



Contents

Special Issue: Organometallics for Energy Conversion

Editorial

Richard D. Adams

J. Organomet. Chem. 694 (2009) 2643

Foreword to special issue on organometallics for energy conversion

The reasons for organizing this special issue of the Journal of Organometallic Chemistry on Energy Conversion are presented.



Review Articles

Wai-Yeung Wong

J. Organomet. Chem. 694 (2009) 2644

Challenges in organometallic research – Great opportunity for solar cells and OLEDs

Organometallic chemistry can and will make an important contribution to the global energy problem. This article presents a critical perspective of the field of

organometallic compounds in molecular devices where light is transformed into electricity (in photovoltaic solar cells) whereas electrical energy is converted into light energy (in organic light-emitting diodes). New synthetic methods need to be developed to produce technologically useful materials with specific functional roles.

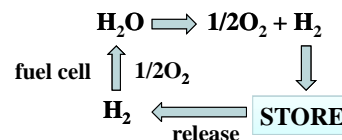


Gregory J. Kubas

J. Organomet. Chem. 694 (2009) 2648

Hydrogen activation on organometallic complexes and H₂ production, utilization, and storage for future energy

This perspective article serves to highlight the contributions to this special volume of Journal of Organometallic Chemistry entitled "Organometallics for Energy Conversion". The key features of dihydrogen coordination to transition metal complexes are discussed in the context of the challenge of producing and utilizing hydrogen as the energy carrier of the future.

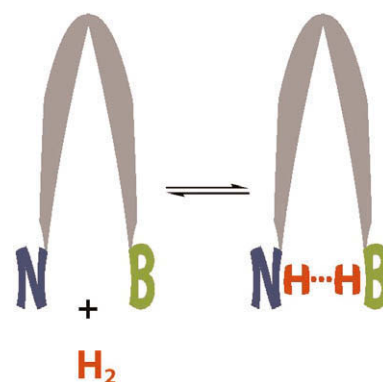


**Victor Sumerin, Felix Schulz,
Martin Nieger, Michiko Atsumi,
Cong Wang, Markku Leskelä,
Pekka Pyykkö, Timo Repo,
Bernhard Rieger**

J. Organomet. Chem. 694 (2009) 2654

Experimental and theoretical treatment of hydrogen splitting and storage in boron–nitrogen systems

Intramolecular boron–nitrogen systems, where the active centers are located close to each other, act like molecular tweezers and are able to reversibly activate hydrogen. The recent experimental and theoretical studies concerning the heterolytic hydrogen splitting and liberation by aminoboranes are presented.

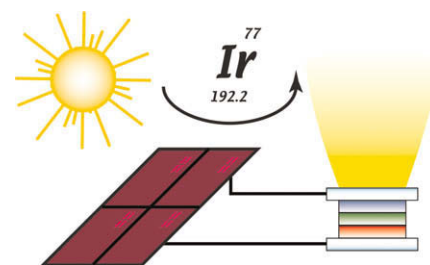


**Etienne Baranoff, Jun-Ho Yum,
Michael Graetzel, Md.K. Nazeeruddin**

J. Organomet. Chem. 694 (2009) 2661

Cyclometallated iridium complexes for conversion of light into electricity and electricity into light

Applications of cyclometallated iridium complexes for energy saving light-emitting devices (OLED's) and energy generating dye-sensitized solar cells (DSSC's) are briefly reviewed.

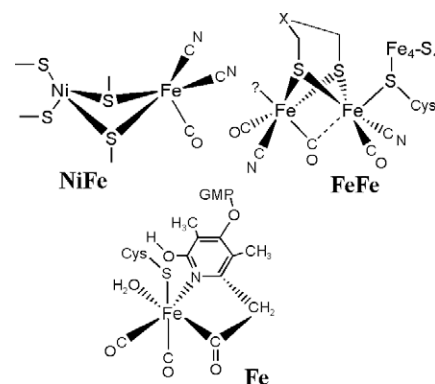


D. Michael Heinekey

J. Organomet. Chem. 694 (2009) 2671

Hydrogenase enzymes: Recent structural studies and active site models

Production and utilization of hydrogen in nature is catalyzed by hydrogenase enzymes. The active site structures of the hydrogenases contain carbon monoxide and cyanide bound to iron. These structures are unprecedented in biology, which has led to intense efforts to generate small molecule model complexes.

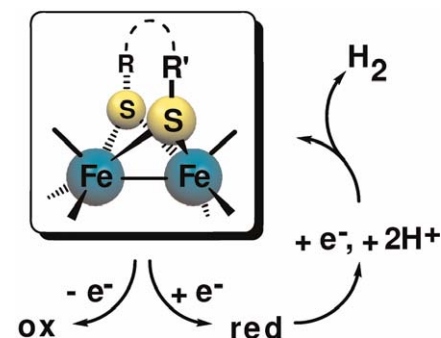


**Greg A.N. Felton, Charles A. Mebi,
Benjamin J. Petro, Aaron K. Vannucci,
Dennis H. Evans, Richard S. Glass,
Dennis L. Lichtenberger**

J. Organomet. Chem. 694 (2009) 2681

Review of electrochemical studies of complexes containing the Fe_2S_2 core characteristic of [FeFe]-hydrogenases including catalysis by these complexes of the reduction of acids to form dihydrogen

A review of published literature on the electrochemical reduction and oxidation of complexes containing the Fe_2S_2 core characteristic of the active site of [FeFe]-hydrogenases. Correlations between reduction and oxidation potentials and molecular structure are developed and catalytic formation of H_2 is also discussed.



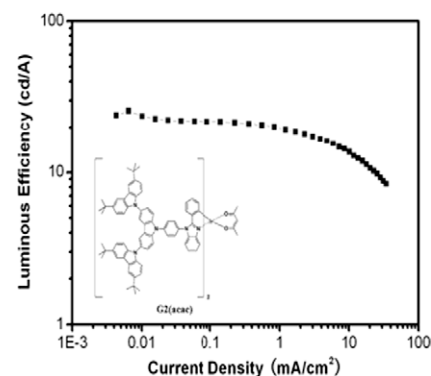
Regular Papers

**Junqiao Ding, Jianhong Lü,
Yanxiang Cheng, Zhiyuan Xie,
Lixiang Wang, Xiabin Jing, Fosong Wang**

J. Organomet. Chem. 694 (2009) 2700

Effect of ancillary ligands on the properties of heteroleptic green iridium dendrimers functionalized with carbazole dendrons

The heteroleptic iridium dendrimer **G2(acac)** can be conveniently synthesized with a total yield as high as 67% and the efficiency of its non-doped electrophosphorescent device reaches to 25.8 cd/A (7.7%).

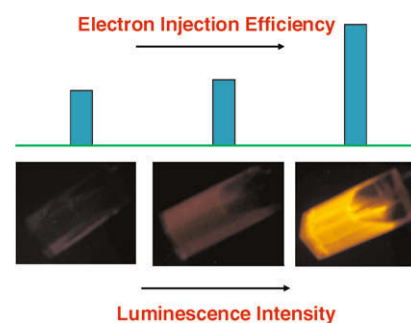


**Zhijun Ning, Qiong Zhang, Wenjun Wu,
He Tian**

J. Organomet. Chem. 694 (2009) 2705

Novel iridium complex with carboxyl pyridyl ligand for dye-sensitized solar cells: High fluorescence intensity, high electron injection efficiency?

Novel iridium-based sensitizers were synthesized for sensitization of dye-sensitized solar cells. By changing the ligand, the absorption spectra can be extended and molar extinction coefficient was enhanced. The highest conversion efficiency reached 2.86%. It was found that the electron injection efficiencies are consistent with their luminescence quantum yields. The high oxidative potential of **Ir3** enables it to be used along with $\text{Br}^-/\text{Br}_3^-$ redox electrolyte and the photovoltage was found to be enhanced greatly.

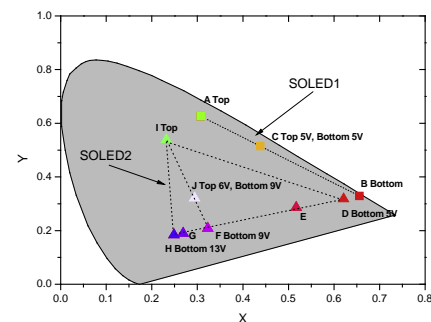


C.J. Liang, Wallace C.H. Choy

J. Organomet. Chem. 694 (2009) 2712

Tunable full-color emission of two-unit stacked organic light emitting diodes with dual-metal intermediate electrode

The color-tunable stacked organic light-emitting devices (SOLEDs) with independently-addressable intermediate Al/Au electrode are examined. Multi- and full-color emissions are achieved in two-unit SOLEDs.

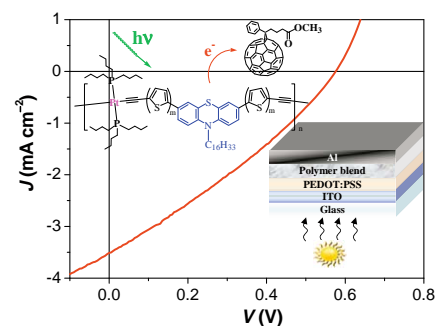


**Wai-Yeung Wong, Wing-Cheong Chow,
Kai-Yin Cheung, Man-Kin Fung,
Aleksandra B. Djurišić, Wai-Kin Chan**

J. Organomet. Chem. 694 (2009) 2717

Harvesting solar energy using conjugated metallopolymers containing electron-rich phenothiazine-oligothiophene moieties

Tuning the properties and polymer solar cell efficiency in polyplatinynes containing the phenothiazine-oligothiophene spacer by varying the chain length of oligothiophenyl components is described. This tuning strategy for solar energy conversion provides an access toward efficient polymer solar cells and demonstrates the potential of conjugated metallopolymers for efficient power generation even at shorter absorption wavelengths.

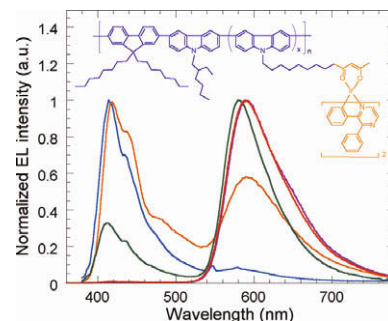


**Lei Ying, Jianhua Zou, Anqi Zhang,
Bing Chen, Wei Yang, Yong Cao**

J. Organomet. Chem. 694 (2009) 2727

Novel orange-red light-emitting polymers with cyclometalated iridium complex grafted in alkyl chain

Novel poly(fluorene-*alt*-carbazole) (PFCz) based copolymers with 3,6-carbazole-*N*-alkyl grafted iridium complex using 2,3-diphenylpyrazine as ligand were synthesized. By complete or incomplete energy transfer from the host polymer to the guest iridium complex, the efficient orange-red or white light-emitting electroluminescence could be achieved.

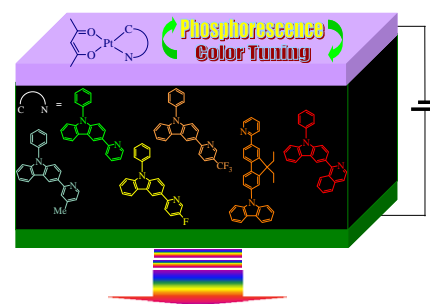


**Cheuk-Lam Ho, Wai-Yeung Wong,
Bing Yao, Zhiyuen Xie, Lixiang Wang,
Zhenyang Lin**

J. Organomet. Chem. 694 (2009) 2735

Synthesis, characterization, photophysics and electrophosphorescent applications of phosphorescent platinum cyclometalated complexes with 9-arylcarbazole moieties

The synthesis, crystal structures, photophysics and electrophosphorescence of some color-tunable platinum-based phosphors with substituted 9-arylcarbazole moieties are reported. This class of new functional metallophosphors shows improved hole-injection/hole-transporting traits relative to the benchmark complex with 2-phenylpyridine. The structure-property-function relationships of these molecules is discussed as a function of the ligand and substituent effects of the carbazolyl chromophore.

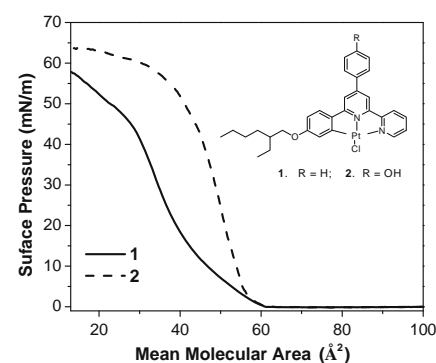


Iswarya Mathew, Wenfang Sun

J. Organomet. Chem. 694 (2009) 2750

Photophysics of Pt(II) 4,6-diphenyl-2,2'-bipyridyl complexes in solution and in LB film

Two amphiphilic platinum(II) 4,6-diphenyl-2,2'-bipyridyl complexes with alkoxy substituent were synthesized and characterized. LB films of these two complexes were prepared and characterized by AFM technique. Electronic absorption and emission characteristics of these complexes in solutions at room temperature, in glassy solutions at 77 K, and in LB films were studied.

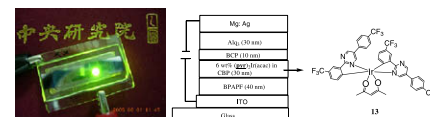


**Cing-Fong Lin, Wei-Sheng Huang,
Hsien-Hsin Chou, Jiann T. Lin**

J. Organomet. Chem. 694 (2009) 2757

Synthesis and characterization of cyclometalated iridium(III) complexes containing pyrimidine-based ligands

Cyclometalated iridium complexes based on pyrimidine derivatives have been synthesized. Green-emitting OLEDs were fabricated using these complexes as the dopants. Computations were also carried out for the complexes.

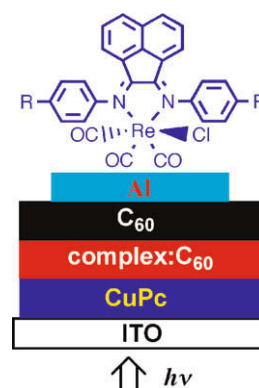


**Chris S.K. Mak, Hei Ling Wong,
Qing Yun Leung, Wing Yan Tam,
Wai Kin Chan, Aleksandra B. Djurišić**

J. Organomet. Chem. 694 (2009) 2770

The use of sublimable chlorotricarbonyl bis(phenylimino)acenaphthene rhenium(I) complexes as photosensitizers in bulk-heterojunction photovoltaic devices

A series of sublimable rhenium complexes was used in the fabrication of bulk-heterojunction photovoltaic cells. The active layer of the devices composes of a blend of rhenium complex and C₆₀, and the optical absorption by the complex plays an important role in photosensitization process.

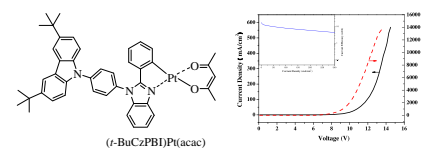


**Hui Li, Junqiao Ding, Zhiyuan Xie,
Yanxiang Cheng, Lixiang Wang**

J. Organomet. Chem. 694 (2009) 2777

Synthesis, characterization and electrophosphorescent properties of mononuclear platinum(II) complexes based on 2-phenylbenzimidazole derivatives

Phosphorescent platinum(II) complexes [(C^N)Pt(acac)] possessing nearly ideal square planar geometry display highly efficient electroluminescent performance. A maximum brightness of 13606 cd/m² and a maximum luminous efficiency of 17.5 cd/A are realized in the solution-processible OLED based on (*t*-BuCzPBI)-Pt(acac).

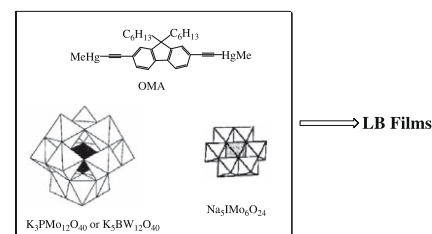


**Li Liu, Jun Yang, Ling-Xiang Qiao,
Ming Chen, Shi-Zhong Liu, Zu-Liang Du,
Zheng-Ji Zhou, Wai-Yeung Wong**

J. Organomet. Chem. 694 (2009) 2786

Preparation, luminescent, structural and electrical properties of Langmuir–Blodgett films of new organomercurial acetylde complex/heteropolyoxometalate hybrid composites

A new class of luminescent organometallic/inorganic nanohybrid Langmuir–Blodgett films based on a dimercury(II) diacetylde complex were prepared and characterized by π -A isotherms, low-angle X-ray diffraction, atomic force microscopy and scanning tunneling microscopy. These hybrid composites display intriguing luminescent and electrical properties and have great potential for various optoelectronic applications.

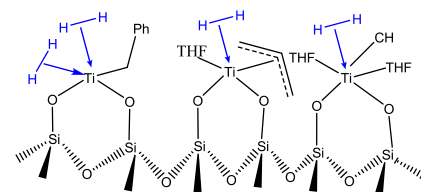


**Ahmad Hamaed, Tuan K.A. Hoang,
Michel Trudeau, David M. Antonelli**

J. Organomet. Chem. 694 (2009) 2793

Optimization of hydrogen storage capacity in silica-supported low valent Ti systems exploiting Kubas binding of hydrogen

Silica framework materials grafted with low valent Ti fragments for Kubas-type binding of hydrogen were optimized for hydrogen adsorption capacity, varying the surface area, pore size, loading levels, and type of organometallic precursor. The optimized silicas were capable to absorb 3.98, 2.40 and 2.27 H₂/Ti center when grafted with TiBz₄, Me₃Ti and Allyl₃Ti, respectively.

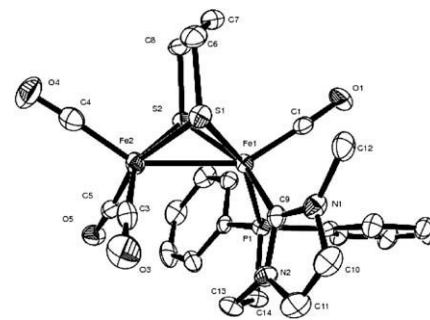


Didier Morvan, Jean-François Capon, Frédéric Gloaguen, François Y. Pétilion, Philippe Schollhammer, Jean Talarmin, Jean-Jacques Yaouanc, François Michaud, Nelly Kervarec

J. Organomet. Chem. 694 (2009) 2801

Modeling [FeFe] hydrogenase: Synthesis and protonation of a diiron dithiolate complex containing a phosphine-N-heterocyclic-carbene ligand

The synthesis of a nonsymmetric compound $[\text{Fe}_2\{\mu\text{-S}(\text{CH}_2)_3\text{S}\}(\text{CO})_4(\text{I}_{\text{Me}}\text{-}(\text{CH}_2)_2\text{-PPh}_2)]$ (I_{Me} = 1-methylimidazol-2-ylidene) with a chelating phosphine-N-heterocyclic-carbene ligand on a single iron atom is described. This complex catalyzes proton reduction. Low temperature NMR studies on the protonation of this chelated complex revealed the formation of a terminal hydride intermediate.

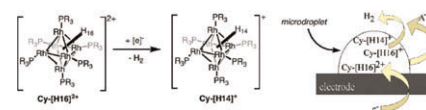


Rachel M. Hiney, Frank Marken, Paul R. Raithby, Andrew S. Weller

J. Organomet. Chem. 694 (2009) 2808

Aqueous-organic biphasic redox-chemistry of high-hydride content rhodium clusters: Towards immobilisation of redox-switchable H_2 binding materials on a surface

The rhodium cluster $[\text{Rh}_6(\text{PCy}_3)_6\text{H}_{12}][\text{BAR}_4^{\text{F}}]_2$ can be immobilised onto suitable electrode surfaces under organic microdroplet | aqueous electrolyte two-phase conditions and shows reversible electrochemical responses that include the redox-switched binding of H_2 .

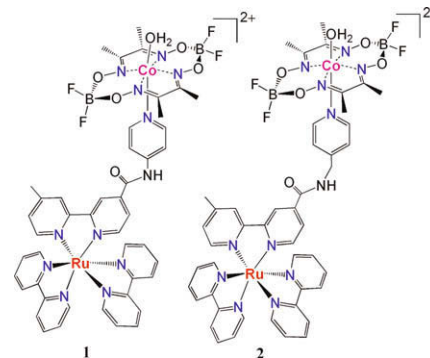


Cheng Li, Mei Wang, Jingxi Pan, Pan Zhang, Rong Zhang, Licheng Sun

J. Organomet. Chem. 694 (2009) 2814

Photochemical hydrogen production catalyzed by polypyridyl ruthenium-cobaloxime heterobinuclear complexes with different bridges

Two polypyridyl ruthenium-cobaloxime heterobinuclear complexes **1** and **2** were prepared and used for photochemical hydrogen generation. Complex **2** containing an unconjugated bridge displayed a higher turnover (48 TON) than complex **1** containing a conjugated bridge (38 TON) under the optimal reaction condition.

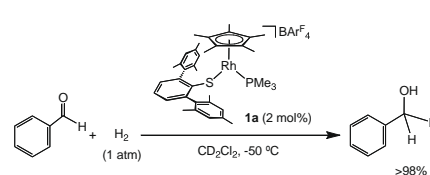


Mayumi Sakamoto, Yasuhiro Ohki, Gerald Kehr, Gerhard Erker, Kazuyuki Tatsumi

J. Organomet. Chem. 694 (2009) 2820

Catalytic hydrogenation of $\text{C}=\text{O}$ and $\text{C}=\text{N}$ bonds via heterolysis of H_2 mediated by metal-sulfur bonds of rhodium and iridium thiolate complexes

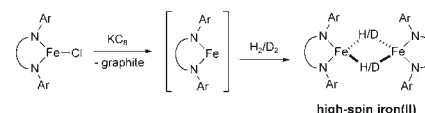
Coordinatively unsaturated rhodium and iridium complexes having a bulky thiolate, $[\text{Cp}^*\text{M}(\text{PMe}_3)(\text{SDmp})](\text{BAR}_4^{\text{F}})$ (**1a**: $\text{M} = \text{Rh}$; **1b**: $\text{M} = \text{Ir}$; $\text{Dmp} = 2,6\text{-}(\text{mesityl})_2\text{C}_6\text{H}_3$, $\text{Ar}^{\text{F}} = 3,5\text{-}(\text{CF}_3)_2\text{C}_6\text{H}_3$), catalyzed the hydrogenation of benzaldehyde, *N*-benzylidene-aniline, and cyclohexanone, under 1 atm of H_2 at low temperatures.



Thomas R. Dugan, Patrick L. Holland*J. Organomet. Chem.* 694 (2009) 2825

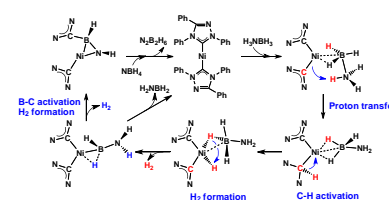
New routes to low-coordinate iron hydride complexes: The binuclear oxidative addition of H₂

Two new routes to [L^{tBu}Fe(μ-H)]₂ are reported. Et₃SiH reacts with L^{tBu}FeF to give [L^{tBu}Fe(μ-H)]₂ in 83% yield. Alternatively, binuclear oxidative addition of H₂ or D₂ to a putative Fe(I) intermediate gives [L^{tBu}Fe(μ-H)]₂ or [L^{tBu}Fe(μ-D)]₂ in ~60% yield. Mössbauer spectra of [L^{tBu}Fe(μ-H)]₂ show that the iron(II) centers are high-spin.

**Xinzheng Yang, Michael B. Hall***J. Organomet. Chem.* 694 (2009) 2831

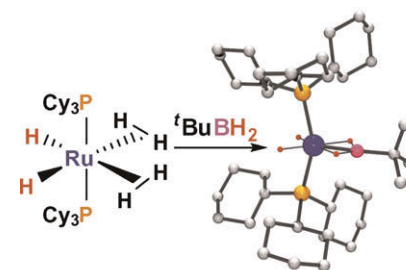
Density functional theory study of the mechanism for Ni(NHC)₂ catalyzed dehydrogenation of ammonia-borane for chemical hydrogen storage

The predicted reaction mechanism which features unexpected ligand participation points the way to finding new catalysts with higher efficiency, as partial unsaturation of the M-L bond may be essential for low energy H transfers.

**Yann Gloaguen, Gilles Alcaraz, Laure Vendier, Sylviane Sabo-Etienne***J. Organomet. Chem.* 694 (2009) 2839

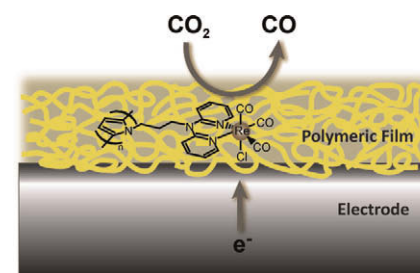
Tert-butylborane: A bis (σ-B-H) ligand in ruthenium hydride chemistry

The reaction of *tert*-butylborane with the bis(dihydrogen) complex RuH₂(η²-H₂)₂(PCy₃)₂ leads to the corresponding bis σ-borane complex which is the first example of a monoalkylborane ruthenium bis σ-complex. An alternative route involves the reaction of RuHCl(η²-H₂)(PCy₃)₂ with lithium *tert*-butylborohydride.

**Kwong-Chak Cheung, Peng Guo, Ming-Him So, Lawrence Yoon Suk Lee, Kam-Piu Ho, Wing-Leung Wong, Kam-Han Lee, Wing-Tak Wong, Zhong-Yuan Zhou, Kwok-Yin Wong***J. Organomet. Chem.* 694 (2009) 2842

Electrocatalytic reduction of carbon dioxide by a polymeric film of rhenium tricarbonyl dipyridylamine

A dipyridylamine ligand with a pendant pyrrole (*N*-(3-*N,N'*-bis(2-pyridyl)propyl)amino)pyrrole, PPP) and its corresponding rhenium(I) complex, Re(CO)₃(κ²-*N,N*-PPP)Cl, have been synthesized and characterized. The electrochemical reduction of CO₂ to CO by poly[Re(CO)₃(κ²-*N,N*-PPP)Cl] film was investigated.

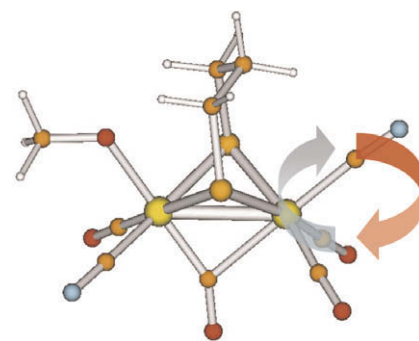


**Claudio Greco, Maurizio Bruschi,
Piercarlo Fantucci, Luca De Gioia**

J. Organomet. Chem. 694 (2009) 2846

Relation between coordination geometry and stereoelectronic properties in DFT models of the CO-inhibited [FeFe]-hydrogenase cofactor

Several models of the CO-inhibited form of [FeFe]-hydrogenases active site have been investigated by means of DFT, showing that the hardness of ligands on the proximal iron atom and the nature of the pendant can affect the coordination geometry of the distal iron atom. Such observations are relevant to the design of novel bio-inspired models which could be valuable for a thorough characterization of the structural properties of the CO-inhibited enzyme.

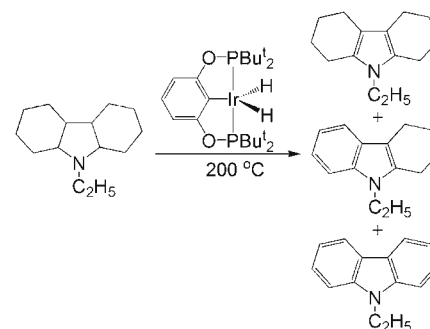


**Zhaohui Wang, Ian Tonks, Jack Belli,
Craig M. Jensen**

J. Organomet. Chem. 694 (2009) 2854

Dehydrogenation of *N*-ethyl perhydrocarbazole catalyzed by PCP pincer iridium complexes: Evaluation of a homogenous hydrogen storage system

The iridium complexes $\text{IrH}_2(\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{P}^i\text{Bu}^t)_2)$ (**1**), $\text{IrH}_2(\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{PP}^i\text{r}^t)_2)$ (**2**), and $\text{IrHCl}(\text{C}_6\text{H}_3\text{-2,6-(OP}^i\text{Bu}^t)_2)$ (**3**) have been found to be highly active catalysts for the dehydrogenation of *N*-ethyl perhydrocarbazole at 200 °C. However, dehydrogenation to the fully unsaturated ethyl carbazole does not occur in most instances. Complex **3** is the most active catalyst and shows a reasonable activity at 150 °C.

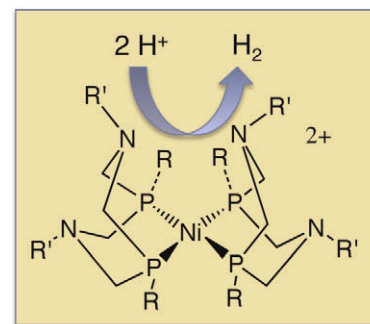


Douglas H. Pool, Daniel L. DuBois

J. Organomet. Chem. 694 (2009) 2858

$[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ar}})_2(\text{NCMe})][\text{BF}_4]_2$ as an electrocatalyst for H_2 production: $(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ar}}) = 1,5\text{-di(4-(thiophene-3-yl)phenyl)-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane}$

A thiophene modified nickel complex containing a cyclic diphosphine ligand with pendant nitrogen bases is shown to be an effective catalyst for the electrochemical reduction of protons to hydrogen.



Note

**Yohan Oudart, Vincent Artero,
Lucie Norel, Cyrille Train, Jacques Pécaut,
Marc Fontecave**

J. Organomet. Chem. 694 (2009) 2866

Synthesis, crystal structure, magnetic properties and reactivity of a Ni–Ru model of NiFe hydrogenases with a pentacoordinated triplet ($S = 1$) Ni^{II} center

$[\text{NiCl}(\text{xbsms})\text{Ru}(\text{CO})_3\text{Cl}]$ is a new functional model of the active site of NiFe hydrogenase. By contrast to other previously reported Ni–Ru complexes, the nickel(II) center coordinates a chloride ligand and adopts a paramagnetic ($S = 1$) electronic configuration.

