

# ORGANOMETALLICS

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**Cr(CO)<sub>5</sub>**

**Ce<sup>IV</sup>Y<sub>2</sub>N@C<sub>80</sub>**

**[Ce<sup>IV</sup>Y<sub>2</sub>N@C<sub>80</sub>]<sup>+</sup>**

**h<sub>v</sub> 254 nm**

**h<sub>v</sub> 541 - 592 nm**

**HOMO**

**LUMO**

**+e**

**-e**

**understanding of mechanism**

redox energy mediators photovoltaics liquid crystals electrocatalysis molecular electronics homogeneous catalysis optoelectronic materials redox markers, labels, probes supramolecular building blocks electrogenerated chemiluminescence

**ELECTROCHEMISTRY**



**ON THE COVER:** Much of the behavior of molecules can be viewed in terms of the movement of electrons. This view is obvious in the case of oxidation and reduction reactions, but so too catalysis can be viewed as the movement of electrons from one set of bonds to another, photophysical behaviors involve the movement of electrons between different energy levels and spatial distributions, and photovoltaics and molecular electronics depend on the transfer of electrons. Synthetic organometallic chemistry is making major strides in all of these areas and more. Electrochemistry represents a complementary approach to electron-transfer-initiated reactivity of organometallic compounds: instead of individual “classic” chemical oxidation/reduction agents, the electrode serves as a “clean” electron donor/acceptor. Moreover, its oxidation/reduction ability can be easily and continuously changed by the applied potential. Electrochemical experiments are thus rich in information concerning thermodynamics, kinetics, equilibria, reversibility, and mechanism. This issue brings together leading organometallic chemists and electrochemists to illustrate the breadth and power of electrochemical studies of organometallic compounds.

## Editor's Page

4513

Introduction to the Special Issue on Organometallic Electrochemistry  
 Jiří Ludvík,\* Dennis H. Evans,\* and Dennis L. Lichtenberger\*

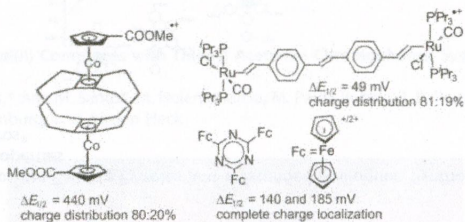
[dx.doi.org/10.1021/om5008709](https://doi.org/10.1021/om5008709)

## Reviews

4517

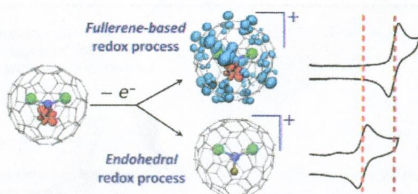
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Half-Wave Potential Splittings  $\Delta E_{1/2}$  as a Measure of Electronic Coupling in Mixed-Valent Systems: Triumphs and Defeats  
 Rainer F. Winter\*

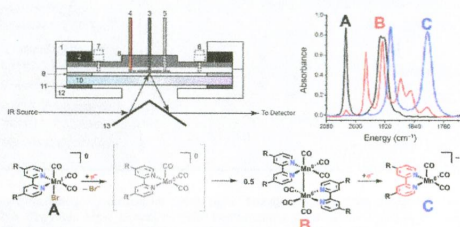
[dx.doi.org/10.1021/om500029x](https://doi.org/10.1021/om500029x)




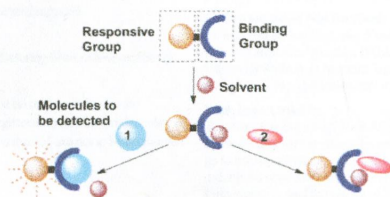
Transition-Metal and Rare-Earth-Metal Redox Couples inside Carbon Cages: Fullerenes Acting as Innocent Ligands  
 Yang Zhang and Alexey A. Popov\*



Developing a Mechanistic Understanding of Molecular Electrocatalysts for CO<sub>2</sub> Reduction using Infrared Spectro-electrochemistry  
 Charles W. Machan, Matthew D. Sampson, Steven A. Chabolla, Tram Dang, and Clifford P. Kubiak\*

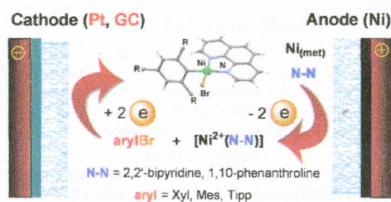


Molecular Recognition and Sensing Based on Ferrocene Derivatives and Ferrocene-Based Polymers  
 Ruoli Sun, Li Wang,\* Haojie Yu,\* Zain-ul- Abdin, Yongsheng Chen, Jin Huang, and Rongbai Tong

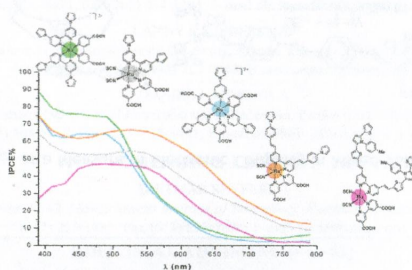


Electrochemical Synthesis and Properties of Organonickel  $\sigma$ -Complexes

Dmitry G. Yakhvarov,\* Aliya F. Khusnuriylova, and Oleg G. Sinyashin

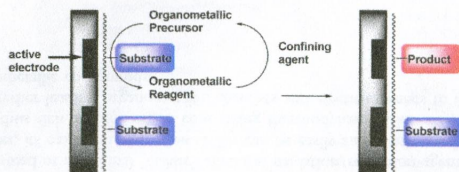
Ruthenium Polypyridine Complexes Bearing Pyrroles and  $\pi$ -Extended Analogues. Synthesis, Spectroelectronic, Electrochemical, and Photovoltaic Properties

Marc Beley\* and Philippe C. Gros\*



## Electrochemically Generated Organometallic Reagents and Site-Selective Synthesis on a Microelectrode Array

Kevin D. Moeller\*

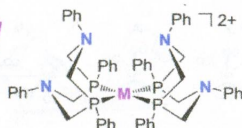


4617 **S**

dx.doi.org/10.1021/om4010669

Comparison of  $[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)_2(\text{CH}_3\text{CN})]^{2+}$  and  $[\text{Pd}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)_2]^{2+}$  as Electrocatalysts for  $\text{H}_2$  Production  
Eric S. Wiedner\* and Monte L. Helm

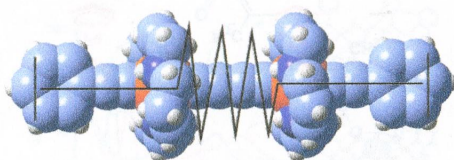
*Ni vs. Pd*



4621 **S**

dx.doi.org/10.1021/om401231j

Unsymmetric Mononuclear and Bridged Dinuclear  $\text{Co}^{\text{III}}$ (cyclam) Acetylides  
Timothy D. Cook, Phillip E. Fanwick, and Tong Ren\*

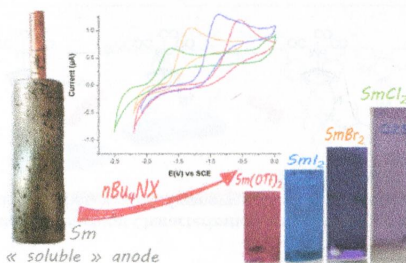


4625 **S**

dx.doi.org/10.1021/om500222a

Efficient Electrosynthesis of  $\text{SmCl}_2$ ,  $\text{SmBr}_2$ , and  $\text{Sm}(\text{OTf})_2$  from a "Sacrificial" Samarium Anode: Effect of  $n\text{Bu}_4\text{NPF}_6$  on the Reactivity  
Linhao Sun and Mohamed Mellah\*

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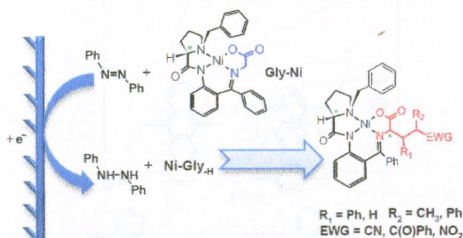


4629

dx.doi.org/10.1021/om500070n

### Electrochemically Deprotonated Chiral Nickel(II) Glycinate in Stereoselective Nucleophilic Addition to Michael Acceptors: Advantages and Limitations

Tatiana V. Magdesieva,\* Oleg A. Levitskiy, Yuri K. Grishin, Asmik A. Ambartsumyan, Mikhail A. Kiskin, Andrei V. Churakov, Konstantin K. Babievsky, and Konstantin A. Kochetkov

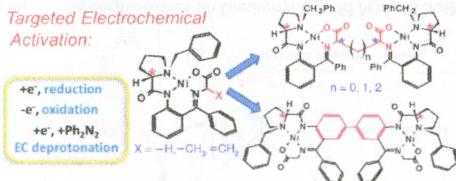


4639

dx.doi.org/10.1021/om500034x

### Chiral Nickel(II) Binuclear Complexes: Targeted Diastereoselective Electrosynthesis

Tatiana V. Magdesieva,\* Oleg A. Levitskiy, Yuri K. Grishin, Asmik A. Ambartsumyan, Ksenia A. Paseshnikchenko, Natalia G. Kolotytkina, and Konstantin A. Kochetkov

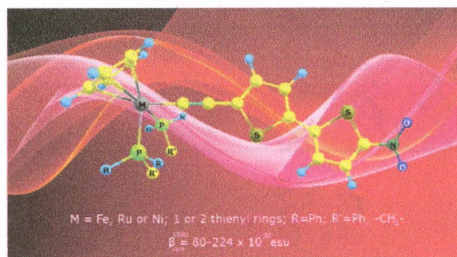


4655

dx.doi.org/10.1021/om4001204

### Mono( $\eta^5$ -cyclopentadienyl)metal(II) Complexes with Thienyl Acetylide Chromophores: Synthesis, Electrochemical Studies, and First Hyperpolarizabilities

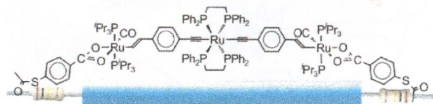
Tiago J. L. Silva, Paulo J. Mendes,\* Ana M. Santos, M. Helena Garcia, M. Paula Robalo, J. P. Prates Ramalho, A. J. Palace Carvalho, Marina Büchert, Christian Wittenburg, and Jürgen Heck





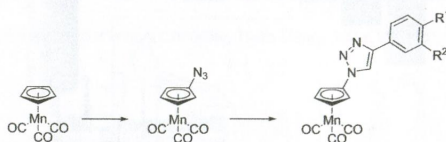
### Divinylphenylene- and Ethynylvinylphenylene-Bridged Mono-, Di-, and Triruthenium Complexes for Covalent Binding to Gold Electrodes

Evelyn Wuttke, Yves-Marie Hervault, Walther Polit, Michael Linseis, Philipp Eler, Stéphane Rigaut,\* and Rainer F. Winter\*



### Cymantrene-Triazole "Click" Products: Structural Characterization and Electrochemical Properties

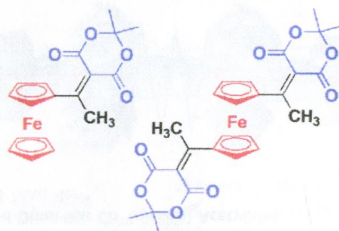
David P. Day, Thomas Dann, David. L. Hughes, Vasily S. Oganessian, Dietmar Steverding, and Gregory G. Wildgoose\*



### Synthesis, Structure, and Spectroelectrochemistry of Ferrocenyl-Meldrum's Acid Donor-Acceptor Systems

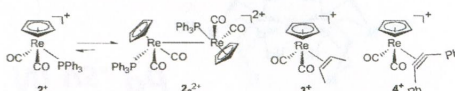
Konrad Kowalski,\* Łukasz Szczupak, Joanna Skiba, Obadah S. Abdel-Rahman, Rainer F. Winter,\* Rafał Czerwieńec, and Bruno Therrien

#### Nonplanar Donor-Acceptor Systems



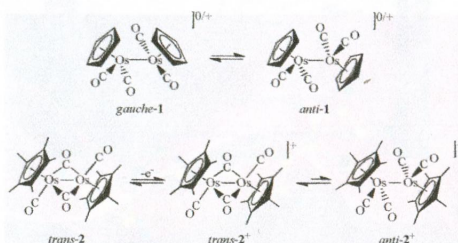
### One-Electron Oxidation of $\text{ReCp}(\text{CO})_2\text{L}$ ( $\text{L} = \text{PPh}_3, \eta^2\text{-2-Butene}, \eta\text{-Diphenylacetylene}$ ): Electrochemical, Spectroscopic, and Computational Studies of the Electronic Properties and Dimerization Tendencies of 17-Electron Rhenium Complexes

Daesung Chong, Vitor H. Teixeira, Maria José Calhorda,\* and William E. Geiger\*



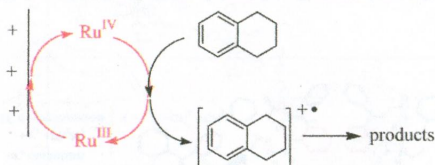
Comparison of the One-Electron Oxidations of CO-Bridged vs Unbridged Bimetallic Complexes: Electron-Transfer Chemistry of  $\text{Os}_2\text{Cp}_2(\text{CO})_4$  and  $\text{Os}_2\text{Cp}^*_2(\mu\text{-CO})_2(\text{CO})_2$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ,  $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ )

Derek R. Laws, R. Morris Bullock,\* Richmond Lee, Kuo-Wei Huang,\* and William E. Geiger\*



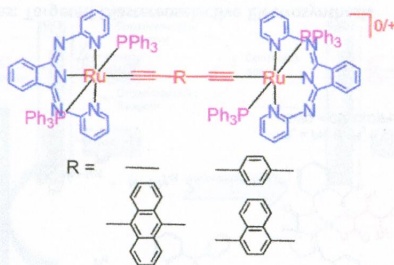
Homogeneous Catalysis and Selectivity in Electrochemistry

Michael Michman,\* Lina Appelbaum, Jenny Gun, Alexander D. Modestov, and Ovadia Lev



Electrochemical, Spectroscopic, and Theoretical Studies on Diethynyl Ligand Bridged Ruthenium Complexes with 1,3-Bis(2-pyridylimino)isoindolate

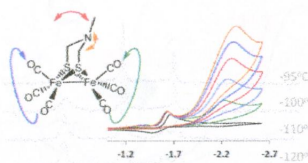
Dao-Bin Zhang, Jin-Yun Wang, Hui-Min Wen, and Zhong-Ning Chen\*





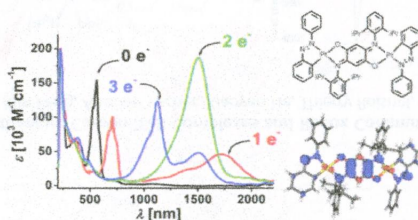
### Conformational Mobility and Pendent Base Effects on Electrochemistry of Synthetic Analogues of the [FeFe]-Hydrogenase Active Site

Danielle J. Crouthers, Jason A. Denny, Ryan D. Bethel, David G. Munoz, and Marcetta Y. Darensbourg\*



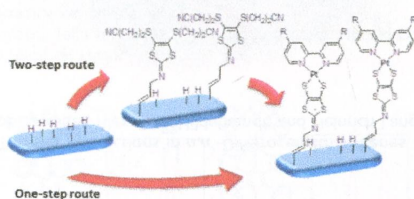
### Dinuclear Quinonoid-Bridged $d^8$ Metal Complexes with Redox-Active Azobenzene Stoppers: Electrochemical Properties and Electrochromic Behavior

Naina Deibel, Michael G. Sommer, Stephan Hohloch, Johannes Schwann, David Schweinfurth, Fabian Ehret, and Biprajit Sarkar\*



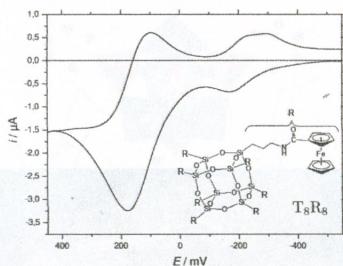
### Assembly of Platinum Diimine Dithiolate Complexes onto Hydrogen-Terminated Silicon Surfaces

Gilles Yzambart, Bruno Fabre,\* Thierry Roisnel, Vincent Dorcet, Soraya Ababou-Girard, Cristelle Meriadec, and Dominique Lorcé\*



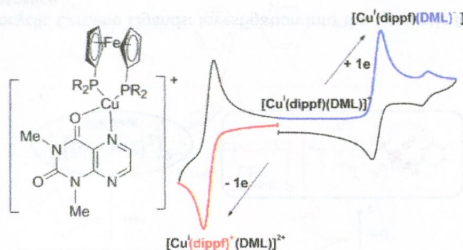
Redox-Active Silica Nanoparticles. 9. Synthesis, Electrochemistry, and Diffusion Properties of Caged Octakis(*N*-ferrocenyl-3-aminopropyl)silsesquioxane

David Ruiz Abad, Jörg Henig, Hermann A. Mayer,\* Thomas Reißig, and Bernd Speiser\*



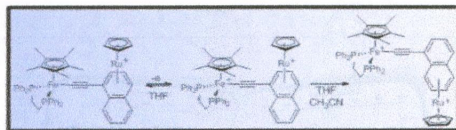
Electrochemical Evidence for Hemilabile Coordination of 1,3-Dimethylumazine to [1,1'-Bis(diorganophosphino)ferrocene]copper(I)

Rajkumar Jana, Biprajit Sarkar, Sabine Strobel, Shaikh M. Mobin, Wolfgang Kaim,\* and Jan Fiedler\*



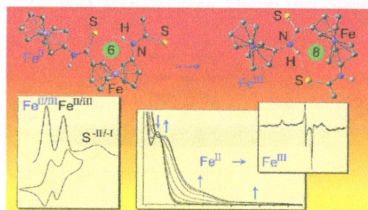
Proton-Controlled Regioselective Synthesis of [Cp\*(dppe)Fe-C≡C-1-( $\eta^5$ -C<sub>10</sub>H<sub>7</sub>)Ru( $\eta^5$ -Cp)](PF<sub>6</sub>) and Electron-Driven Haptotropic Rearrangement of the ( $\eta^5$ -Cp)Ru<sup>+</sup> Arenophile

Rim Makhoul, Hiba Sahnoun, Thomas Davin, Samia Kahlal, Vincent Dorcet, Thierry Roisnel, Jean-François Halet,\* Jean-René Hamon,\* and Claude Lapinte\*



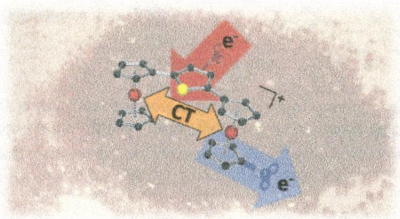
### Impact of O → S Exchange in Ferrocenyl Amides on the Structure and Redox Chemistry

Torben Kienz, Christoph Förster, and Katja Heinze\*



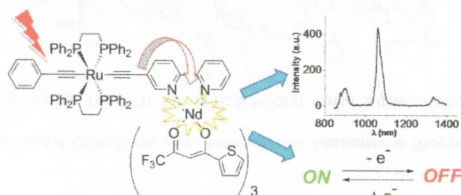
### Substituent Influence on Charge Transfer Interactions in $\alpha,\alpha'$ -Diferrocenylthiophenes

J. Matthäus Speck, Marcus Korb, Tobias Rüfer, Alexander Hildebrandt, and Heinrich Lang\*



### Lanthanide Sensitization with Ruthenium Carbon-Rich Complexes and Redox Commutation of Near-IR Luminescence

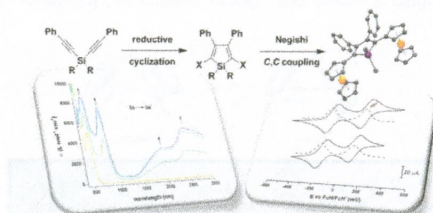
Lucie Norel,\* Emmanuel Di Piazza, Min Feng, Antoine Vacher, Xiaoyan He, Thierry Roisnel, Olivier Maury, and Stéphane Rigaut\*





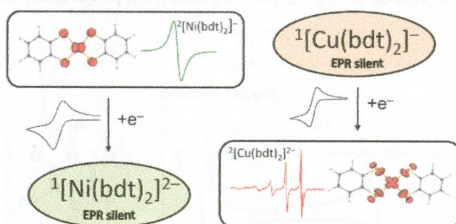
### Synthesis, Characterization, Electrochemistry, and Computational Studies of Ferrocenyl-Substituted Siloles

Steve W. Lehigh, Alexander Hildebrandt, Tobias Rüffer, Marcus Korb, Paul J. Low, and Heinrich Lang\*



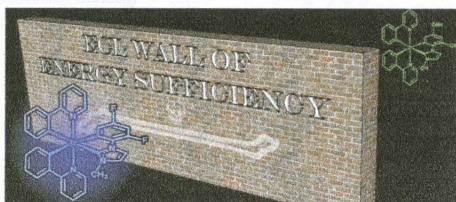
### Redox Reactions of Nickel, Copper, and Cobalt Complexes with "Noninnocent" Dithiolate Ligands: Combined in Situ Spectroelectrochemical and Theoretical Study

Peter Machata, Peter Herich, Karol Lušpai, Lukas Bucinsky, Stanislava Šoralová, Martin Breza, Jozef Kozisek, and Peter Raptá\*

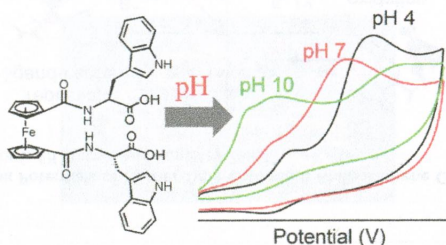


### Iridium Complexes of N-Heterocyclic Carbene Ligands: Investigation into the Energetic Requirements for Efficient Electrogenenerated Chemiluminescence

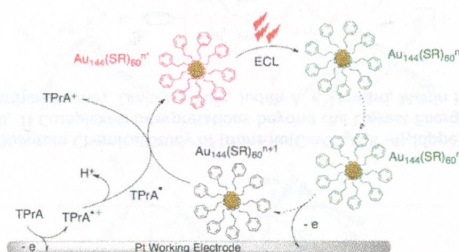
Bradley D. Stringer, Linh M. Quan, Peter J. Barnard,\* David J. D. Wilson, and Conor F. Hogan\*



**Bis-amino Acid Derivatives of 1,1'-Ferrocenedicarboxylic Acid: Structural, Electrochemical, and Metal Ion Binding Studies**  
 Bimalendu Adhikari, Alan J. Lough, Bryan Barker, Afzal Shah, Cuili Xiang, and Heinz-Bernhard Kraatz\*

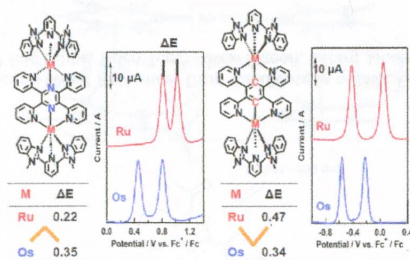


**Electrogenerated Chemiluminescence of Monodisperse  $Au_{144}(SC_2H_4Ph)_{60}$  Clusters**  
 Mahdi Hesari, Zhifeng Ding,\* and Mark S. Workentin\*

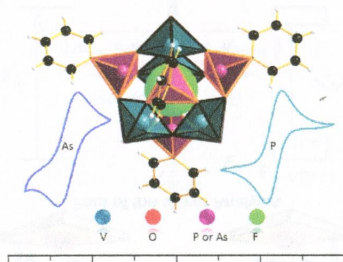


**Tuning of Metal–Metal Interactions in Mixed-Valence States of Cyclometalated Dinuclear Ruthenium and Osmium Complexes Bearing Tetrapyridylpyrazine or –benzene**

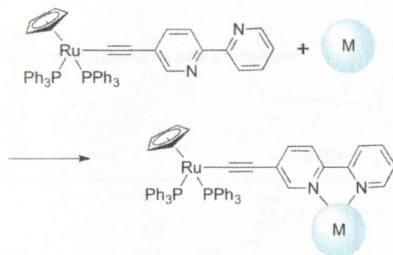
Takumi Nagashima, Takuya Nakabayashi, Takashi Suzuki, Katsuhiko Kanaizuka, Hiroaki Ozawa, Yu-Wu Zhong, Shigeyuki Masaoka, Ken Sakai, and Masa-aki Haga\*



**Control of Bridging Ligands in  $[(V_2O_3)_2(RXO_3)_4CF]^-$  Cage Complexes: A Unique Way To Tune Their Chemical Properties**  
 Jabor Rabeah,\* Anton Dimitrov, Annette-Enrica Surkus, Haijun Jiao, Wolfgang Baumann, Reinhard Stöber, Jörg Radnik, Ursula Bentrup, and Angelika Brückner\*

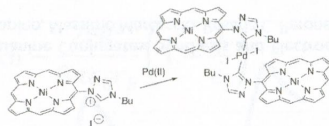


**Coordinating Tectons: Bimetallic Complexes from Bipyridyl Terminated Group 8 Alkynyl Complexes**  
 George A. Koutsantonis,\* Paul J. Low,\* Campbell F. R. Mackenzie, Brian W. Skelton, and Dmitry S. Yuft



**Synthesis and Electrochemical Studies of Porphyrin Dimers Linked by Metallocarbenes**

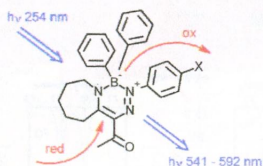
Julien Haumesser, Jean-Paul Gisselbrecht, Lydia Karmazin-Brelot, Corinne Bailly, Jean Weiss, and Romain Ruppert\*





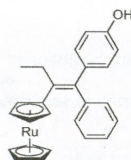
### New Triazaborine Chromophores: Their Synthesis via Oxazaborines and Electrochemical and DFT Study of Their Fundamental Properties

František Josefík, Tomáš Mikysek,\* Markéta Svobodová, Petr Šimůnek, Hana Kvapilová, and Jiří Ludvík



### Oxidative Sequence of a Ruthenocene-Based Anticancer Drug Candidate in a Basic Environment

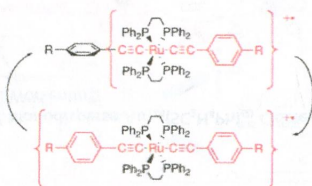
Hui Zhi Shirley Lee, Olivier Buriez,\* Eric Labbé, Siden Top,\* Pascal Pigeon, Gérard Jaouen, Christian Amatore,\* and Weng Kee Leong



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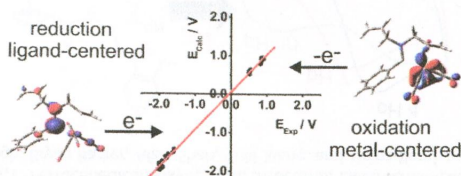
### Combined Spectroscopic and Quantum Chemical Study of $[trans\text{-Ru}(\text{C}\equiv\text{CC}_6\text{H}_4\text{R}^1\text{-4})_2(\text{dppe})_2]^{n+}$ and $[trans\text{-Ru}(\text{C}\equiv\text{CC}_6\text{H}_4\text{R}^1\text{-4})(\text{C}\equiv\text{CC}_6\text{H}_4\text{R}^2\text{-4})(\text{dppf})_2]^{n+}$ ( $n = 0, 1$ ) Complexes: Interpretations beyond the Lowest Energy Conformer Paradigm

Santiago Marqués-González, Matthias Parthey, Dmitry S. Yufit, Judith A. K. Howard, Martin Kaupp,\* and Paul J. Low\*



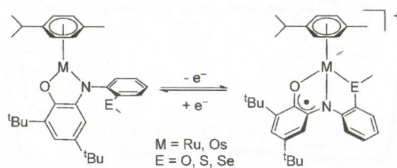
### Theoretical Predictions of Redox Potentials of Fischer-Type Chromium Aminocarbene Complexes

Hana Kvapilová,\* Irena Hoskocová, Jiří Ludvík, and Stanislav Zálšíš\*



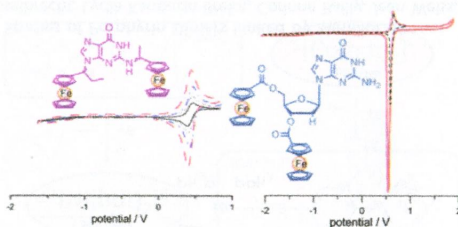
### Structure and Spectroelectrochemical Response of Arene–Ruthenium and Arene–Osmium Complexes with Potentially Hemilabile Noninnocent Ligands

Martina Bubrin, David Schweinfurth, Fabian Ehret, Stanislav Zálaiš, Hana Kvapilová, Jan Fiedler, Qiang Zeng, František Hartl,\* and Wolfgang Kaim\*



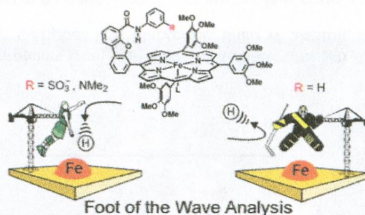
### New Approaches toward Ferrocene–Guanine Conjugates: Synthesis and Electrochemical Behavior

Matteo Iurlo,\* Luca Mengozzi, Stefania Rapino, Massimo Marcaccio, Rosaria C. Perone, Stefano Masiero,\* Piergiorgio Cozzi,\* and Francesco Paolucci\*



### Electrocatalytic H<sub>2</sub> Evolution by Proton-Gated Hangman Iron Porphyrins

Daniel J. Graham and Daniel G. Nocera\*



5002

Electrocatalytic Reduction of Carbon Dioxide with a Manganese(I) Tricarbonyl Complex Containing a Nonaromatic  $\alpha$ -Diimine Ligand

Qiang Zeng, Joanne Tory, and František Hartl\*

dx.doi.org/10.1021/om500389y



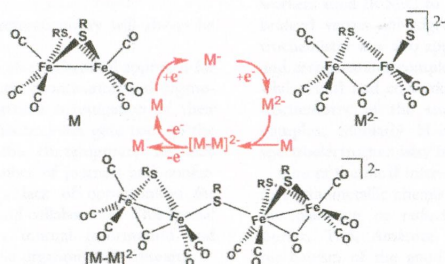
5009

S

Electrochemical, Spectroscopic, and Computational Study of Bis( $\mu$ -methylthiolato)diironhexacarbonyl: Homoassociative Stabilization of the Dianion and a Chemically Reversible Reduction/Reoxidation Cycle

Orrasa In-noi, Kenneth J. Haller,\* Gabriel B. Hall, William P. Brezinski, Jacob M. Marx, Taka Sakamoto, Dennis H. Evans, Richard S. Glass, and Dennis L. Lichtenberger\*

dx.doi.org/10.1021/om5004122



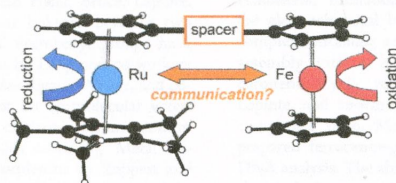
5020

S

Synthesis, Crystal Structures, and Electrochemical Behavior of Fe–Ru Heterobimetallic Complexes with Bridged Metallocene Units

Jiří Schulz, Filip Uhlík, J. Matthäus Speck, Ivana Císařová, Heinrich Lang, and Petr Štěpnička\*

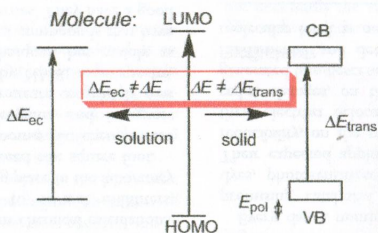
dx.doi.org/10.1021/om500505n





## Optical and Electrochemical Band Gaps in Mono-, Oligo-, and Polymeric Systems: A Critical Reassessment

Rudolf Holze\*

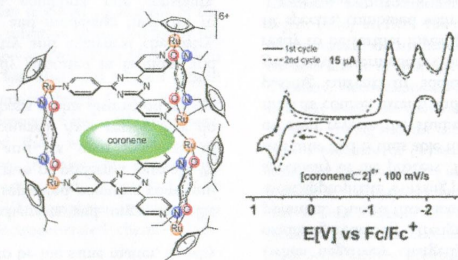


## Notes



### Synthesis and Electrochemical Behavior of a Zwitterion-Bridged Metalla-Cage

Minghui Yuan, Fritz Weisser, Biprajit Sarkar, Amine Garci, Pierre Braunstein,\* Lucie Routaboul,\* and Bruno Therrien\*



### Electrostatic Modeling of the Tunable Potential Difference between the Two Consecutive Oxidation Steps of Dinickel Bisfulvalene

Frédéric Barrière\*

$$\text{Born} - \frac{Z^2 e^2}{8\pi\epsilon_0 r_B} \left(1 - \frac{1}{\epsilon_r}\right)$$

$$\frac{q_1 q_2}{4\pi\epsilon_0 r^2} \text{Coulomb}$$