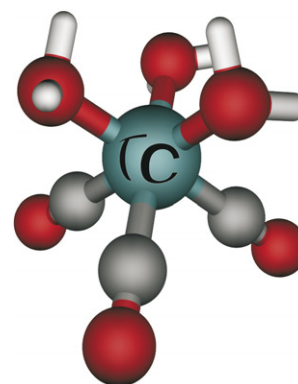
Reviews

Roger Alberto

J. Organomet. Chem. 692 (2007) 1179

The particular role of radiopharmacy within bioorganometallic chemistry

Basic insights into the different directions of bioorganometallic chemistry and some facets of the $[M(CO)_3]^+$ ($M = Tc, Re$) moiety are reviewed in general. Specifically, the synthesis of $[M(OH_2)_3(CO)_3]^+$ and its impact on radiopharmaceutical chemistry is described. The formation of additional M–C bonds in water is exemplified with cyclopentadienyl chemistry, the perspectives on targeted molecular imaging with the labelling of amino acids and the reactivity towards essential biomolecules such as guanine is shown.

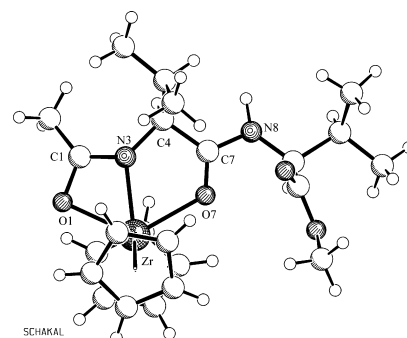


Gerhard Erker

J. Organomet. Chem. 692 (2007) 1187

Group 4 metallocenes in bioorganometallic chemistry

Titanocenes and zirconocenes have been modified in various ways by attachment of biogenic groups or ligands. The interaction of reactive bent metallocene systems with derivatives of typical bio-molecules was investigated.

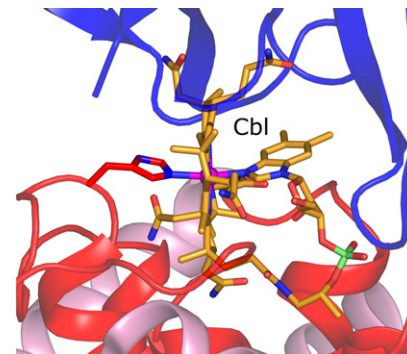


Lucio Randaccio, Silvano Geremia, Jochen Wuerges

J. Organomet. Chem. 692 (2007) 1198

Crystallography of vitamin B₁₂ proteins

This review deals with results from crystallographic studies on proteins that interact with the essential micronutrient cobalamin (vitamin B₁₂). Both B₁₂-dependent enzymes and B₁₂-transport proteins are described with an emphasis on structural aspects of cobalamin and its protein environment.



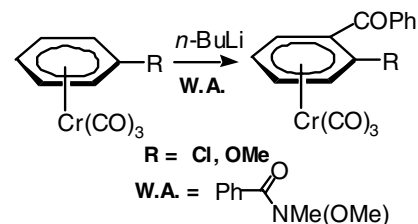
Communications

**Antoine Eloi, Françoise Rose-Munch,
Eric Rose, Patrick Herson**

J. Organomet. Chem. 692 (2007) 1216

Benzoyl-substituted (η^6 -arene)tricarbonylchromium complexes: Synthesis and structure

Lithiation of chloro- and methoxy-(η^6 -benzene)tricarbonylchromium complexes yielded, after electrophilic quench with a Weinreb amide, the corresponding benzoyl-substituted complexes. One of them has been investigated by an X-ray diffraction study.

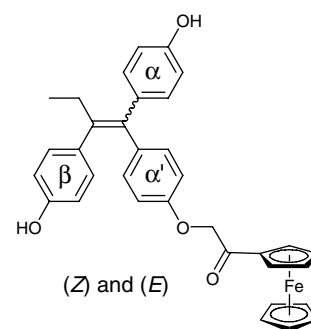


**Anh Nguyen, Siden Top, Anne Vessières,
Pascal Pigeon, Michel Huché,
Elizabeth A. Hillard, Gérard Jaouen**

J. Organomet. Chem. 692 (2007) 1219

Organometallic analogues of tamoxifen: Effect of the amino side-chain replacement by a carbonyl ferrocenyl moiety in hydroxytamoxifen

Ferrocenyl analogues of tamoxifen, obtained from the replacement of amino side chain by a ferrocenyl group, exhibit a good affinity with the estrogen receptor α and β , and an anti-proliferative activity on MCF-7 and PC-3 cancer cell lines.



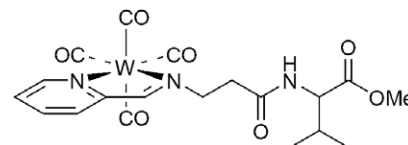
Regular papers

**Richard S. Herrick, Julie Dupont,
Iwona Wrona, Julia Pilloni, Matthew Beaver,
Mark Benotti, Frank Powers,
Christopher J. Ziegler**

J. Organomet. Chem. 692 (2007) 1226

Preparation and characterization of d^6 tungsten compounds with amino acid derivatized diimine ligands and preparation of dipeptide derivatives using peptide coupling agents

Condensation of pyridine-2-carboxaldehyde and α -amino acids in the presence of $\text{W}(\text{CO})_4(\text{pip})_2$ causes decarboxylation. Decarboxylation does not occur for β -alanine or GABA. Preparation of dipeptide compounds by coupling $[\text{Hpip}][\text{W}(\text{CO})_4(\text{pyca}-(\text{CH}_2)_n-\text{CO}_2)]$, $n = 2$ or 3 , with amino acid esters is reported along with the molecular structure of $\text{W}(\text{CO})_4(\text{pyca}-\beta\text{-Ala}-\text{Val}-\text{OMe})$.

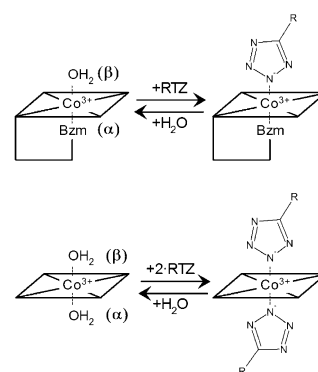


**Sergey N. Fedosov, Lars Berglund, Ebba Nexø,
Torben E. Petersen**

J. Organomet. Chem. 692 (2007) 1234

Tetrazole derivatives and matrices as novel cobalamin coordinating compounds

We have found that tetrazole derivatives can coordinate to $\text{H}_2\text{O} \cdot \text{cobalamin}$. A specific group (presumably tetrazole) can be easily created in CNBr-activated Sepharose by treatment with azide. The prepared matrix contained ≈ 10 mM of the active groups, which bound $\text{H}_2\text{O} \cdot \text{cobalamin}$ with $K_d = 10^{-5}$ – 10^{-6} M.

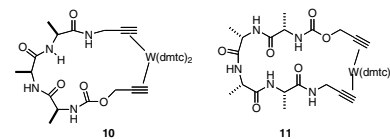


Timothy P. Curran, Adam B. Lesser,
Richard S.H. Yoon

J. Organomet. Chem. 692 (2007) 1243

Turn conformations in a metallacyclitriptide and a metallacyclitetrapeptide induced by tungsten–alkyne coordination

Tungsten–alkyne coordination yields metallacyclicpeptides possessing turn structures.

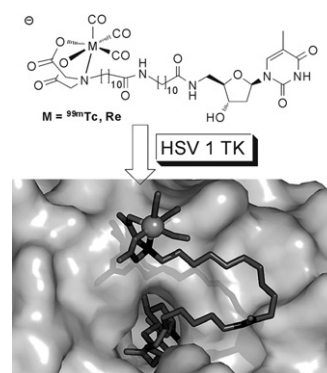


M. Stichelberger, D. Desbouis, V. Spiwok,
L. Scapozza, P.A. Schubiger, R. Schibli

J. Organomet. Chem. 692 (2007) 1255

Synthesis, *in vitro* and *in silico* assessment of organometallic Rhenium(I) and Technetium(I) thymidine complexes

Organometallic technetium and rhenium complexes of 5'-amino-5'-deoxythymidine derivatives were synthesized. Enzyme kinetic studies revealed mixed (uncompetitive) inhibition of human TK for all complexes. The complex with a spatial separation of the thymidine and the metal entities by ~30 Å revealed competitive inhibition of HSV1 TK. Molecular dynamic calculations confirmed these experimental findings.

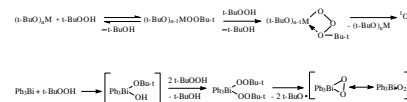


Elena A. Ziburdaeva, Viktor A. Dodonov,
Larisa P. Stepovik

J. Organomet. Chem. 692 (2007) 1265

Oxygen activation on metallic centers and oxidizing abilities of such oxygen

Tri-*tert*-butoxyaluminium (tetra-*tert*-butoxytitanium) and *tert*-butylhydroperoxide (1:2) under mild conditions (20 °C) in C₆H₆, C₆H₅Cl or CCl₄ generate oxygen in a yield ~80%. ~50% of the oxygen is in the electron-excited singlet state. System triphenylbismuth-*tert*-butylhydroperoxide (1:3) forms an η²-peroxocomplex. XOOBu-*t* [X = (*t*-BuO)₂Al, (*t*-BuO)₃Ti] and Ph₃Bi(η²O₂) demonstrate high oxidizing activity.

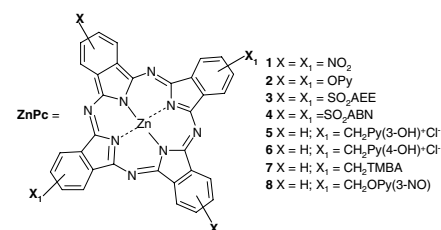


Stefano Banfi, Enrico Caruso,
Loredana Buccafurni, Raffaella Ravizza,
Marzia Gariboldi, Elena Monti

J. Organomet. Chem. 692 (2007) 1269

Zinc phthalocyanines-mediated photodynamic therapy induces cell death in adenocarcinoma cells

A panel of eight Zn-phthalocyanines (1)–(8), differently substituted on the benzo units, was synthesized either by direct cyclic-tetramerization of substituted phthalonitriles, or by chemical transformations of available Zn-phthalocyanines. The phototoxicity of compounds 1–8 was evaluated *in vitro* on tumor cells, and their effect compared with those induced by porfimer sodium.

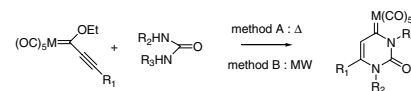


**Antonietta Artillo, Giorgio Della Sala,
Marco De Santis, Anna Llordes,
Susagna Ricart, Aldo Spinella**

J. Organomet. Chem. 692 (2007) 1277

Preparation of organometallic uracil-analogue Fischer carbene complexes: Comparative study of conventional heating vs microwave irradiation

Organometallic uracil-analogues of Fischer carbene complexes are readily accessible through reaction of alkynyl alkoxy carbene metal complexes with mono and dimethylureas. The synthetic utility of this methodology was demonstrated by the preparation of a variety of Fischer carbene complexes incorporating the uracil skeleton, and applied to the synthesis of the organometallic analog of the commercial dimethyl uracil.

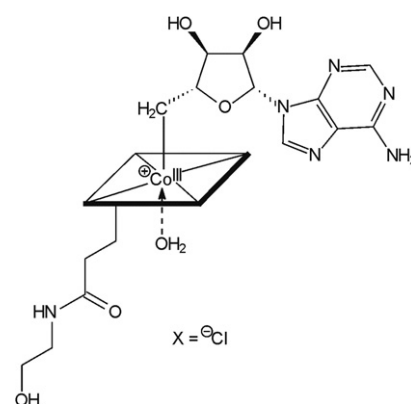


Philip A. Butler, Bernhard Kräutler

J. Organomet. Chem. 692 (2007) 1285

Adenosyl-176-norcobinamide – A likely biosynthetic precursor to natural 176-norvitamin B₁₂ derivatives

Co_β-5'-adenosyl-176-norcobinamide – a likely biosynthetic intermediate of the complete 176-norcobinamides – was synthesized by *in situ* alkylation of electrochemically prepared Co(I)-176-norcobinamide.

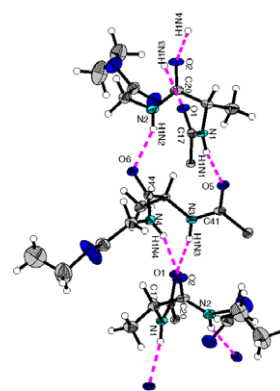


**Alok Goel, David Savage, Steven R. Alley,
Paula N. Kelly, Dermot O'Sullivan,
Helge Mueller-Bunz, Peter T.M. Kenny**

J. Organomet. Chem. 692 (2007) 1292

The synthesis and structural characterization of novel *N-meta*-ferrocenyl benzoyl dipeptide esters: The X-ray crystal structure and *in vitro* anti-cancer activity of *N*-{*meta*-ferrocenyl}-benzoyl}-L-alanine-glycine ethyl ester

A series of *N-meta*-ferrocenyl benzoyl dipeptide esters were prepared by coupling *meta*-ferrocenyl benzoic acid to the dipeptide ethyl esters using the conventional 1,3-dicyclohexylcarbodiimide (DCC), 1-hydroxybenzotriazole (HOBt) protocol. The dipeptides employed in the synthesis were AlaGly(OEt), AlaAla(OEt), AlaLeu(OEt) and AlaPhe(OEt). The compounds were fully characterized by a range of NMR spectroscopic techniques, mass spectrometry (MALDI-MS, ESI-MS), and cyclic voltammetry (CV). In addition, the X-ray crystal structure and cytotoxicity of *N*-{*meta*-(ferrocenyl)-benzoyl}-L-alanine-glycine ethyl ester (**2**) towards lung cancer cells has been determined.

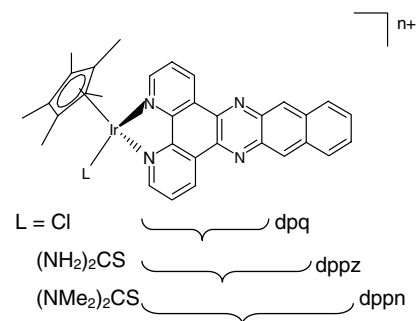


Sven Schäfer, William S. Sheldrick

J. Organomet. Chem. 692 (2007) 1300

Coligand tuning of the DNA binding properties of half-sandwich organometallic intercalators: Influence of polypyridyl (pp) and monodentate ligands (L = Cl, (NH₂)₂CS, (NMe₂)₂CS) on the intercalation of (η⁵-pentamethylcyclopentadienyl)-iridium(III)-dipyridoquinoxaline and -dipyridophenazine complexes

The DNA binding of novel organoiridium(III) polypyridyl (pp) complexes of the types [(η⁵-C₅Me₅)Ir(L)(pp)](CF₃SO₃) (**1–3**) and [(η⁵-C₅Me₅)Ir(L)(pp)](CF₃SO₃)₂ (L = (NH₂)₂CS, (NMe₂)₂CS) (**4–9**) has been studied by UV/Vis spectroscopy, CD and viscosometric titrations. The mode of binding (coordinative, surface or intercalative) can be tuned by the nucleophilicity and bulkiness of the monodentate ligand L. For L=(NH₂)₂CS, dppz presents an optimum aromatic surface area for side-on intercalation into DNA.

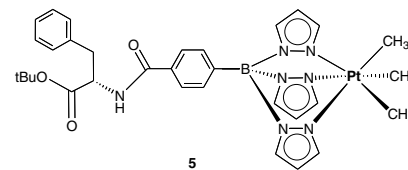


Matthew C. Kuchta, Christian Gemel,
Nils Metzler-Nolte

J. Organomet. Chem. 692 (2007) 1310

An amino acid bioconjugate of an organoplatinum tris(pyrazolyl)borate complex: Synthesis and structure of $[p\text{-}({}^t\text{BuO-Phe-CO})\text{C}_6\text{H}_4\text{Tp}]\text{PtMe}_3$

A tetravalent organoplatinum complex of a benzoic acid-functionalized-Tp ligand $p\text{-}(\text{HO}_2\text{C})\text{C}_6\text{H}_4\text{TpPtMe}_3$ has been synthesized and shown to undergo coupling to phenylalanine-*tert*-butylester to provide the first tris-(pyrazolyl)borate bioconjugate $[p\text{-}({}^t\text{BuO-Phe-CO})\text{C}_6\text{H}_4\text{Tp}]\text{PtMe}_3$ which has been structurally characterized by X-ray diffraction.

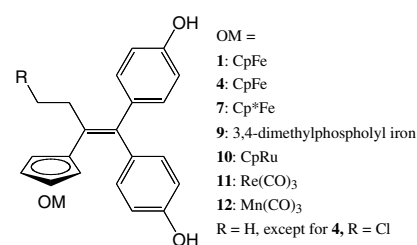


Elizabeth A. Hillard, Anne Vessières,
Siden Top, Pascal Pigeon, Konrad Kowalski,
Michel Huché, Gérard Jaouen

J. Organomet. Chem. 692 (2007) 1315

Organometallic diphenols: The importance of the organometallic moiety on the expression of a cytotoxic effect on breast cancer cells

The diphenol ferrocenyl compounds **1** and **4** uniquely exhibited cytotoxic effects against breast cancer cells, and displayed distinctive oxidation chemistry, while the non-ferrocenyl compounds were estrogenic (**9–12**) or inactive (**7**).

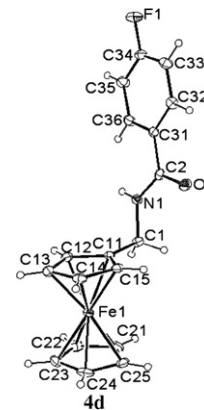


Paula N. Kelly, Adeline Prêtre, Siobhan Devoy,
Isobel O'Rielly, Rosaleen Devery, Alok Goel,
John F. Gallagher, Alan J. Lough,
Peter T.M. Kenny

J. Organomet. Chem. 692 (2007) 1327

Synthesis, structural characterisation and biological activity of novel *N*-(ferrocenylmethyl)benzene-carboxamide derivatives

A series of *N*-(ferrocenylmethyl)benzene-carboxamide derivatives (**4a–f**) have been synthesised by coupling ferrocenylmethyl amine **3** with benzoic acid and various substituted fluorobenzoic acids using the standard 1,3-dicyclohexylcarbodiimide (DCC), 1-hydroxybenzotriazole (HOBt) protocol. All the compounds were fully characterised using a combination of ¹H NMR, ¹³C NMR, ¹⁹F NMR, DEPT-135, ¹H–¹H COSY and ¹H–¹³C COSY (HMQC) spectroscopy and electrospray ionisation mass spectrometry (ESI-MS). The compounds **4a**, **4d**, **4e** and **4f** exhibited cytotoxic effects on the MDA-MB-435-S-F breast cancer cell line. Single crystal X-ray crystallographic data for **4d** is also presented.

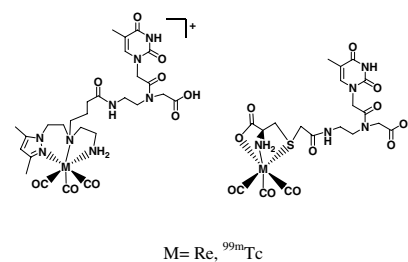


Catarina Xavier, Jae-Kyoung Pak,
Isabel Santos, Roger Alberto

J. Organomet. Chem. 692 (2007) 1332

Evaluation of two chelators for labelling a PNA monomer with the $fac\text{-}[^{99\text{m}}\text{Tc}(\text{CO})_3]^+$ moiety

Two bifunctional chelators bearing a PNA monomer containing a thymine as nucleobase were synthesized and characterized. These bifunctional chelators allowed the synthesis of the tricarbonyl complexes $fac\text{-}[\text{M}(\text{CO})_3(\kappa^3\text{-6})]^+$ (M = Re (**8**), M = ^{99m}Tc (**8a**)) and $fac\text{-}[\text{M}(\text{CO})_3(\kappa^3\text{-7})]$ (M = Re (**9**), M = ^{99m}Tc (**9a**)). The possibility of preparing these model complexes encourages to pursue the labelling of PNAs with clinical relevance, using these bifunctional chelators.

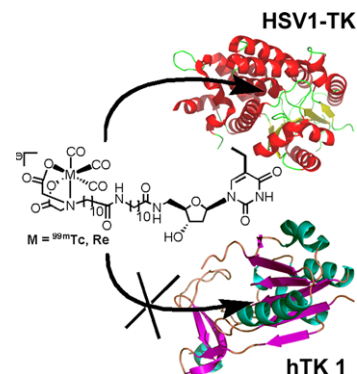


D. Desbouis, P.A. Schubiger, R. Schibli

J. Organomet. Chem. 692 (2007) 1340

Synthesis of tricarbonyl rhenium and technetium complexes of a 5'-carboxamide 5-ethyl-2'-deoxyuridine for selective inhibition of herpes simplex virus thymidine kinase 1

The first organo-technetium and organo-rhenium complexes of 5-ethyl-2'-deoxyuridine have been prepared. They selectively inhibit the viral HSV1-TK in a competitive manner but do not display any activity against human TK 1. The potency of inhibition is significantly improved compared to the isostructural thymidine derivative by virtue of exchange of the methyl group by an ethyl group at position 5 of the base functionality. In vitro cell experiments revealed a low uptake of the radioactive complex in HSV1 TK-positive cells.

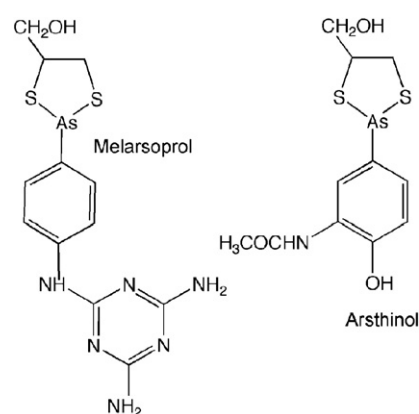


Siham Ben Zirar, Stéphane Gibaud, Alexandra Camut, Alain Astier

J. Organomet. Chem. 692 (2007) 1348

Pharmacokinetics and tissue distribution of the antileukaemic organoarsenicals arsthinol and melarsoprol in mice

A pharmacokinetics study of antileukaemic melarsoprol and arsthinol has been done. In the bone marrow, arsenic concentrations were very high, especially that of melarsoprol. The brain concentrations were high, although lower than in the bone marrow. This fact is in accordance with the antileukaemic activity and the brain toxicity of these organoarsenicals.

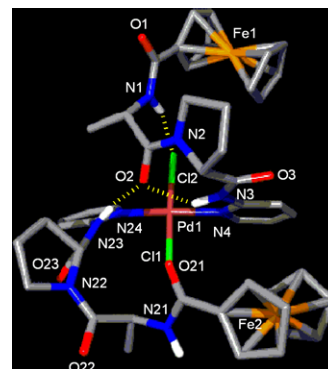


Toshiyuki Moriuchi, Takashi Fujiwara, Toshikazu Hirao

J. Organomet. Chem. 692 (2007) 1353

Complexation-induced conformational regulation of ferrocene-dipeptide conjugates to nucleate γ -turn-like structure

The complexation of the ferrocene-dipeptide conjugate bearing one dipeptide chain of heterochiral sequence (-L-Ala-D-Pro-NHPy) with $\text{PdCl}_2(\text{MeCN})_2$ was demonstrated to afford the 2:1 *trans* palladium complex, which is present in the pseudo-helical conformation and γ -turn-like structure in the crystal structure through complexation and intramolecular hydrogen bonding. Furthermore, the left-handed pseudo-helical molecular arrangement was formed through a network of intermolecular hydrogen bonds.

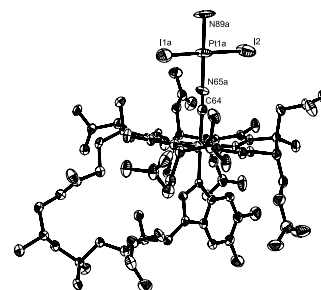


Pilar Ruiz-Sánchez, Stefan Mundwiler, Alfredo Medina-Molner, Bernhard Spingler, Roger Alberto

J. Organomet. Chem. 692 (2007) 1358

Iodination of cisplatin adduct of Vitamin B₁₂ [$\{\text{B}_{12}\}\text{-CN-}\{cis\text{-PtCl}(\text{NH}_3)_2\}^+$]

The reaction of the cisplatin-vitamin B₁₂ adduct [$\{\text{B}_{12}\}\text{-CN-}\{cis\text{-PtCl}(\text{NH}_3)_2\}^+$] with iodide results in the rapid substitution of one chloride and one ammonia ligand by iodide and the formation of [$\{\text{B}_{12}\}\text{-CN-}\{trans\text{-PtI}_2(\text{NH}_3)\}$]. The analogous reaction with ¹³¹I gave only mono-substitution and represents a straight forward way for platinum mediated radiolabeling of B₁₂.

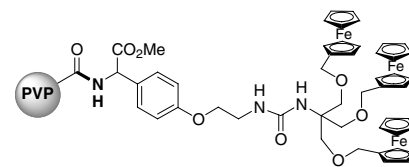


**Clara Baldoli, Claudio Oldani,
Emanuela Licandro, Prasanna Ramani,
Antonio Valerio, Paolo Ferruti, Luigi Falcicola,
Patrizia Mussini**

J. Organomet. Chem. 692 (2007) 1363

Ferrocene derivatives supported on poly(*N*-vinylpyrrolidin-2-one) (PVP): Synthesis of new water-soluble electrochemically active probes for biomolecules

End-carboxy functionalized poly(*N*-vinylpyrrolidin-2-one) (PVP) has been used as new water-soluble and biocompatible polymeric support for a series of ferrocene labeled amino acid and PNA monomer derivatives. The organometallic polymer-conjugates thus obtained are new and potentially useful as water-soluble electrochemically active probes for biomolecules.

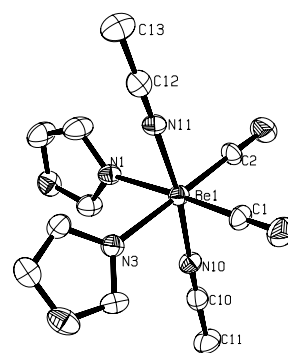


**Lukas Kromer, Bernhard Spingler,
Roger Alberto**

J. Organomet. Chem. 692 (2007) 1372

Synthesis and reactivity of $[\text{ReBr}_2(\text{NCCH}_3)_2(\text{CO})_2]^-$: A new precursor for bioorganometallic chemistry

The water soluble complex $[\text{ReBr}_2(\text{NCCH}_3)_2(\text{CO})_2]^-$ has been prepared. Substitution reactions in water with mono- and bidentate ligands resulted in the exclusive exchange of bromide. The $[\text{Re}(\text{NCCH}_3)_2(\text{CO})_2]^+$ core represent a new building block in bioorganometallic chemistry.

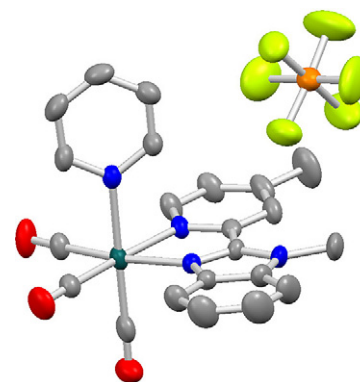


**Andrea Albertino, Claudio Garino,
Simona Ghiani, Roberto Gobetto, Carlo Nervi,
Luca Salassa, Edward Rosenberg,
Ayesha Sharmin, Guido Viscardi,
Roberto Buscaino, Gianluca Croce,
Marco Milanese**

J. Organomet. Chem. 692 (2007) 1377

Photophysical properties and computational investigations of tricarbonylrhenium(I)[2-(4-methylpyridin-2-yl)benzo[*d*]-*X*-azole]L and tricarbonylrhenium(I)[2-(benzo[*d*]-*X*-azol-2-yl)-4-methylquinoline]L derivatives (X = N-CH₃, O, or S; L = Cl⁻, pyridine)

A series of novel tricarbonylrhenium(I) complexes with 2-(4-methylpyridin-2-yl)benzo[*d*]-*X*-azole or 2-(benzo[*d*]-*X*-azol-2-yl)-4-methylquinoline (X = N-CH₃, O, or S) as ligands were synthesized and fully characterized. Their photophysical and electrochemiluminescent properties were studied. DFT and time-dependent (TD) DFT calculations were carried out for investigating the effect of the organic ligand on the optical properties and electronic structure of the reported complexes.

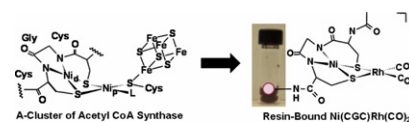


**Kayla N. Green, William D. James,
Angelica V. Cantillo, Marcetta Y. Darensbourg**

J. Organomet. Chem. 692 (2007) 1392

The acetyl CoA synthase paradigm for hybrid bio-organometallics: Quantitative measures for resin-bound Ni-Rh complexes

Inspired by the active site of Acetyl CoA Synthase we have constructed the resin-bound ligand $\text{Ni}(\text{CGC})^{2-}$ and derivatized it with $\text{Rh}^1(\text{CO})_2$. Through UV-Vis spectroscopy and Neutron Activation Analysis, the loading of CGC, Ni, and Rh have been established. The ability of $\text{O-Ni}(\text{CGC})\text{Rh}(\text{CO})_2^{1-}$ to withstand stress (i.e., leaching studies) was also investigated.

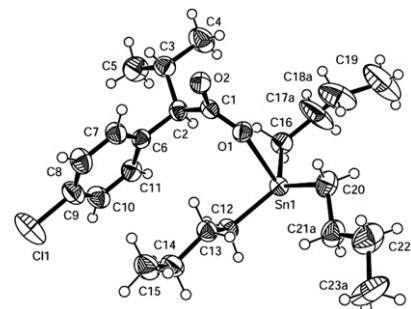


George Eng, Xueqing Song, Alejandra Zapata, Angel C. de Dios, Leah Casabianca, Robert D. Pike

J. Organomet. Chem. 692 (2007) 1398

Synthesis, structural and larvicidal studies of some triorganotin 2-(*p*-chlorophenyl)-3-methylbutyrates

A series of triorganotin 2-(*p*-chlorophenyl)-3-methylbutyrates, $(R_3SnO_2CCH(CH_2)_2C_6H_4Cl-4)$, where R = methyl, ethyl, *n*-propyl, *n*-butyl, phenyl and *cyclo*-hexyl, have been synthesized. Their structures have been determined by various spectroscopic techniques in both solution and solid states. Larvicidal activities of the complexes were evaluated against three species of mosquito larvae.



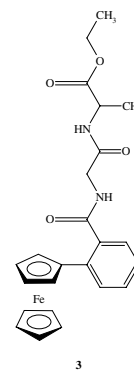
Note

Alan J. Corry, Alok Goel, Steven R. Alley, Paula N. Kelly, Dermot O'Sullivan, David Savage, Peter T.M. Kenny

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N-*ortho*-Ferrocenyl benzoyl dipeptide esters: Synthesis, structural characterization and *in vitro* anti-cancer activity of *N*-{*ortho*-(ferrocenyl)benzoyl}-glycine-L-alanine ethyl ester and *N*-{*ortho*-(ferrocenyl)benzoyl}-L-alanine-glycine ethyl ester

N-*ortho*-ferrocenyl benzoyl dipeptide ethyl esters **2–6** have been prepared by coupling *ortho*-ferrocenyl benzoic acid to the dipeptide ethyl esters GlyGly(OEt) (**2**), GlyAla(OEt) (**3**), GlyPhe(OEt) (**4**), AlaGly(OEt) (**5**) and AlaPhe(OEt) (**6**) using the conventional 1,3-dicyclohexylcarbodiimide (DCC), 1-hydroxybenzotriazole (HOBt) procedure. The compounds were fully characterized by a range of NMR spectroscopic techniques, mass spectrometry and cyclic voltammetry. The IC_{50} values of **3** and **5** were found to be 5.3 and 21 μ M, respectively, against highly invasive/super invasive lung cancer cells.



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