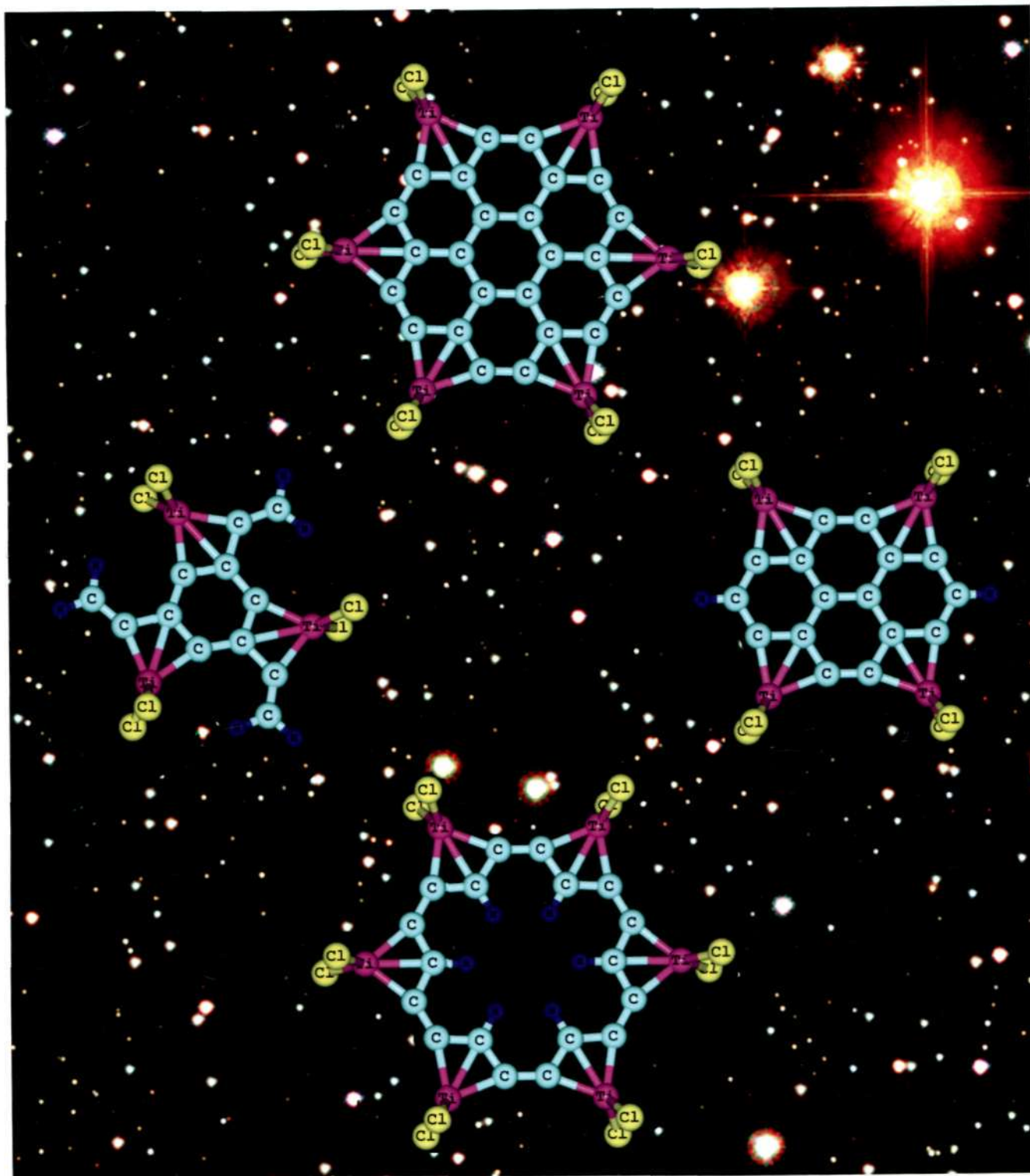


# ORGANOMETALLICS

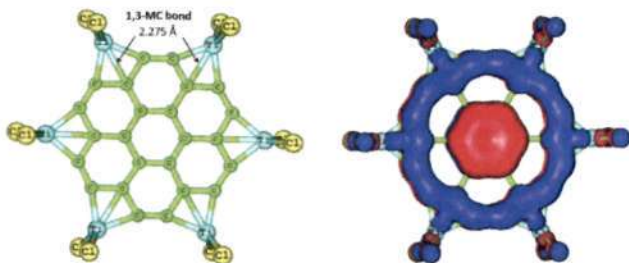


**ON THE COVER:** Strong evidence for the existence of hitherto unrecognized 1,3-metal–carbon bonding in organometallic chemistry has been obtained. Inspired by this finding, Suresh and Frenking have predicted the formation of star-shaped metalloaromatic “edge complexes”. The molecular images on the cover page show such complexes with characteristic 1,3-MC bonds between the metals and the  $\beta$ -carbon atoms, which render the  $\beta$ -carbon atoms planar and tetracoordinate. The background image is a NASA/ESA Hubble space telescopic view of a planetary host star (<http://www.spacetelescope.org/images/opo0638c/>). Further details may be found in the article on pages 1531–1536.

## Articles

1531 [dx.doi.org/10.1021/om301037a](http://dx.doi.org/10.1021/om301037a)

### 1,3-Metal–Carbon Bonding Predicts Rich Chemistry at the Edges of Aromatic Hydrocarbons Cherumuttathu H. Suresh\* and Gernot Frenking



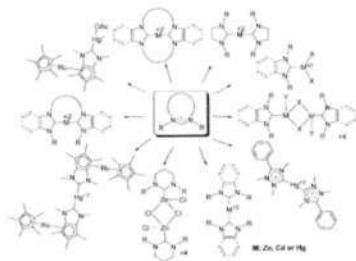
## Reviews

1537

[dx.doi.org/10.1021/om301091p](http://dx.doi.org/10.1021/om301091p)

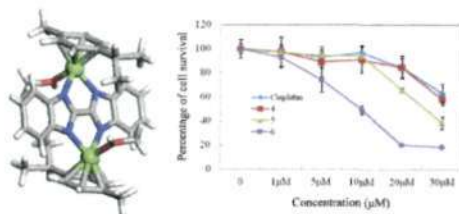
### Group XII Metal–N-Heterocyclic Carbene Complexes: Synthesis, Structural Diversity, Intramolecular Interactions, and Applications

Srinivasa Budagumpi\* and Salasiah Endud



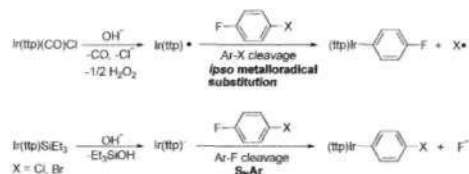
1563 **S** dx.doi.org/10.1021/om301174s

**Growth Inhibitory Activity of a Bis-Benzimidazole-Bridged Arene Ruthenium Metalla-Rectangle and -Prism**  
 Vaishali Vajpayee, Sun mi Lee, Joeng Woo Park, Abhishek Dubey, Hyunuk Kim, Timothy R. Cook, Peter J. Stang, and Ki-Whan Chi\*



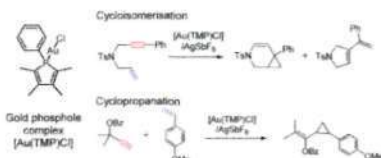
1567 **S** dx.doi.org/10.1021/om301196t

**Competitive Aryl-Fluorine and Aryl-Halogen (Halogen = Cl, Br) Bond Cleavage with Iridium Porphyrin Complexes**  
 Ying Ying Qian, Bao Zhu Li, and Kin Shing Chan\*



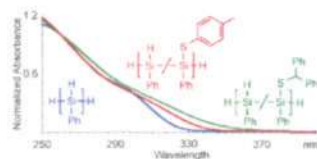
1571 **S** dx.doi.org/10.1021/om301244m

**Gold Phosphole Complexes as Efficient Catalysts for Alkyne Activation**  
 Kévin Fourmy, Sonia Mallet-Ladeira, Odile Dechy-Cabaret,\* and Maryse Gouygou\*



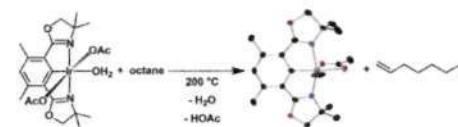
1575 **S** dx.doi.org/10.1021/om301246z

**Borane-Catalyzed Si-H Activation Routes to Polysilanes Containing Thiolato Side Chains**  
 Peter T. K. Lee, Miranda K. Skjel, and Lisa Rosenberg\*



1579 **S** dx.doi.org/10.1021/om301267c

**Alkane Dehydrogenation by C-H Activation at Iridium(III)**  
 Kate E. Allen, D. Michael Heinekey, Alan S. Goldman, and Karen I. Goldberg\*



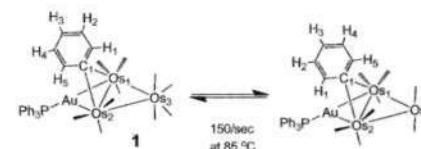
1583 **S** dx.doi.org/10.1021/om400040q

**Aminoborane σ Complexes: Significance of Hydride Co-ligands in Dynamic Processes and Dehydrogenative Borylene Formation**  
 David A. Addy, Joshua I. Bates, Michael J. Kelly, Ian M. Riddlestone, and Simon Aldridge\*



1587 **S** dx.doi.org/10.1021/om400059c

**Dynamic Rotation of Bridging Aryl Ligands in Unsaturated Metal Carbonyl Cluster Complexes**  
 Richard D. Adams,\* Vitaly Rassolov,\* and Qiang Zhang



1591 **S** dx.doi.org/10.1021/om400054u

**Functionalized Cyclic Disilenes via Ring Expansion of Cyclotrisilenes with Isocyanides**  
 Yu Ohmori, Masaaki Ichinohe, Akira Sekiguchi,\* Michael J. Cowley, Volker Huch, and David Scheschkewitz\*



R = aryl, silyl  
 R' = aryl, alkyl

1595

dx.doi.org/10.1021/om301088x

## Diastereoselective Synthesis of Chiral Octahedral Iridium(III) Phosphano–Oxazoline Complexes

Daniel Carmona,\* Joaquina Ferrer,\* Néstor García, Paola Ramírez, Fernando J. Lahoz, Pilar García-Orduña, and Luis A. Oro

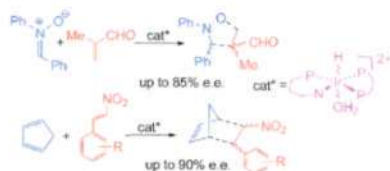


1609

dx.doi.org/10.1021/om301089c

## Chiral Octahedral Phosphano–Oxazoline Iridium(III) Complexes as Catalysts in Asymmetric Cycloaddition Reactions

Daniel Carmona,\* Joaquina Ferrer,\* Néstor García, Paola Ramírez, Fernando J. Lahoz, Pilar García-Orduña, and Luis A. Oro

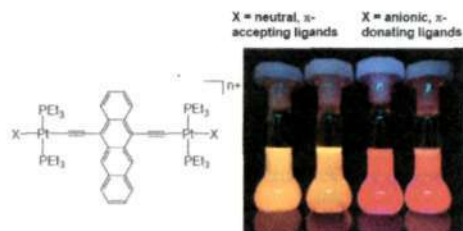


1620

dx.doi.org/10.1021/om300904b

## Ligand Perturbations on Fluorescence of Dinuclear Platinum Complexes of 5,12-Diethynyltetracene: A Spectroscopic and Computational Study

Minh-Hai Nguyen, Chun-Yuen Wong,\* and John H. K. Yip\*

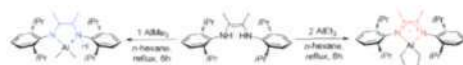


1630

dx.doi.org/10.1021/om300920y

Synthesis and Reactions of a Redox-Active  $\alpha$ -Diimine Aluminum Complex

Jianfeng Li, Kun Zhang, Hanmin Huang, Ao Yu, Hongfan Hu, Haiyan Cui, and Chunming Cui\*



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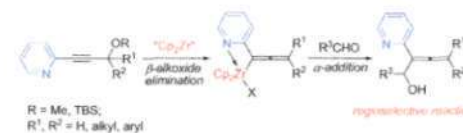
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1636

dx.doi.org/10.1021/om301007z

Unusual Regioselectivity in the Aldehyde Addition Reactions of Allenyl/Propargyl Zirconium Complexes Derived from  $\gamma$ -(2-Pyridyl)propargyl Ethers: Synthesis of Multisubstituted  $\alpha$ -Hydroxyallenes

Guoqin Fan, Xin Xie, Yuanhong Liu,\* and Yuxue Li\*



1643

dx.doi.org/10.1021/om301021j

## Influence of Electronically and Sterically Tunable Cinnamate Ligands on the Spectroscopic Properties and Reactivity of Bis(triphenylphosphine)platinum(0) Olefin Complexes

Magnus R. Buchner, Bettina Bechlers, Bernhard Wahl, and Klaus Ruhland\*

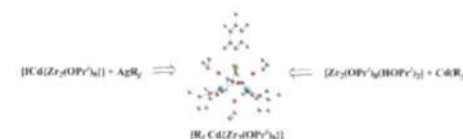


1654

dx.doi.org/10.1021/om301053b

Synthetic and Structural Investigations on the Reactivity of the Cd–I Bond in [ICd(Zr<sub>2</sub>(OPr)<sub>6</sub>)] to Construct New Mixed-Metal Alkoxides

Corinna Hegemann, Wieland Tyrre, Jörg-Martin Neudörfl, and Sanjay Mathur\*

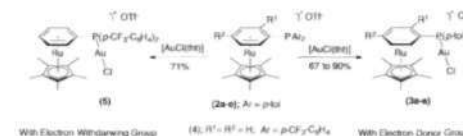


1665

dx.doi.org/10.1021/om301101z

## Gold Compounds Anchored to a Metalated Arene Scaffold: Synthesis, X-ray Molecular Structures, and Cycloisomerization of Enyne

Julien Dubarle-Offner, Marion Barbazanges, Mylène Augé, Christophe Desmaret, Jamal Moussa, M. Rosa Axet, Cyril Olivier, Corinne Aubert,\* Louis Fensterbank, Vincent Gandon, Max Malacria, Geoffrey Gontard, and Hani Amouri\*

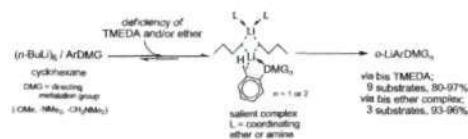


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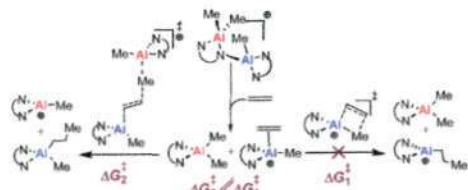
## ortho-Lithiations Reassessed: the Advantages of Deficiency Catalysis in Hydrocarbon Media

D. W. Slocum,\* Thomas K. Reinscheld, Christopher B. White, Michael D. Timmons, Philip A. Shelton, Matthew G. Slocum, Rebecca D. Sandlin, Erica G. Holland, Damir Kusmic, John A. Jennings, Kristen C. Tekin, Quang Nguyen, Steven J. Bush, Julia M. Keller, and Paul E. Whitley\*



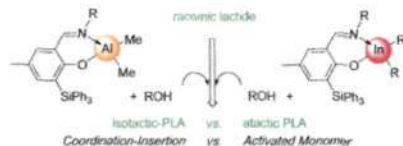
## Theoretical Investigation into the Mechanism of Ethylene Polymerization by a Cationic Dinuclear Aluminum Complex: A Longstanding Unresolved Issue

Nafiseh Ghorbani, Narges Mahdizadeh Ghohe, Shirin Torabi, Brian F. Yates,\* and Alireza Ariafard\*



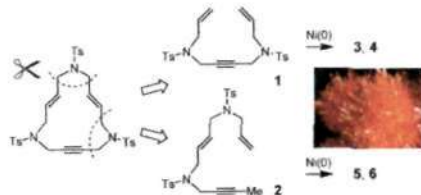
## [Phenoxy-imine]aluminum versus -indium Complexes for the Immortal ROP of Lactide: Different Stereocontrol, Different Mechanisms

Mickael Normand, Vincent Dorcet, Evgeny Kirillov,\* and Jean-François Carpentier\*



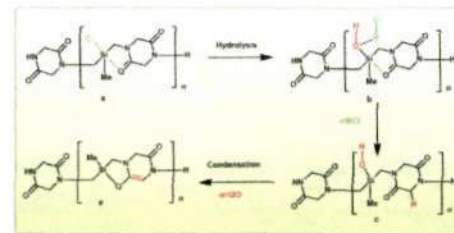
## Nickel(0) Complexes of Acyclic Polyunsaturated Aza Ligands

Sandra Brun, Oscar Torres, Anna Pla-Quintana, Anna Roglans,\* Richard Goddard, and Klaus-Richard Pörschke\*



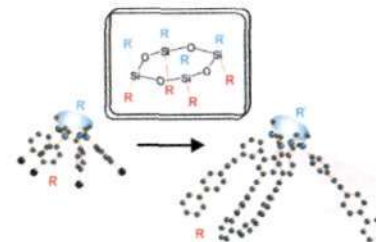
## Synthesis and Hydrolysis-Condensation Study of Water-Soluble Self-Assembled Pentacoordinate Polysilylamides

Muhammad Sohail,\* Alan R. Bassindale, Peter G. Taylor, Alexander A. Koryukov, Dmitry E. Arkhipov, Louise Male, Simon J. Coles, and Michael B. Hursthouse

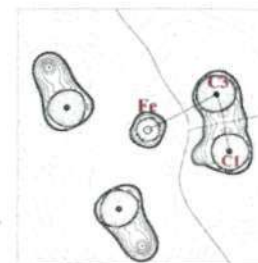


## Selective Derivatization and Characterization of Bifunctional "Janus-Type" Cyclotetrasiloxanes

Robin Panisch,\* Alan R. Bassindale, Alexander A. Koryukov, Mateusz B. Pitak, Simon J. Coles, and Peter G. Taylor\*

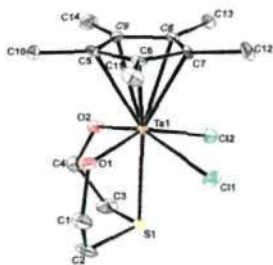
Bonding Analysis of the Trimethylenemethane (TMM) Complexes  $[\eta^6-C_6H_6]M-TMM$  ( $M = Fe, Ru, Os$ ),  $[\eta^5-C_5H_5]M-TMM$  ( $M = Co, Rh, Ir$ ), and  $[\eta^4-C_4H_4]M-TMM$  ( $M = Ni, Pd, Pt$ )

Masoumeh Mousavi and Gernot Frenking\*

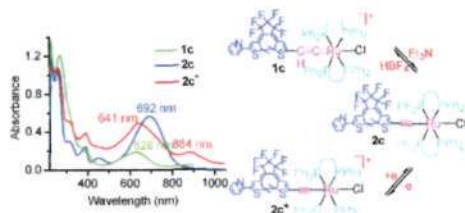


**Insertion Reactions in Ta–H and Ta–Me Bonds in Complexes Containing Tridentate  $\alpha^2\text{O}_2\text{S}_2\text{O}$ -Type Ligands**

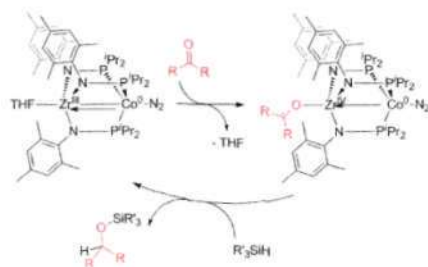
Jacob Fernández-Gallardo, Ángel Bajo, Rosa Fandos, Antonio Otero,\* Ana Rodríguez, and María José Ruiz\*

**Multistate Photochromism in a Ruthenium Complex with Dithienylethene–Acetylide**

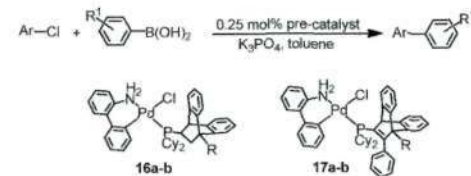
Hui-Min Wen, Bin Li, Jin-Yun Wang, Lin-Xi Shi, Chang-Neng Chen, and Zhong-Ning Chen\*

**Catalytic Hydrosilylation of Ketones Using a Co/Zr Heterobimetallic Complex: Evidence for an Unusual Mechanism Involving Ketyl Radicals**

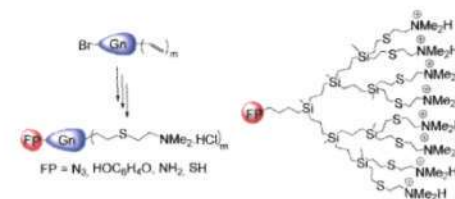
Wen Zhou, Seth L. Marquard, Mark W. Bezpalko, Bruce M. Foxman, and Christine M. Thomas\*

**Electron-Rich Trialkyl-Type Dihydro-KITPHOS Monophosphines: Efficient Ligands for Palladium-Catalyzed Suzuki–Miyaura Cross-Coupling. Comparison with Their Biaryl-Like KITPHOS Monophosphine Counterparts**

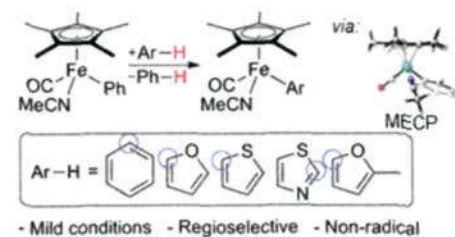
Simon Doherty,\* Julian G. Knight, Nicholas A. B. Ward, Dror M. Bittner, Corinne Wills, William McFarlane, William Clegg, and Ross W. Harrington

**Thiol-Ene Synthesis of Cationic Carbosilane Dendrons: a New Family of Synthons**

Elena Fuentes-Paniagua, Cornelia E. Peña-González, Marta Galán, Rafael Gómez,\* F. Javier de la Mata,\* and Javier Sánchez-Nieves\*

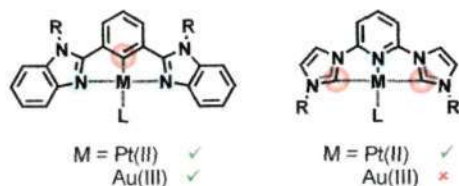
**Facile and Regioselective C–H Bond Activation of Aromatic Substrates by an Fe(II) Complex Involving a Spin-Forbidden Pathway**

Steven E. Kalman, Alban Petit, T. Brent Gunnoe,\* Daniel H. Ess,\* Thomas R. Cundari,\* and Michal Sabat



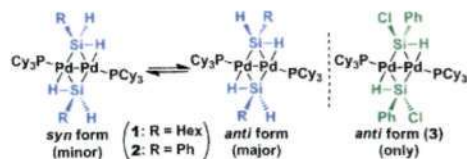
### Gold Complexes with Tridentate Cyclometalating and NHC Ligands: A Search for New Photoluminescent Gold(III) Compounds

Annika Herbst, Catherine Bronner, Pierre Dechambenoit, and Oliver S. Wenger\*



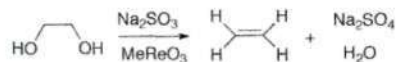
### Dipalladium Complexes with Bridging Monoalkyl or Monophenyl Silyl Ligands in the Solid State and in Solution

Makoto Tanabe, Atsushi Takahashi, Tetsuyuki Yamada, and Kohtaro Osakada\*



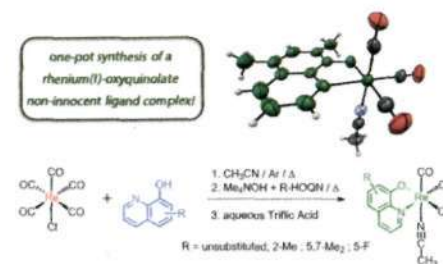
### Mechanism of Sulfite-Driven, $\text{MeReO}_3$ -Catalyzed Deoxydehydration of Glycols

Peng Liu and Kenneth M. Nicholas\*



### Investigation of Monomeric versus Dimeric *fac*-Rhenium(I) Tricarbonyl Systems Containing the Noninnocent 8-Oxyquinolate Ligand

Helen C. Zhao, Barbara Mello, Bi-Li Fu, Hara Chowdhury, David J. Szalda, Ming-Kang Tsai, David C. Grills, and Jonathan Rochford\*



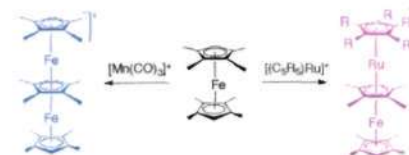
### Angular Distortions at Benzylic Carbons Due to Intramolecular Polarization-Induced Metal–Arene Interactions: A Case Study with Open-Shell Chromium(II) NHC Complexes

Andreas A. Danopoulos,\* Kirill Yu. Monakhov, Vincent Robert,\* Pierre Braunstein,\* Roberto Pattacini, Susana Conde-Guadaño, Martin Hanton, and Robert P. Toozé

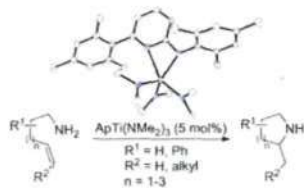


### Synthesis and Structures of Triple-Decker Complexes with a Bridging Tetramethylcyclopentadienyl Ligand

Sonam K. Ghag, Michael L. Tarlton, Ernst A. Henle, Elizabeth M. Ochoa, Alex W. Watson, Lev N. Zakharov, and Eric J. Watson\*

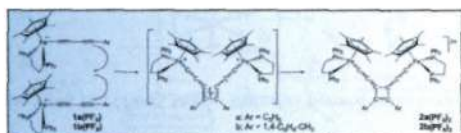


**2-Aminopyridinate Titanium Complexes for the Catalytic Hydroamination of Primary Aminoalkenes**  
Eugene Chong, Sadaf Qayyum, Laurel L. Schafer,\* and Rhett Kempe



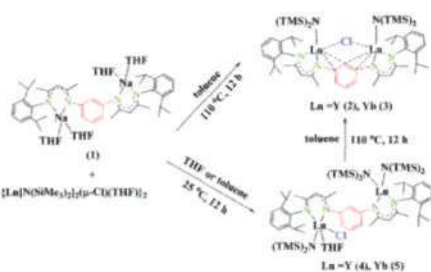
**Oxidative Activation of Aryldiynyl-Iron Complexes: Regioselective Dimerization**

Alexandre Burgun, Frédéric Gendron, Thierry Roisnel, Sourisak Sinbandhit, Karine Costuas,\* Jean-François Halet,\* Michael I. Bruce,\* and Claude Lapinte\*



**Unexpected C–H Bond Activation Promoted by Bimetallic Lanthanide Amido Complexes Bearing a META-Phenylene-Bridged Bis(beta-diketiminato) Ligand**

Song Sun, Qiu Sun, Bei Zhao,\* Yong Zhang, Qi Shen, and Yingming Yao\*

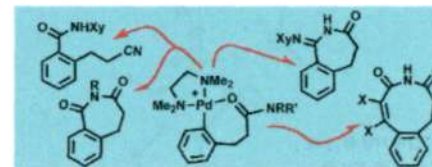


**Platinum-Catalyzed Assembly of Quinaldine from Aniline and Ethylene**

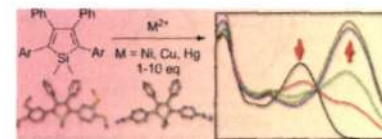
Aurélien Béthegnies, Pavel A. Dub, and Rinaldo Poli\*



**Synthesis and Reactivity of Ortho-Palladated 3-Phenylpropanamides. Insertion of CO, XyNC, and Alkynes into the Pd–C Bond. Synthesis of Seven- and Nine-Membered Palladacycles and Benzazepine- and Benzazonine-Based Heterocycles**  
Roberto Frutos-Pedreño, Pablo González-Herrero,\* José Vicente,\* and Peter G. Jones

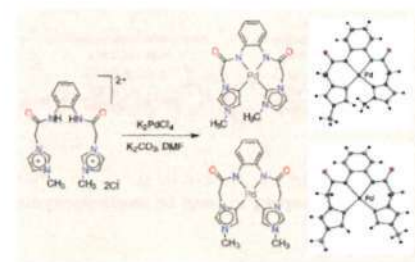


**Synthesis of 2,5-Substituted Siloles and Optical Study of Interactions with Mercury(II), Copper(II), and Nickel(II) Cations**  
James B. Carroll and Janet Braddock-Wilking\*



**Nickel(II) and Palladium(II) Complexes with Chelating N-Heterocyclic Carbene Amidate Ligands: Interplay between Normal and Abnormal Coordination Modes**

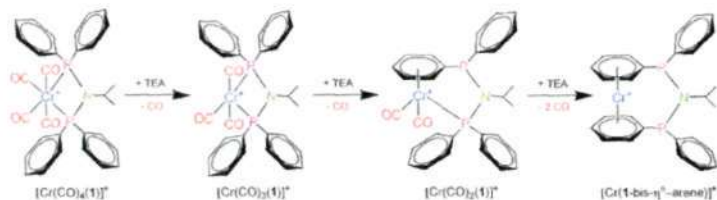
Kel Vin Tan, Jason L. Dutton, Brian W. Skelton, David J. D. Wilson, and Peter J. Barnard\*





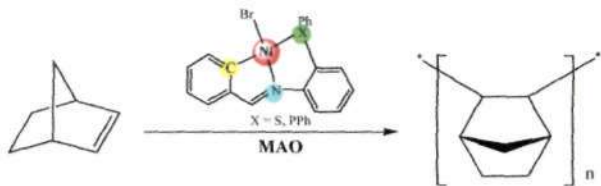
Formation of  $[\text{Cr}(\text{CO})_4(\text{Ph}_2\text{PN}(\text{iPr})\text{PPh}_2)]^+$  Structural Isomers by Reaction of Triethylaluminum with a Chromium *N,N*-Bis(diarylphosphino)amine Complex  $[\text{Cr}(\text{CO})_4(\text{Ph}_2\text{PN}(\text{iPr})\text{PPh}_2)]^+$ : An EPR and DFT Investigation

Emma Carter,\* Kingsley J. Cavell,\* William F. Gabrielli, Martin J. Hanton, Andrew J. Hallett, Lucia McDyre, James A. Platts, David M. Smith, and Damien M. Murphy\*



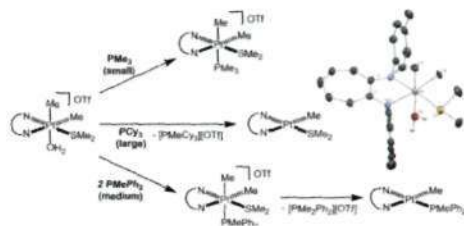
Nickel(II) and Palladium(II) Complexes with Tridentate [C,N,S] and [C,N,P] Ligands: Syntheses, Characterization, and Catalytic Norbornene Polymerization

Ya-Lin Qiao and Guo-Xin Jin\*



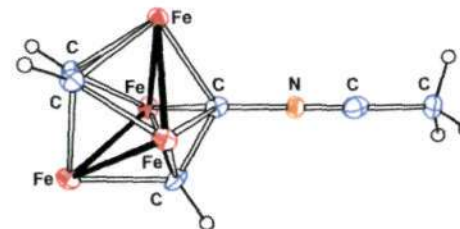
Reductive Elimination from Platinum(IV) Aminotroponimate Dimethyl Complexes Promoted by Sterically Hindered Lewis Bases

Elise Traversa, Joseph L. Templeton,\* Hiu Yan Cheng, Megan Mohadjer Beromi, Peter S. White, and Nathan M. West\*



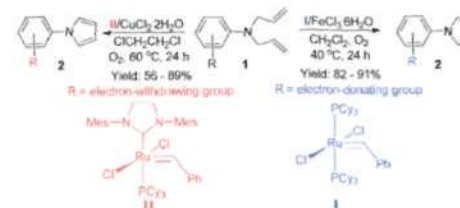
Lewis Acid Chemistry of a Cationic [CCH] Subunit in a Bisdisphenoidal Eight-Atom Tetrairon–Tetracarbon Cluster

Masaaki Okazaki,\* Wataru Taniwaki, Kazuki Miyagi, Masato Takano, Satoshi Kaneko, and Fumiyuki Ozawa\*



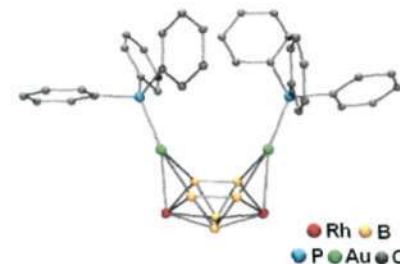
Synthesis of Pyrrole Derivatives from Dialkylamines by One-Pot Tandem Ring-Closing Metathesis and Metal-Catalyzed Oxidative Dehydrogenation

Weiqliang Chen and Jianhui Wang\*



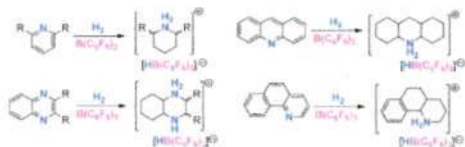
Reactivity of Dirhodium Analogues of Octaborane-12 and Decaborane-14 towards Transition-Metal Moieties

Dipak Kumar Roy, R. S. Anju, Babu Varghese, and Sundargopal Ghosh\*



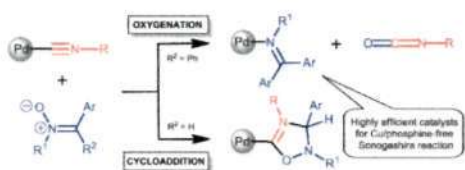
Metal-Free Hydrogenation of *N*-Based Heterocycles

Tayseer Mahdi, Jon Nathaniel del Castillo, and Douglas W. Stephan\*

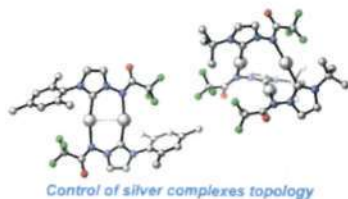


## Selective Nucleophilic Oxygenation of Palladium-Bound Isocyanide Ligands: Route to Imine Complexes That Serve as Efficient Catalysts for Copper-/Phosphine-Free Sonogashira Reactions

Andrei S. Kritchenkov, Konstantin V. Luzyanin, Nadezhda A. Bokach, Maxim L. Kuznetsov, Vladislav V. Gurzhiy, and Vadim Yu. Kukushkin\*

*N*-Acyliminoimidazolium Ylides as Precursors to Anionic *N*-Heterocyclic Carbene Ligands: Control of Topology and Reactivity

Hannah Guernon and Claude Y. Legault\*

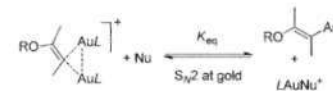


## Stabilization of Three-Coordinated Germanium(II) and Tin(II) Cations by a Neutral Chelating Ligand

Marek Bouška, Libor Dostál, Aleš Růžička, and Roman Jambor\*

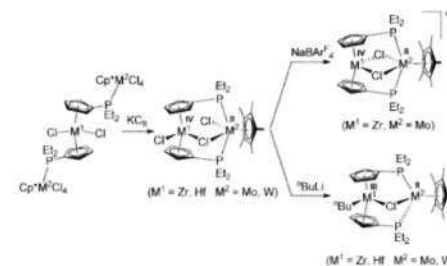
Quantitative Evaluation of the Stability of *gem*-Diaurated Species in Reactions with Nucleophiles

Alexander Zhdanko and Martin E. Maier\*

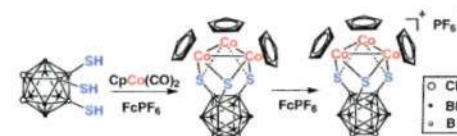


## Synthesis, Structure, and Reactivity of Group VI Metal Complexes Bearing Group IV Metalloacyldiphosphine Moieties and a Pentamethylcyclopentadienyl Ligand

Takama Miyazaki, Yoshiaki Tanabe, Masahiro Yuki, Yoshihiro Miyake, and Yoshiaki Nishibayashi\*

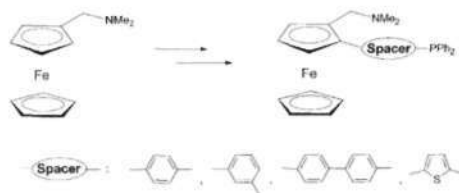
Boron-Substituted *o*-Carboranetrithiol To Construct Trimeric Cobalt Clusters

Xiaolei Zhang, Xiao Tang, Jiajia Yang, Yizhi Li, Hong Yan,\* and Vladimir I. Bregadze\*



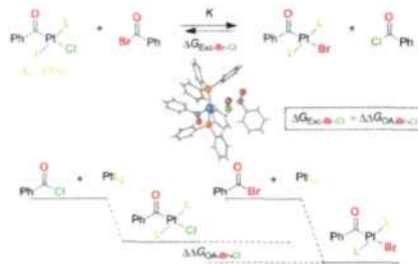
### 1,2-Disubstituted Aryl-Based Ferrocenyl Phosphines

Martyna Madalska, Peter Lönnecke, and Evamarie Hey-Hawkins\*



### $\sigma$ -Bond Metathesis between M–X and RC(O)X' (M = Pt, Pd; X, X' = Cl, Br, I): Facile Determination of the Relative $\Delta G$ Values of the Oxidative Additions of RC(O)X to an M(0) Complex, Evidence by Density Functional Theory Calculations, and Synthetic Applications

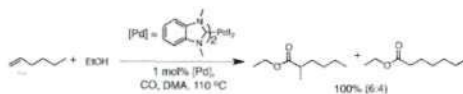
Hitoshi Kuniyasu,\* Atsushi Sanagawa, Daisuke Nakane, Takanori Iwasaki, Nobuaki Kambe,\* Karan Bobuatong, Yunpeng Lu, and Masahiro Ehara\*



## Notes

### Palladium Complexes with N-Heterocyclic Carbene Ligands As Catalysts for the Alkoxycarbonylation of Olefins

Gina M. Roberts, Philip J. Pierce, and L. Keith Woo\*



### An Environmentally Benign and Cost-Effective Synthesis of Aminoferrocene and Aminoruthenocene

Anna Leonidova, Tanmaya Joshi, David Nipkow, Angelo Frei, Johanna-Elena Penner, Sandro Konatschnig, Malay Patra, and Gilles Gasser\*

