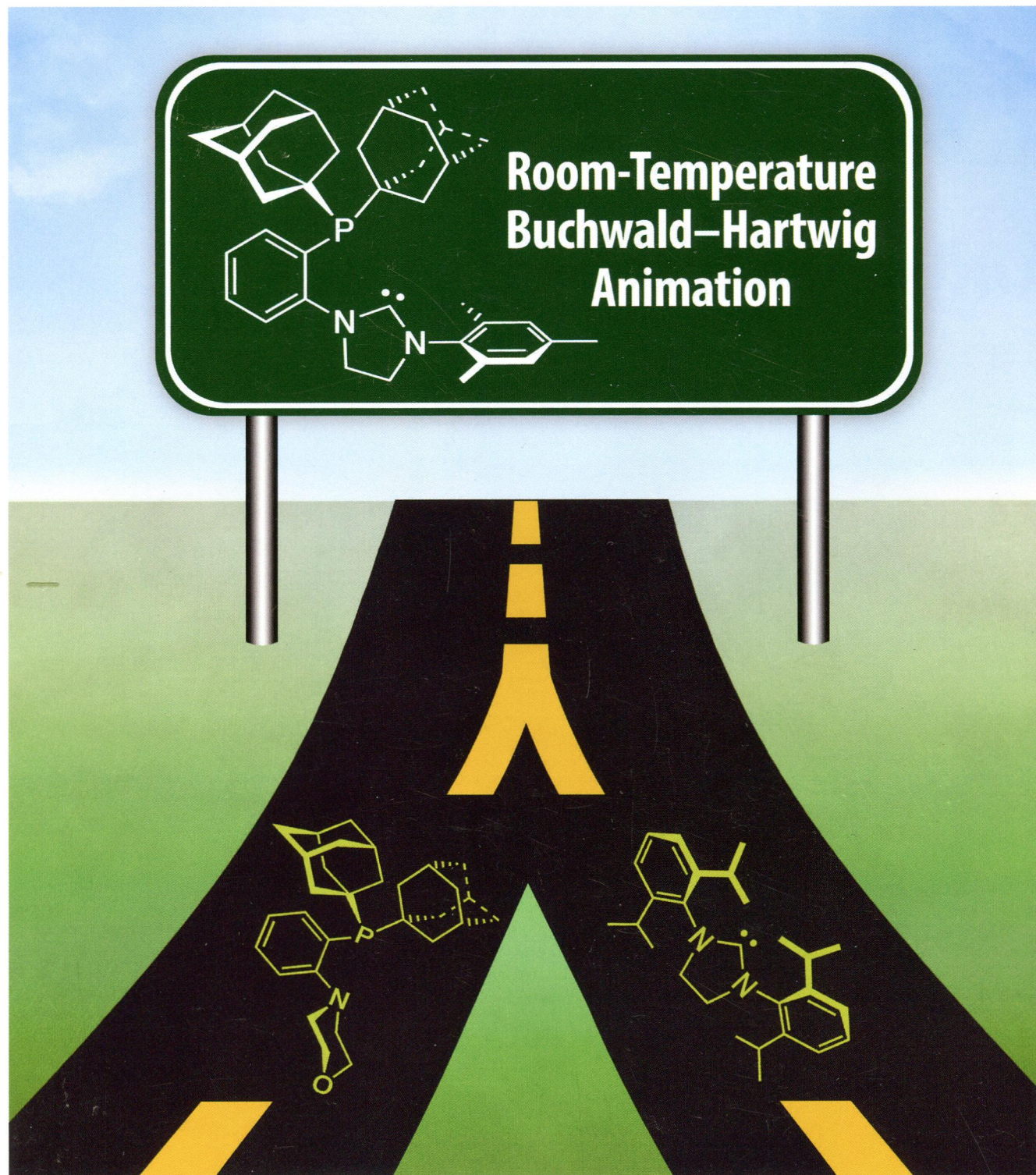


# ORGANOMETALLICS



**ON THE COVER:** The cover page depicts the conceptual merging of sterically demanding P,N and carbene ligands to afford a new hybrid P<sub>2</sub>carbene ligand that enables, for the first time, the Buchwald–Hartwig amination of aryl chlorides with both primary and secondary amines at room temperature using a single ligand. See the paper by Stradiotto and co-workers on pages 6148–6161.

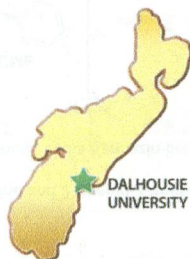
## Editor's Page

6147

[dx.doi.org/10.1021/om400947y](https://doi.org/10.1021/om400947y)

**Award-Winning Organometallic Chemistry: The 2012 Strem Chemicals Award for Pure or Applied Inorganic Chemistry of the Canadian Society for Chemistry**

John A. Gladysz



DALHOUSIE  
UNIVERSITY

## Articles

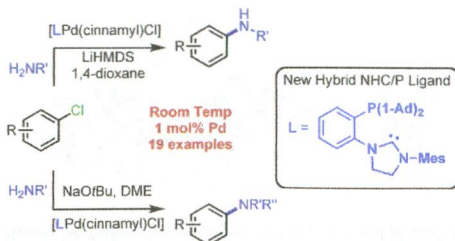
### Cover Paper

6148


[dx.doi.org/10.1021/om400684n](https://doi.org/10.1021/om400684n)

**New Phosphine-Functionalized NHC Ligands: Discovery of an Effective Catalyst for the Room-Temperature Amination of Aryl Chlorides with Primary and Secondary Amines**

Craig A. Wheaton, John-Paul J. Bow, and Mark Stradiotto\*

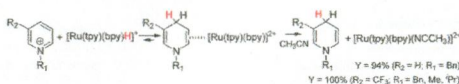


6162 **S**

dx.doi.org/10.1021/om400862n

Formation of  $\eta^2$ -Coordinated Dihydropyridine–Ruthenium(II) Complexes by Hydride Transfer from Ruthenium(II) to Pyridinium Cations

Yasuo Matsubara, Tatsumi Kosaka, Kichitaro Koga, Akira Nagasawa, Atsuo Kobayashi, Hideo Konno, Carol Creutz, Kazuhiko Sakamoto, and Osamu Ishitani\*

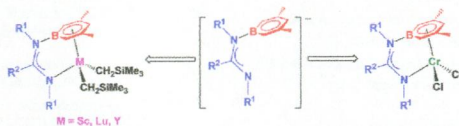


6166 **S**

dx.doi.org/10.1021/om400893c

Synthesis and Catalytic Activity of Amido-Boratabenzene Complexes of Rare-Earth Metals and Zirconium and Chromium

Xiufang Wang, Weijie Peng, Peng Cui, Xuebing Leng, Wei Xia, and Yaofeng Chen\*

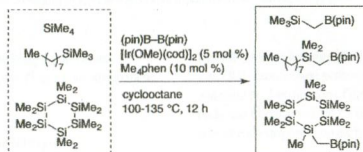


6170 **S**

dx.doi.org/10.1021/om400900z

Functionalization of Tetraorganosilanes and Permethyloligosilanes at a Methyl Group on Silicon via Iridium-Catalyzed C(sp<sup>3</sup>)–H Borylation

Toshimichi Ohmura,\* Takeru Torigoe, and Michinori Suginome\*

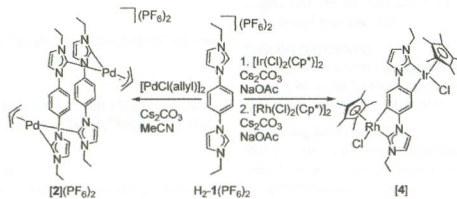


6174 **S**

dx.doi.org/10.1021/om400921c

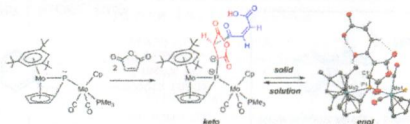
Two Different, Metal-Dependent Coordination Modes of a Dicarbene Ligand

Ramananda Maity, Arnab Rit, Christian Schulte to Brinke, Jutta Kösters, and F. Ekkehardt Hahn\*



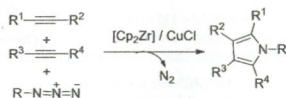
### Novel Dimerization of Maleic Anhydride at a Mo<sub>2</sub> Complex: Phase-Driven Keto/Enol Tautomerism in a Phosphinidenium–Ylide Complex

Isabel G. Albuero, M. Angeles Alvarez, M. Esther García, Daniel García-Vivó,\* and Miguel A. Ruiz\*



### Copper-Mediated Reaction of Zirconacyclopentadienes with Azides: A One-Pot Three-Component Synthesis of Multiply Substituted Pyrroles from One Azide and Two Alkynes

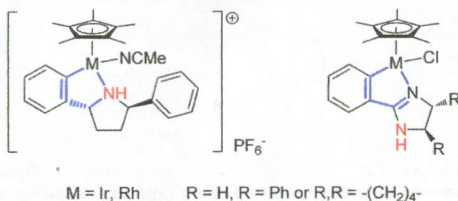
Yiqing Zhou, Xiaoyu Yan, Chao Chen, and Chanjuan Xi\*



## Articles

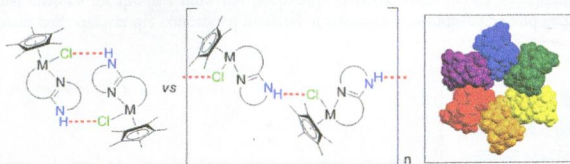
### Cyclometalation of (2*R*,5*R*)-2,5-Diphenylpyrrolidine and 2-Phenyl-2-imidazoline Ligands with Half-Sandwich Iridium(III) and Rhodium(III) Complexes

Elias Féghali, Laurent Barloy,\* Jean-Thomas Issenuth, Lydia Karmazin-Brelot, Corinne Bailly, and Michel Pfeffer\*



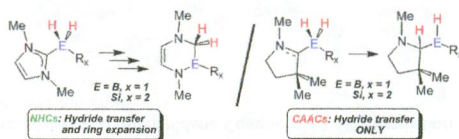
### Serendipitous Self-Assembly of Cyclometalated Complexes through Hydrogen Bonds: Dimers or Chains within Compact or Porous Networks

Laurent Barloy,\* Elias Féghali, Marc Henry, Lydia Karmazin-Brelot, Corinne Bailly, and Michel Pfeffer\*



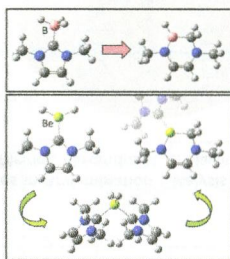
### Carbene-Bound Borane and Silane Adducts: A Comprehensive DFT Study on Their Stability and Propensity for Hydride-Mediated Ring Expansion

Mohammad R. Momeni, Eric Rivard, and Alex Brown\*



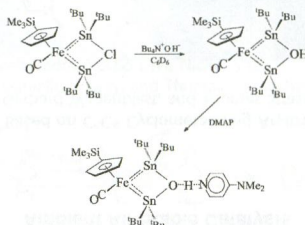
### Comparison of the Mechanism of Borane, Silane, and Beryllium Hydride Ring Insertion into N-Heterocyclic Carbene C–N Bonds: A Computational Study

Kalon J. Iversen, David J. D. Wilson,\* and Jason L. Dutton\*



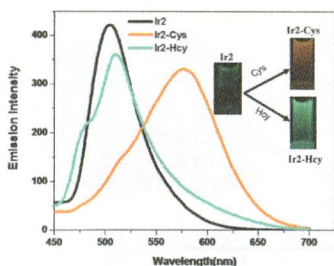
### Reactions of an Iron Chlorodistannane with Hydroxide: Isolation and Structural Characterization of $\{(t\text{r}^3\text{-Me}_3\text{SiC}_5\text{H}_4)\text{Fe}(\text{CO})\}[(\text{Sn}^t\text{Bu}_2)_2(\mu\text{-OH})]\text{-DMAP}$ , DMAP = 4-(*N,N*-Dimethylamino)pyridine, a $\mu\text{-OH}$ -Stannyl(stannylene)–Iron Complex

Hemant K. Sharma, Alejandro J. Metta-Magaña, and Keith H. Pannell\*



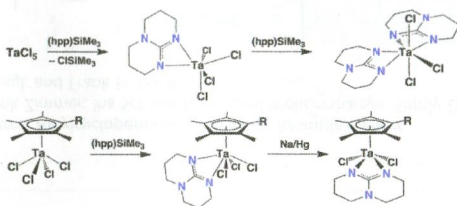
## Discrimination of Cys from Hcy by an Iridium(III) Complex Based on Time-Dependent Luminescence

Huili Chen,\* Xiaokai Li, Ruichun Bai, Yanbo Wu, Yingfang Fan, and Jianbin Chao



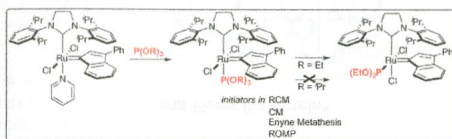
## High- and Mid-Valent Tantalum and Mono(peralkylcyclopentadienyl)tantalum Complexes of the Bicyclic Guanidinate Hexahydropyrimidopyrimidinate

Adil Mohammad, Justine R. Olson, David A. Rotsch, Ross D. Bemowski, Dale C. Swenson, and Louis Messerle\*



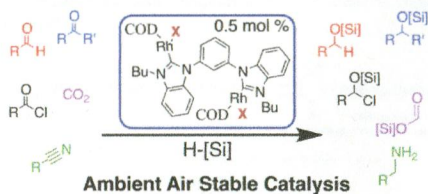
## Mixed N-Heterocyclic Carbene/Phosphite Ruthenium Complexes: The Effect of a Bulkier NHC.

César A. Urbina-Blanco, Xavier Bantreil, Julia Wappel, Thibault E. Schmid, Alexandra M. Z. Slawin, Christian Slugovc, and Catherine S. J. Cazin\*



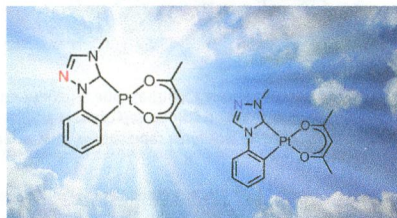
### Homobimetallic Rhodium NHC Complexes as Versatile Catalysts for Hydrosilylation of a Multitude of Substrates in the Presence of Ambient Air

Aron J. Huckaba, T. Keith Hollis,\* and Sean W. Reilly



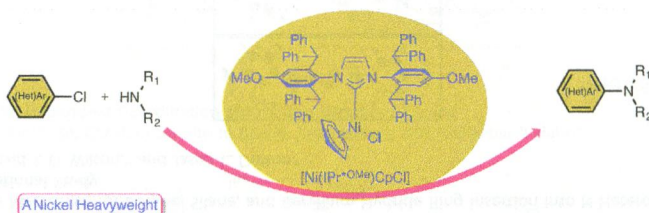
### Phosphorescent Platinum(II) Complexes Based on C<sup>∗</sup>C<sup>∗</sup> Cyclometalating Aryltriazol-5-ylidenes

Mario Tenne, Stefan Metz, Ingo Münster, Gerhard Wagenblast, and Thomas Strassner\*



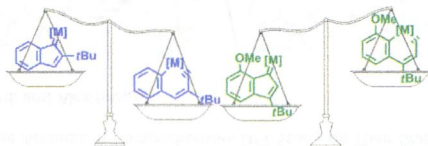
### Enhanced Activity of [Ni(NHC)CpCl] Complexes in Arylation Catalysis

Anthony R. Martin, Yusuke Makida, Sébastien Meiries, Alexandra M. Z. Slawin, and Steven P. Nolan\*



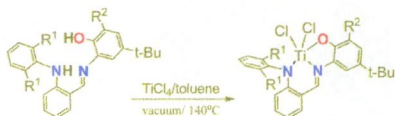
### Interconversion of Metalla-naphthalynes and Indenylidene Complexes: A DFT Prediction

Jinglan Fan, Ke An, Xuerui Wang, and Jun Zhu\*



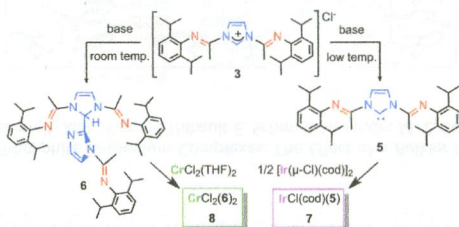
### Efficient Synthesis of Titanium Complexes Bearing Tridentate [N<sup>-</sup>,N,O<sup>-</sup>] Anilido-Imine Ligands and Their Catalytic Properties for Ethylene Polymerization

Lei Zhang, Xuyang Luo, Wei Gao,\* Jingshun Zhang, and Ying Mu\*



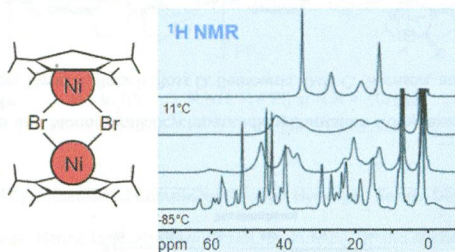
### Elusive Free Bisimino-N-heterocyclic Carbene and Its Rearrangement by C–C Coupling. Characterization of Relevant Iridium(I) and Chromium(II) Complexes

Ping Liu, Marcel Wesolek, Andreas A. Danopoulos,\* and Pierre Braunstein\*



### Paramagnetic 18-Valence-Electron Alkylcyclopentadienylnickel(II) Bromide Dimers

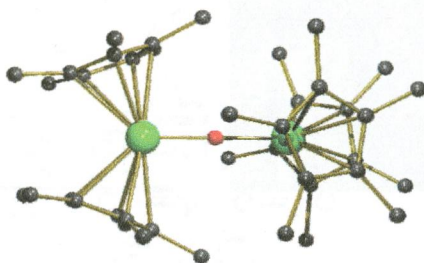
Marion Schär, Dirk Saurenz, Frank Zimmer, Ina Schädlich, Gotthelf Wolmershäuser, Serhiy Demeshko, Franc Meyer, Helmut Sitzmann,\* Oliver M. Heigl, and Frank H. Köhler\*





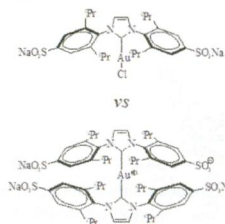
### Synthesis and Structure of Titanium(III) Bis(decamethyltitanocene) Oxide

Jiří Pinkas, Ivana Císařová, Róbert Gyepes, Jiří Kubišta, Michal Horáček, and Karel Mach\*

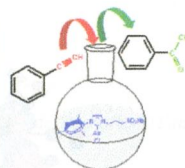
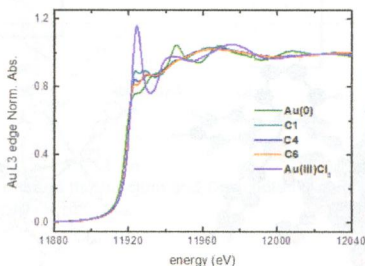


### Synthesis and Structural Characterization of Water-Soluble Gold(I) N-Heterocyclic Carbene Complexes. An X-ray Absorption Fine Structure Spectroscopy (XAFS) Study

Gabriela A. Fernández, Agustín S. Picco, Marcelo R. Ceolín, Alicia B. Chopá, and Gustavo F. Silbestrí\*

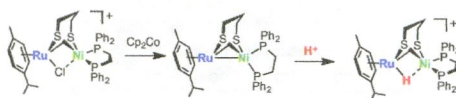


Characterized by XAFS, NMR, MS and UV-Vis



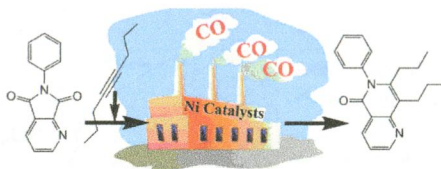
### Organo Ruthenium–Nickel Dithiolates with Redox-Responsive Nickel Sites

Geoffrey M. Chambers, Raja Angamuthu, Danielle L. Gray, and Thomas B. Rauchfuss\*



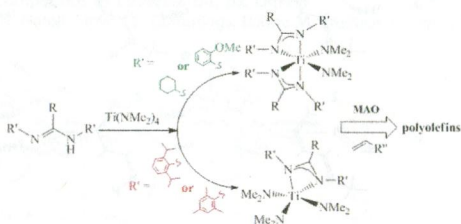
### Catalytic Role of Nickel in the Decarbonylative Addition of Phthalimides to Alkynes

Albert Poater,\* Sai Vikrama Chaitanya Vummaleti, and Luigi Cavallo



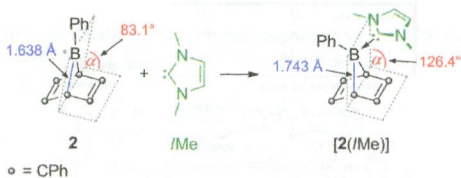
### Synthesis and Structure of Group 4 Symmetric Amidinate Complexes and Their Reactivity in the Polymerization of $\alpha$ -Olefins

Tatyana Elkin, Naveen V. Kulkarni, Boris Tumanskii, Mark Botoshansky, Linda J. W. Shimon, and Moris S. Eisen\*



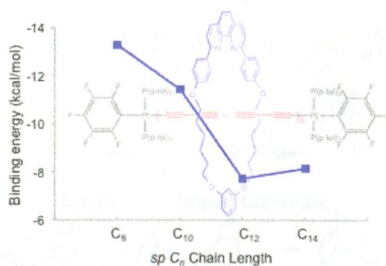
### Ring Expansion of 7-Boranorbornadienes by Coordination with an N-Heterocyclic Carbene

Holger Braunschweig,\* Jonathan Maier, Krzysztof Radacki, and Johannes Wahler



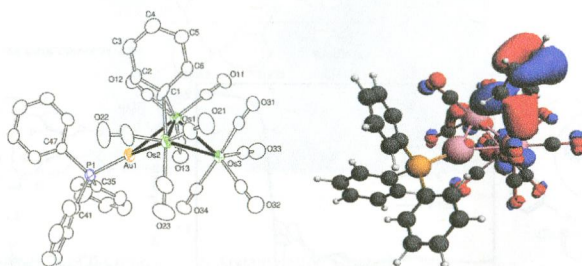
### A Metal-Capped Conjugated Polyene Threaded through a Phenanthroline-Based Macrocycle. Probing beyond the Mechanical Bond to Interactions in Interlocked Molecular Architectures

Hiba Sahnouné, Zuzana Baranová, Nattamai Bhuvanesh, John A. Gladysz,\* and Jean-François Halet\*



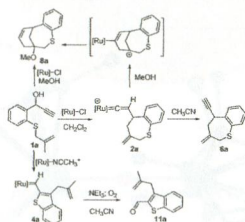
### Unsaturated Triosmium Carbonyl Cluster Complexes with Bridging Aryl Ligands: Structures, Bonding, and Transformations

Richard D. Adams,\* Vitaly Rassolov,\* and Qiang Zhang

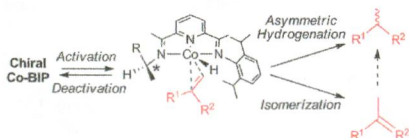


### Tandem Cyclization of Enynes Containing a Thioether or Ether Linkage via Ruthenium Allenylidene and Vinylidene Complexes

Yi-Jhen Feng, Ji-Xian Lo, Ying-Chih Lin,\* Shou-Ling Huang, Yu Wang, and Yi-Hung Liu

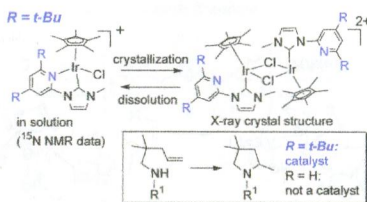


**Cobalt–Bis(imino)pyridine-Catalyzed Asymmetric Hydrogenation: Electronic Structure, Mechanism, and Stereoselectivity**  
Kathrin H. Hopmann\*



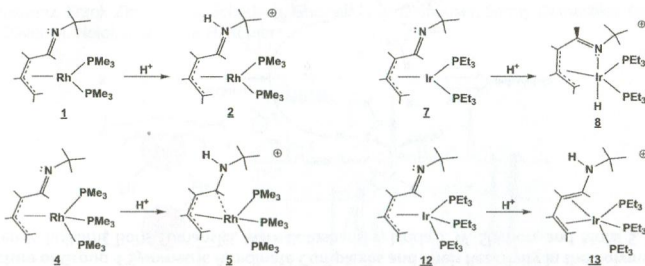
**Effects of Hindrance in N-Pyridyl Imidazolylidenes Coordinated to Iridium on Structure and Catalysis**

Zephen G. Specht, Douglas B. Grotjahn,\* Curtis E. Moore, and Arnold L. Rheingold



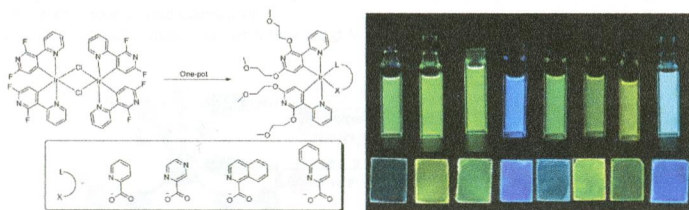
**Synthesis, Spectroscopy, Structure, and Reactivity of Azapentadienyl-Rhodium-Phosphine and Azapentadienyl-Iridium-Phosphine Complexes**

John R. Bleeke,\* Wipark Anutrasakda, and Nigam P. Rath



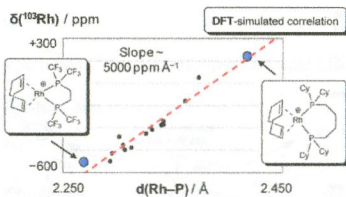
### Effective Alkoxylation of Phosphorescent Heteroleptic Iridium(III) Compounds Bearing Fluorinated Bipyridine Ligands

Hankook Oh, Ki-Min Park, Hyonseok Hwang, Sihyun Oh, Ji Hye Lee, Jia-Sheng Lu, Suning Wang,\* and Youngjin Kang\*



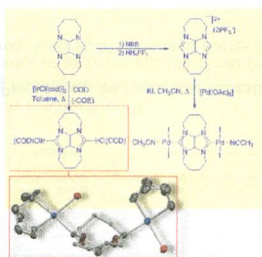
### Computational Insight into $^{103}\text{Rh}$ Chemical Shift–Structure Correlations in Rhodium Bis(phosphine) Complexes

Manuel A. Ortuño, Ludovic Castro, and Michael Bühl\*

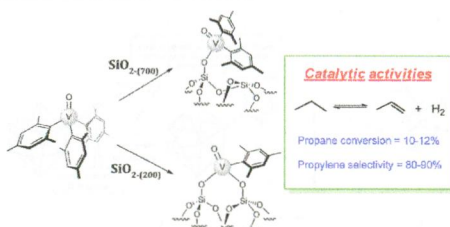


### A Tetracyclic Bis(imidazolindiyliene) Ligand and Its Diiridium and Dipalladium Complexes

Hugo Valdés, Macarena Poyatos,\* and Eduardo Peris\*

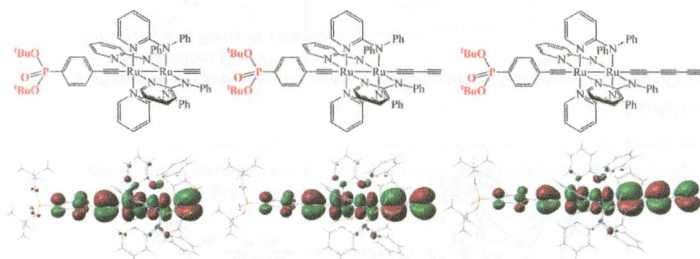


**Vanadium Oxo Organometallic Species Supported on Silica for the Selective Non-oxidative Dehydrogenation of Propane**  
 Kai C. Szeto, Björn Loges, Nicolas Merle, Nicolas Popoff, Alessandra Quadrelli, Hongpeng Jia, Elise Berrier, Aimey De Mallmann,\*  
 Laurent Delevoe, Régis M. Gauvin, and Mostafa Taoufik\*



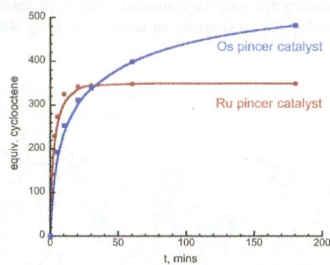
**New Diruthenium Bis-alkynyl Compounds as Potential Ditopic Linkers**

Julia Savchenko, Zhi Cao, Sean N. Natoli, Steven P. Cummings, Boone M. Prentice, Phillip E. Fanwick, and Tong Ren\*



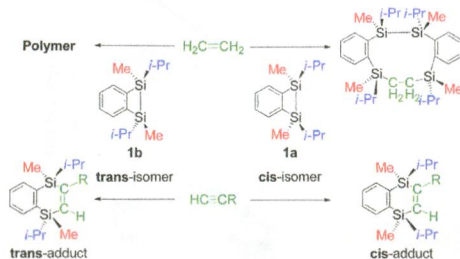
**Acceptor Pincer Chemistry of Osmium: Catalytic Alkane Dehydrogenation by  $(^{CF_3}PCP)Os(cod)(H)$**

Brian C. Gruver, Jeramie J. Adams, Navamoney Arulsamy, and Dean M. Roddick\*



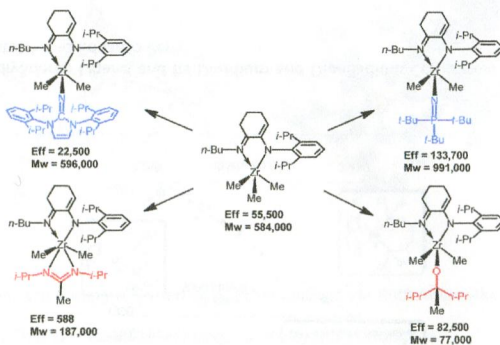
### Stereochemistry of Disilanylene-Containing Cyclic Compounds. Thermal Reactions of *cis*- and *trans*-3,4-Benzo-1,2-diisopropyl-1,2-dimethyl-1,2-disilacyclobut-3-ene

Akinobu Naka,\* Junnai Ikada, Jun Sakata, Mitsuo Ishikawa,\* Yoshihiro Hayashi, Liudmil Antonov, Susumu Kawauchi,\* and Tokio Yamabe



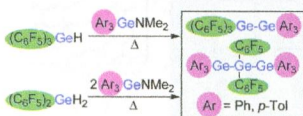
### Preparation of New Olefin Polymerization Precatalysts by Facile Derivatization of Imino–Enamido $\text{ZrMe}_3$ and $\text{HfMe}_3$ Complexes

Jerzy Klosin,\* Philip P. Fontaine, Ruth Figueroa, Scott D. McCann, and Darrek Mort



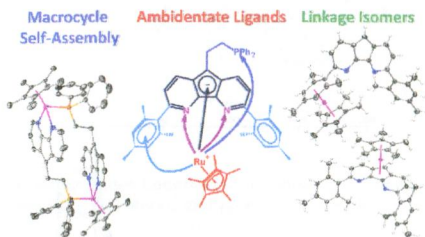
### "Donor–Acceptor" Oligogermanes: Synthesis, Structure, and Electronic Properties

Kirill V. Zaitsev,\* Andrey A. Kapranov, Andrei V. Churakov, Oleg Kh. Poleshchuk, Yuri F. Oprunenko, Boris N. Tarasevich, Galina S. Zaitseva, and Sergey S. Karlov



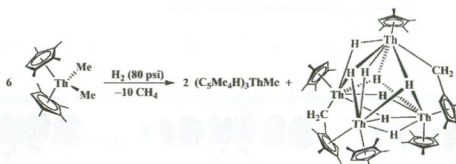
### RuCp\* Complexes of Ambidentate 4,5-Diazafluorene Derivatives: From Linkage Isomers to Coordination-Driven Self-Assembly

Vincent T. Annibale, Rhys Batcup, Tao Bai, Sarah J. Hughes, and Datong Song\*



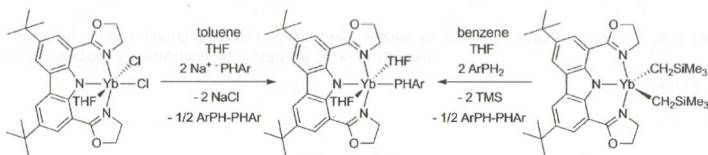
### Actinide Metallocene Hydride Chemistry: C–H Activation in Tetramethylcyclopentadienyl Ligands to Form $[\mu-\eta^5-C_5Me_3H(CH_2)-\kappa-C]^{2-}$ Tuck-over Ligands in a Tetrathorium Octahydride Complex

Nathan A. Siladke, Christopher L. Webster, Justin R. Walensky, Michael K. Takase, Joseph W. Ziller, Daniel J. Grant, Laura Gagliardi,\* and William J. Evans\*



### Unusual Redox Chemistry of Ytterbium Carbazole–Bis(oxazoline) Compounds: Oxidative Coupling of Primary Phosphines by an Ytterbium Carbazole–Bis(oxazoline) Dialkyl

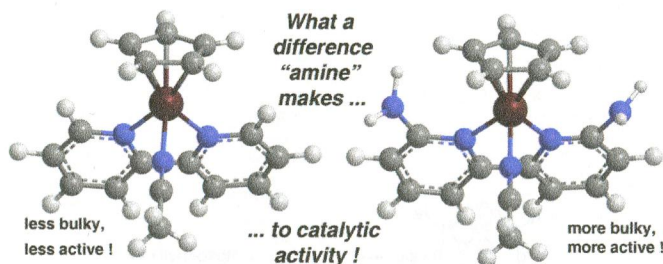
Jin Zou, David J. Berg,\* Allen Oliver, and Brendan Twamley





Comparison of the Catalytic Activity of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}(2,2'\text{-bipyridine})(\text{L})]\text{OTf}$  versus  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}(6,6'\text{-diamino-2,2'\text{-bipyridine})(\text{L})]\text{OTf}$  (L = labile ligand) in the Hydrogenation of Cyclohexanone. Evidence for the Presence of a Metal–Ligand Bifunctional Mechanism under Acidic Conditions

Domenico DiMondo, Michelle E. Thibault, James Britten, and Marcel Schlaf\*



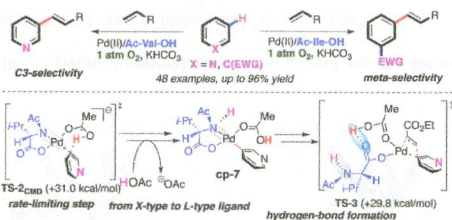
Electron Transfer Behavior of Pincer-Type  $\{\text{RhNO}\}^8$  Complexes: Spectroscopic Characterization and Reactivity of Paramagnetic  $\{\text{RhNO}\}^9$  Complexes

Juan Pellegrino, Carina Gaviglio, David Milstein, and Fabio Doctorovich\*



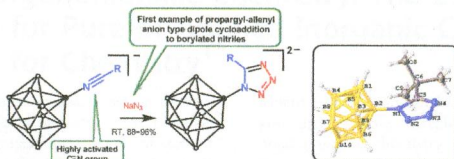
Role of Mono-N-protected Amino Acid Ligands in Palladium(II)-Catalyzed Dehydrogenative Heck Reactions of Electron-Deficient (Hetero)arenes: Experimental and Computational Studies

Xuefeng Cong, Huarong Tang, Chao Wu,\* and Xiaoming Zeng\*

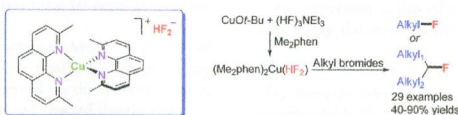


Borylated Tetrazoles from Cycloaddition of Azide Anions to Nitrilium Derivatives of *closo*-Decaborate Clusters

Aleksey L. Mindich, Nadezhda A. Bokach,\* Maxim L. Kuznetsov, Galina L. Starova, Andrey P. Zhdanov, Konstantin Yu. Zhizhin, Serguei A. Miltsov, Nikolay T. Kuznetsov, and Vadim Yu. Kukushkin\*

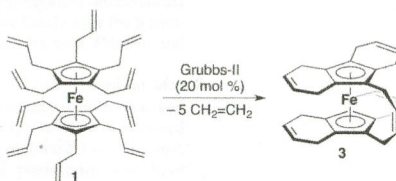
Efficient  $S_N2$  Fluorination of Primary and Secondary Alkyl Bromides by Copper(I) Fluoride Complexes

Yanpin Liu, Chaohuang Chen, Huaifeng Li, Kuo-Wei Huang,\* Jianwei Tan, and Zhiqiang Weng\*



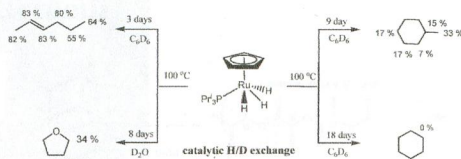
## Inter- versus Intraannular Ring-Closing Metathesis of Polyallylferrocenes: Five-Fold RCM within a Single Molecule

Masamichi Ogasawara,\* Wei-Yi Wu, Sachie Arai, Kiyohiko Nakajima, and Tamotsu Takahashi\*



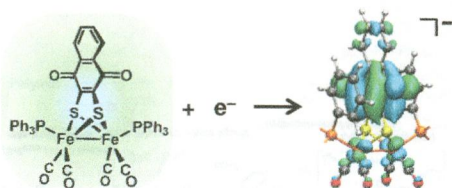
## Catalytic H/D Exchange of Unactivated Aliphatic C-H Bonds

Sun Hwa Lee, Serge I. Gorelsky,\* and Georgii I. Nikonov\*

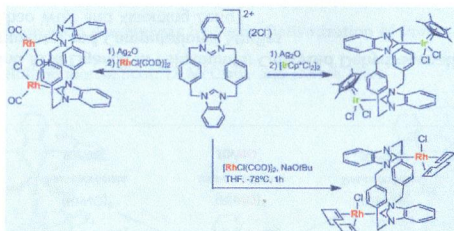


**Redox Chemistry of Noninnocent Quinones Annulated to 2Fe2S Cores**

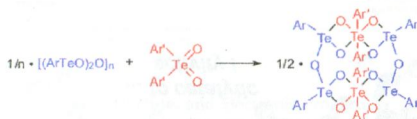
Gabriel B. Hall, Jinzhu Chen, Charles A. Mebi, Noriko Okumura, Matthew T. Swenson, Stephanie E. Ossowski, Uzma I. Zakai, Gary S. Nichol, Dennis L. Lichtenberger,\* Dennis H. Evans,\* and Richard S. Glass\*

**Coordination Singularities of a Bis(*p*-xylyl)bis(benzimidazolylidene) Ligand and the Bis-iridium and -rhodium-Related Complexes**

Sheila Ruiz-Botella, Gregorio Guisado-Barrios, José A. Mata,\* and Eduardo Peris\*

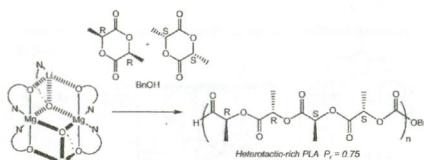
**Notes****Synthesis and Properties of Tellurinic Anhydride–Tellurone Adducts**

Makoto Oba,\* Kozaburo Nishiyama, Shinichi Koguchi, Shigeru Shimada, and Wataru Ando



**Synthesis and Structure of Homo- and Heterometallic Lithium–Magnesium Complexes and Their Reactivity in the ROP of *rac*-Lactide**

Carlos Gallegos, Vanessa Taberner, Francisco M. García-Valle, Marta E. G. Mosquera, Tomás Cuenca,\* and Jesús Cano\*

**Additions and Corrections****Correction to Thermal versus Photochemical Reductive Elimination of Aryl Chlorides from NHC-Gold Complexes**

Michael J. Ghidui, Allen J. Pistner, Glenn P. A. Yap, Daniel A. Lutterman, and Joel Rosenthal\*