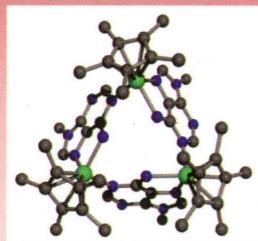
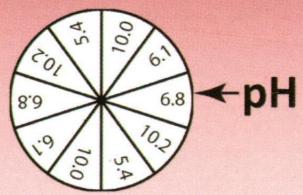
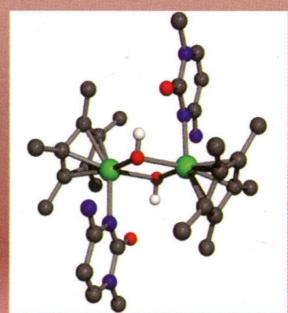
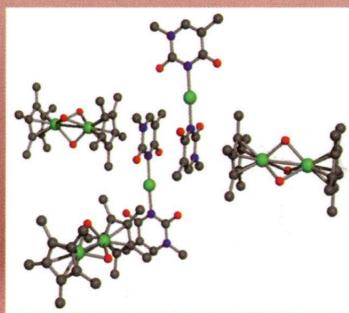
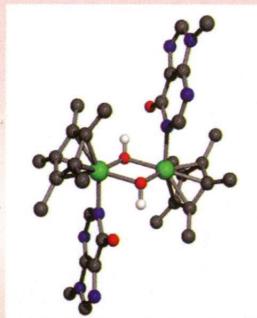
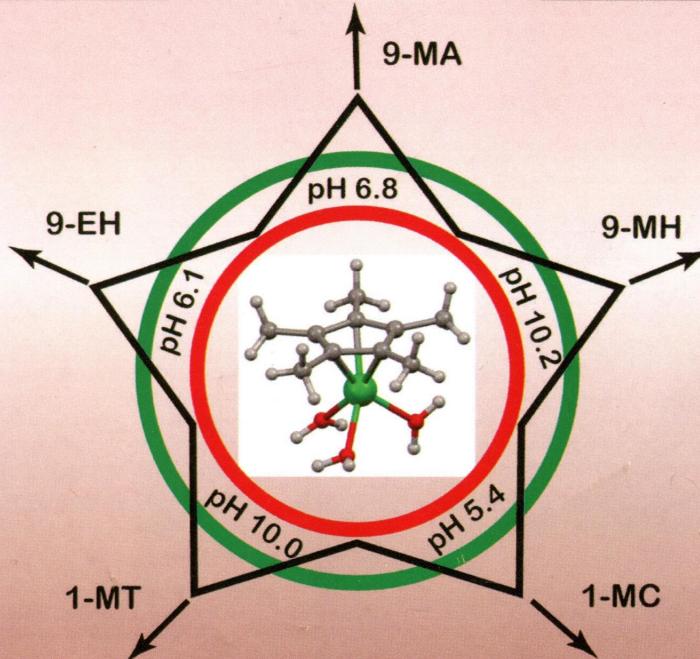


ORGANOMETALLICS

pH "Wheel of Fortune"



*Cp*Rh-DNA* Base Complexes



ORGANOMETALLICS

MAY 26, 2014

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ON THE COVER: The reactions of $[\text{Cp}^*\text{Rh}(\text{H}_2\text{O})_3](\text{OTf})_2$ with DNA nucleobases as a function of pH are reminiscent of a "Wheel of Fortune". As the Wheel spins, the pH changes, and thus, a different Cp^*Rh -DNA nucleobase structure is obtained. This paper shows that pH changes in aqueous solution profoundly affect DNA nucleobase NH protons. For example, 9-MA and 9-EH at pH = ~6 form cyclic trimer complexes that are thermodynamically the most stable, $[\text{Cp}^*\text{Rh}(9\text{-MA})_3](\text{OTf})_3$ and $[\text{Cp}^*\text{Rh}(9\text{-EH})_3](\text{OTf})_3$, respectively, while 1-MC forms an intramolecular H-bonded μ -OH dimer at pH = 5.6, along with 9-MH at pH = 10.2, *trans*- $[\text{Cp}^*\text{Rh}\text{-MC}(\mu\text{-OH})_2](\text{OTf})_2$ and *trans*- $[\text{Cp}^*\text{Rh}(9\text{-MH})(\mu\text{-OH})_2](\text{OTf})_2$, respectively. The reaction of $[\text{Cp}^*\text{Rh}(\text{H}_2\text{O})_3](\text{OTf})_2$ with 1-MT at pH = 10 provides a unique complex of anion and cation components, with dominant electrostatic and $\pi\text{-}\pi$ interactions, namely, $\{[\text{Rh}^*(1\text{-MT})_2][(\text{Cp}^*\text{Rh})(\mu\text{-OH})_3]\}\text{OH}$. The moral of this story is that, when the pH Wheel of Fortune spins, no one knows what to expect, and that is the charm of bioorganometallic chemistry. See the paper by Fish et al. on pages 2389–2404.

Articles

Cover Paper

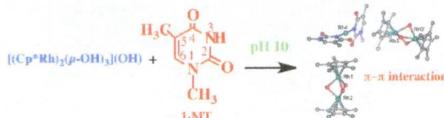
2389



[dx.doi.org/10.1021/om500106](https://doi.org/10.1021/om500106)

Bioorganometallic Chemistry. 27. Synthetic, X-ray Crystallographic, and Competitive Binding Studies in the Reactions of Nucleobases, Nucleosides, and Nucleotides with $[\text{Cp}^*\text{Rh}(\text{H}_2\text{O})_3](\text{OTf})_2$, as a Function of pH, and the Utilization of Several Cp^*Rh -DNA Base Complexes in Host–Guest Chemistry

David P. Smith, Hong Chen, Seiji Ogo, Ana I. Elduque, Miriam Eisenstein, Marilyn M. Olmstead,* and Richard H. Fish*



Communications

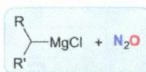
2405



[dx.doi.org/10.1021/om500333](https://doi.org/10.1021/om500333)

Reactions of Grignard Reagents with Nitrous Oxide

Alexander G. Tskhovrebov, Euro Solari, Rosario Scopelliti, and Kay Severin*



Articles

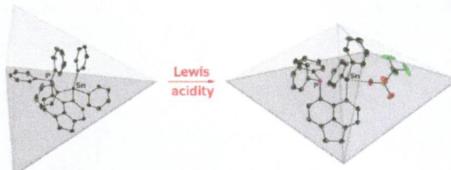
2409



dx.doi.org/10.1021/om500133a

Intramolecularly Coordinated (6-(Diphenylphosphino)acenaphth-5-yl)stannanes. Repulsion vs Attraction of P- and Sn-Containing Substituents in the *peri* Positions

Emanuel Hupf, Enno Lork, Stefan Mebs,* and Jens Beckmann*



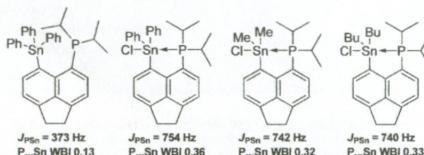
2424



dx.doi.org/10.1021/om500289b

Sterically Restricted Tin Phosphines, Stabilized by Weak Intramolecular Donor–Acceptor Interactions

Kasun S. Athukorala Arachchige, Paula Sanz Camacho, Matthew J. Ray, Brian A. Chalmers, Fergus R. Knight, Sharon E. Ashbrook, Michael Bühl, Petr Kilian, Alexandra M. Z. Slawin, and J. Derek Woollins*



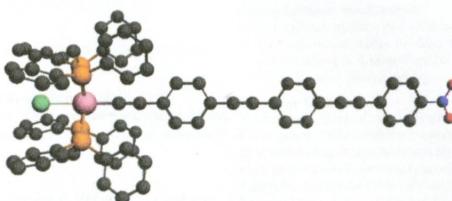
2434



dx.doi.org/10.1021/om500124c

DFT Calculation of Static First Hyperpolarizabilities and Linear Optical Properties of Metal Alkynyl Complexes

Erandi Kulasekera, Simon Petrie, Robert Stranger,* and Mark G. Humphrey



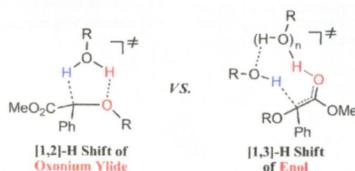
2448



dx.doi.org/10.1021/om401092h

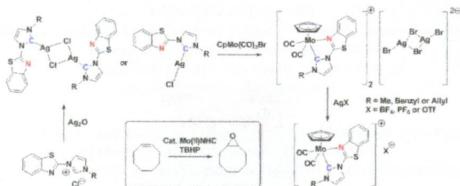
Mechanistic Insight into the Rhodium-Catalyzed O–H Insertion Reaction: A DFT Study

Zhi-Zhong Xie,* Wen-Juan Liao, Jun Cao, Li-Ping Guo, Francis Verpoort,* and Weihai Fang*



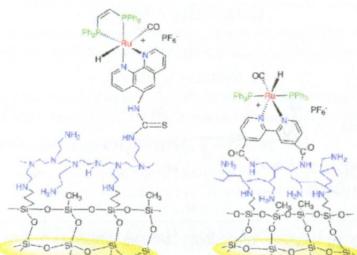
Cyclopentadienyl Molybdenum(II) N,C-Chelating Benzothiazole-Carbene Complexes: Synthesis, Structure, and Application in Cyclooctene Epoxidation Catalysis

Zhe Wang, Sin Wee Benny Ng, Lu Jiang, Wen Jin Leong, Jin Zhao,* and T. S. Andy Hor*



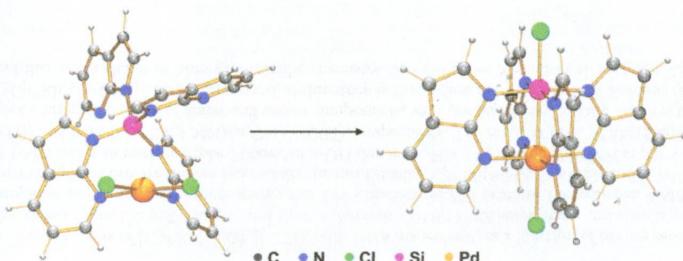
Surface-Bound Ruthenium Diimine Organometallic Complexes: Excited-State Properties

Geoffrey Abbott, Robert Brooks, Edward Rosenberg,* Michelle Terwilliger, J. B. Alexander Ross,* and Ogar O. L. Ichire

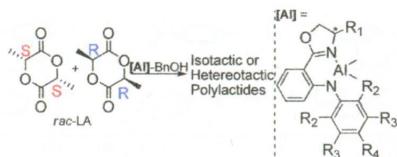


7-Azaindol-1-yl(organo)silanes and Their PdCl_2 Complexes: Pd-Capped Tetrahedral Silicon Coordination Spheres and Paddlewheels with a Pd–Si Axis

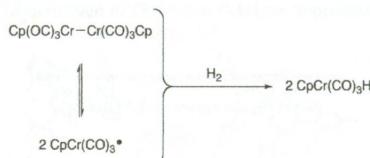
Sven Wahlick, Erica Brendler, Thomas Heine, Lyuben Zhechkov, and Jörg Wagler*



Ring-Opening Polymerization of *rac*-Lactide with Aluminum Chiral Anilido-Oxazolinate Complexes
Shi Bian, Srinivas Abbina, Zhengliang Lu, Edward Kolodka, and Guodong Du*

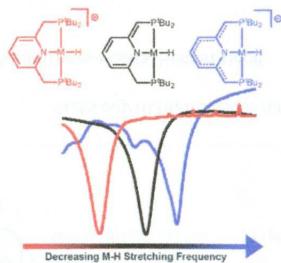


Kinetics and Mechanism of the Hydrogenation of the $\text{CpCr}(\text{CO})_3$ – $\text{Cr}(\text{CO})_3\text{Cp}$ Equilibrium to $\text{CpCr}(\text{CO})_3\text{H}$
Jack R. Norton,* Tudor Spataru, Donald M. Camaioni,* Suh-Jane Lee, Gang Li, Jongwook Choi, and James A. Franz



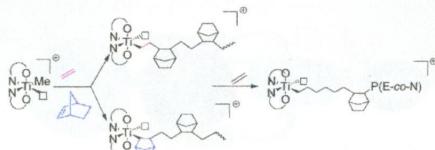
Synthesis and Characterization of Anionic, Neutral, and Cationic PNP Pincer Pd^{II} and Pt^{II} Hydrides
Wilson D. Bailey, Werner Kaminsky, Richard A. Kemp,* and Karen I. Goldberg*

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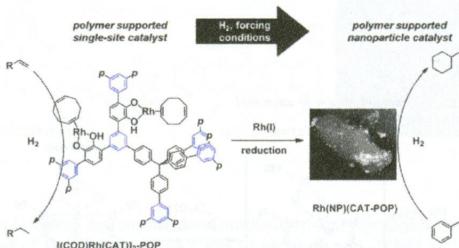
Multinuclear NMR Spectroscopic Characterization of a Fluorinated Enolatoimine Titanium Polymeryl Species in the Living Ethylene-*co*-Norbornene Polymerization

Antonella C. Boccia, Giulia Scalcione, Laura Boggioni, and Incoronata Tritto*



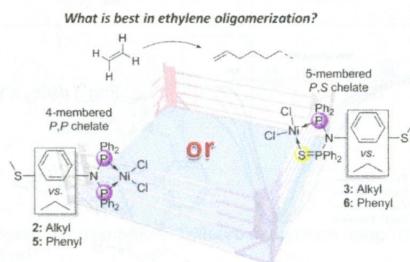
Rhodium Catechol Containing Porous Organic Polymers: Defined Catalysis for Single-Site and Supported Nanoparticulate Materials

Steven J. Kraft, Guanghui Zhang, David Childers, Fulya Dogan, Jeffrey T. Miller, SonBinh T. Nguyen, and Adam S. Hock*



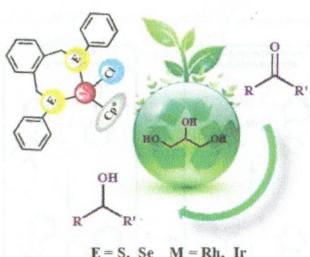
Combined Experimental and Theoretical Study of Bis(diphenylphosphino)(N-thioether)amine-Type Ligands in Nickel(II) Complexes for Catalytic Ethylene Oligomerization

Alessio Ghisolfi, Christophe Fiedel,* Vitor Rosa, Kirill Yu. Monakhov, and Pierre Braunstein*



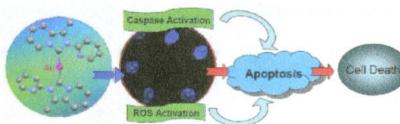
Half-Sandwich Rhodium/Iridium(III) Complexes Designed with Cp^* and 1,2-Bis(phenylchalcogenomethyl)benzene as Catalysts for Transfer Hydrogenation in Glycerol

Om Prakash, Kamal Nayan Sharma, Hemant Joshi, Pancham L. Gupta, and Ajai K. Singh*

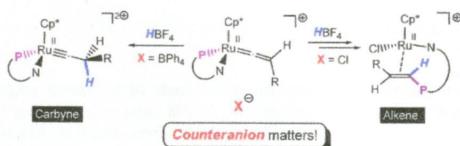


$E = S, Se$ $M = Rh, Ir$

Novel Gold(I)– and Gold(III)–N-Heterocyclic Carbene Complexes: Synthesis and Evaluation of Their Anticancer Properties
Bidyut Kumar Rana, Abhishek Nandy, Valerio Bertolasi, Christopher W. Bielawski, Krishna Das Saha,* and Joydev Dinda*

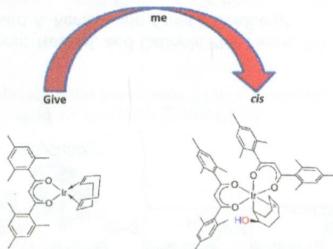


Counterion-Dependent Reaction Pathways in the Protonation of Cationic Ruthenium–Vinylidene Complexes
Manuel Jiménez-Tenorio,* M. Carmen Puerta,* Pedro Valerga, Manuel A. Ortúno, Gregori Ujaque, and Agustí Lledós*

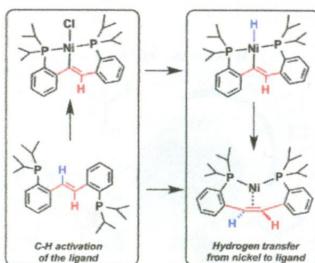


Synthesis and Characterization of $[Ir(Acac^{BiMs})_3](COD)$ and $[cis\text{-}Ir(Acac^{BiMs})_2(COEt\text{-}OH)]$

Oracio Serrano,* Juan Nicasio-Collazo, Guadalupe Morales, J. Carlos Alvarado-Monzón, Aarón Torres-Huerta, Herbert Höpf, Jorge A. López, and Ana C. Esqueda

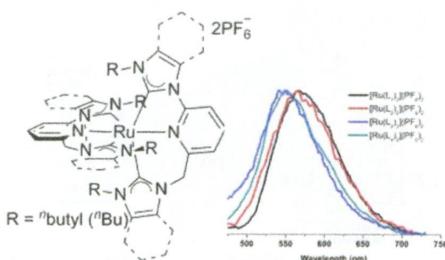


Group 10 Metal Complexes Supported by Pincer Ligands with an Olefinic Backbone
 Brittany J. Barrett and Vlad M. Iluc*



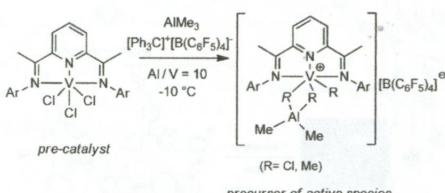
Ruthenium Complexes Bearing Unsymmetric CNC' Pincer Ligands: Molecular Structures and Electronic Properties

Abbas Raja Naziruddin, Chia-Liang Kuo, Wan-Jung Lin, Wei-Hao Lo, Chen-Shiang Lee, Bian-Jian Sun, A. Hsiao Hwa Chang, and Wen-Shu Hwang*



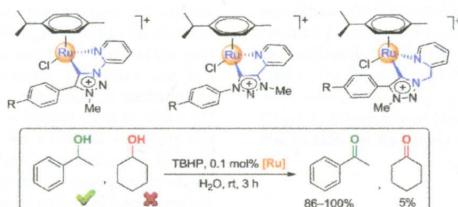
^1H and ^{2}H NMR Spectroscopic Characterization of Heterobinuclear Ion Pairs Formed upon the Activation of Bis(imino)pyridine Vanadium(III) Precatalysts with $\text{AlMe}_3/[\text{Ph}_3\text{C}]^+\text{[B}(\text{C}_6\text{F}_5)_4]^-$ and MAO

Igor E. Soshnikov, Nina V. Semikolenova, Artem A. Antonov, Konstantin P. Bryliakov, Vladimir A. Zakharov, and Evgenii P. Talsi*



Exploring the Scope of Pyridyl- and Picolyl-Functionalized 1,2,3-Triazol-5-ylidenes in Bidentate Coordination to Ruthenium(II) Cymene Chloride Complexes

Aljoša Bolje, Stephan Hohloch, Damijana Urankar, Andrej Pevec, Martin Gazvoda, Biprajit Sarkar, and Janez Košmrlj*

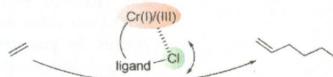


Mechanistic DFT Study on Ethylene Trimerization of Chromium Catalysts Supported by a Versatile Pyrrole Ligand System

Yun Yang, Zhen Liu,* Ruihua Cheng, Xuelian He, and Boping Liu*

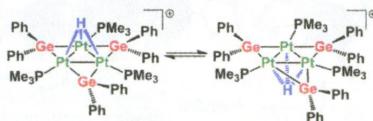
Chevron-Phillips ethylene trimerization system

$\text{Cr}(\text{2-EH})_3 / 2,5\text{-dimethylpyrrole} / \text{TEA} / \text{DEAC}$



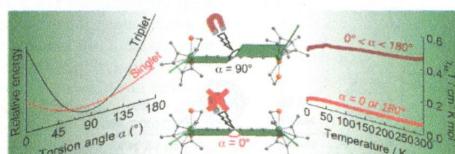
Cationic Hydridotriplatinum Complex with Bridging Germylene Ligands

Kimiya Tanaka, Makoto Tanabe, Tomohito Ide, and Kohtaro Osakada*



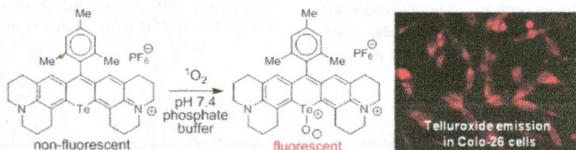
Hexatriynediyl Chain Spanning Two $\text{Cp}^*(\text{dppe})\text{M}$ Termini ($\text{M} = \text{Fe}, \text{Ru}$): Evidence for the Dependence of Electronic and Magnetic Couplings on the Relative Orientation of the Termini

Alexandre Burgun, Frédéric Gendron, Christopher J. Sumby, Thierry Roisnel, Olivier Cadot, Karine Costuas, Jean-François Halet,* Michael I. Bruce,* and Claude Lapinte*



Synthesis and Properties of Heavy Chalcogen Analogues of the Texas Reds and Related Rhodamines

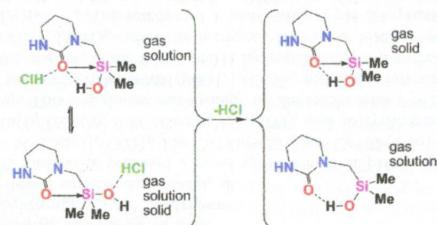
Mark W. Kryman, Gregory A. Schamerhorn, Jacqueline E. Hill, Brandon D. Calitree, Kellie S. Davies, Michelle K. Linder, Tymish Y. Ohulchansky, and Michael R. Detty*



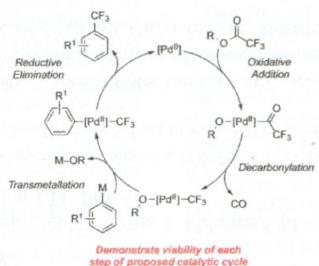
Apicophilicity versus Hydrogen Bonding, Intramolecular Coordination and Hydrogen Bonds in *N*-[(Hydroxydimethylsilyl)methyl]-*N,N*-propyleneurea and Its Hydrochloride, DFT and FT-IR Study and QTAIM and NBO Analysis

Nina N. Chipanina, Nataliya F. Lazareva, Tamara N. Aksamentova, Alexey Yu. Nikonorov, and Bagrat A. Shainyan*

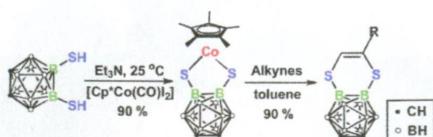
H-Bonding versus apicophilicity rule. Which wins?



Catalytic Cycle for Palladium-Catalyzed Decarbonylative Trifluoromethylation using Trifluoroacetic Esters as the CF₃ Source Ansiai Maleckis and Melanie S. Sanford*



Synthesis of Boron-Fused 1,4-Dithiin via Cob



Notes

[Ru₄(CO)₈(μ-OOCCH₂CH₃)₄(THF)₂] and [Ru₃(μ₃-OH)(CO)₆(μ-OOC'Bu)₄(OOC'Bu)]: Novel Multinuclear Ruthenium Carbonyl Carboxylates

Teresa K. Zimmermann, Jennifer Ziriakus, Eberhardt Herdtweck, Alexander Pöthig, and Fritz E. Kühn*

