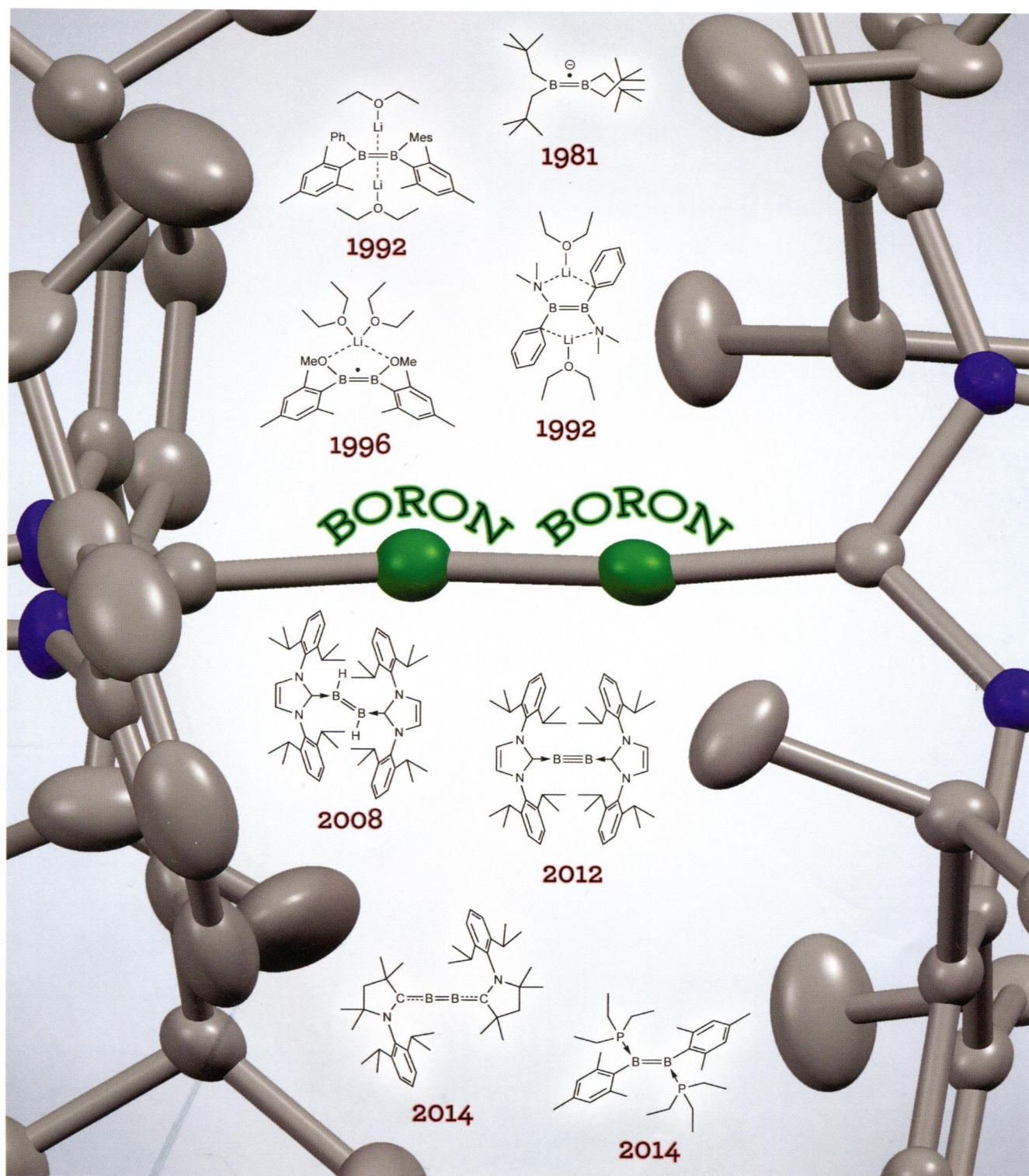


# ORGANOMETALLICS



**ON THE COVER:** Like most discoveries, the synthesis of neutral compounds featuring boron–boron double and triple bonds by the research groups of Robinson and Braunschweig did not come out of the blue. These recent developments make an appreciation of the deep roots and history of the field an imperative, as illustrated by the long time line of unusual compounds featuring element–element multiple bonding. This cover graphic shows just a handful of these compounds, set inside the single-crystal X-ray crystal structure of the first compound prepared with a boron–boron triple bond. The account herein by Braunschweig and Dewhurst gives a historical perspective to this chemistry and summarizes recent work. See the paper on pages 6271–6277.

## Editor's Page

6269

DOI: 10.1021/om501102m

**Award-Winning Organometallic Chemistry: The 2014 RSC Main Group Chemistry Award**  
John A. Gladysz



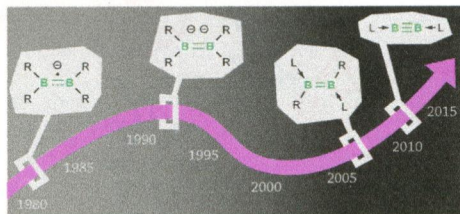
## Reviews

### Cover Paper

6271

DOI: 10.1021/om500875g

**Boron–Boron Multiple Bonding: From Charged to Neutral and Back Again**  
Holger Braunschweig\* and Rian D. Dewhurst



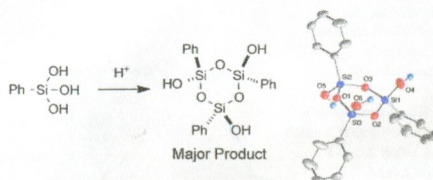


6278 **S**

DOI: 10.1021/om500691c

Acid-Catalyzed Condensation Reaction of Phenylsilanetriol: Unexpected Formation of *cis,trans*-1,3,5-Trihydroxy-1,3,5-triphenylcyclotrisiloxane as the Main Product and Its Isolation

Fujio Yagihashi,\* Masayasu Igarashi, Yumiko Nakajima, Wataru Ando, Kazuhiko Sato, Yoshiyuki Yumoto, Chinami Matsui, and Shigeru Shimada\*

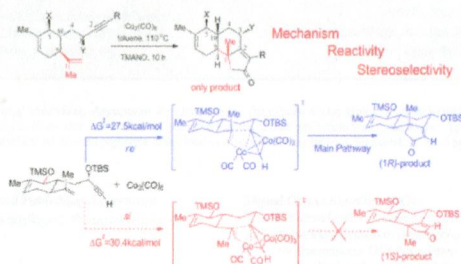


6282 **S**

DOI: 10.1021/om500840q

What Controls Stereoselectivity and Reactivity in the Synthesis of a *trans*-Decalin with a Quaternary Chiral Center via the Intramolecular Pauson–Khand Reaction: A Theoretical Study

Song Liu, Hongjuan Shen, Zhaoyuan Yu, Lili Shi, Zhen Yang,\* and Yu Lan\*

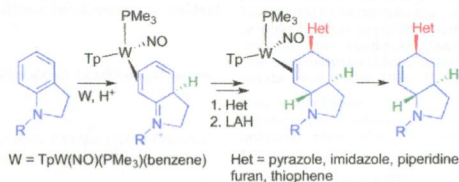


6286 **S**

DOI: 10.1021/om501012q

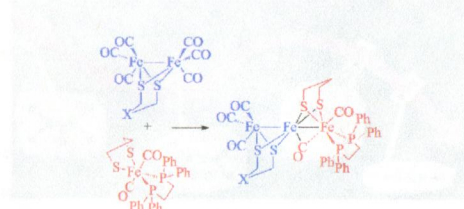
Stereoselective Synthesis of *trans*-Tetrahydroindolines Promoted by a Tungsten  $\pi$  Base

Brianna L. MacLeod, Jared A. Pienkos, Jeffery T. Myers, Michal Sabat, William H. Myers, and W. Dean Harman\*



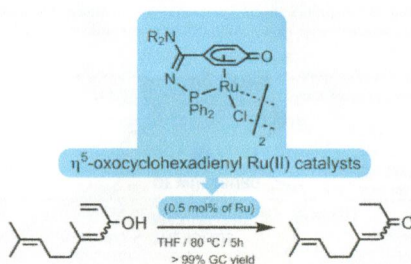
### New Systematic Route to Mixed-Valence Triiron Clusters Derived from Dinuclear Models of the Active Site of [Fe–Fe]-Hydrogenases

Laetitia Beaume, Martin Clémancey, Geneviève Blondin,\* Claudio Greco,\* François Y. Pétillon, Philippe Schollhammer,\* and Jean Talarmin\*



### Tethered $\eta^5$ -Oxocyclohexadienyl Piano-Stool Ruthenium(II) Complexes: A New Class of Catalysts?

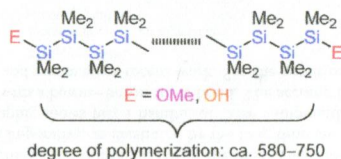
Manel Kechaou-Perrot, Laure Vendier, Stéphanie Bastin, Jean-Marc Sotiropoulos, Karinne Miqueu, Lucía Menéndez-Rodríguez, Pascale Crochet, Victorio Cadierno, and Alain Igau\*



## Articles

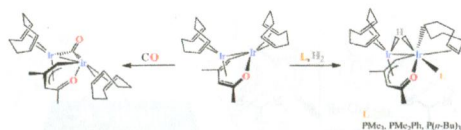
### Studies on the Detailed Structure of Poly(dimethylsilylene)

Soichiro Kyushin,\* Keisuke Ichikawa, Yu Koyama, Hiroyuki Shiraiwa, Hiroshi Ichikawa, Kiyohito Okamura, and Kenji Suzuki



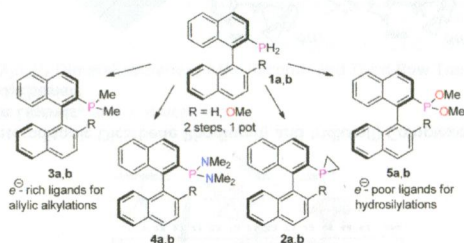
**Iridioxacyclohexadiene-Bridged Mixed-Valence Iridium Cyclooctadiene Complex: Oxidative Addition and Hydrogen-Transfer to Coordinated Cyclooctadiene**

Itzia Irene Padilla-Martínez, Marisol Cervantes-Vásquez, Marco Antonio Leyva-Ramírez, and M. Angeles Paz-Sandoval\*



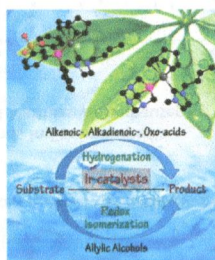
**Air-Stable Chiral Primary Phosphines: A Gateway to MOP Ligands with Previously Inaccessible Stereoelectronic Profiles**

Arne Ficks, William Clegg, Ross W. Harrington, and Lee J. Higham\*



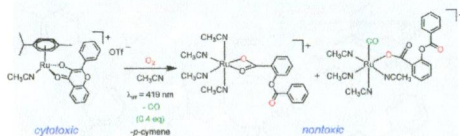
**New Water-Soluble Iridium(I)-N-Heterocyclic Carbene-Tertiary Phosphine Mixed-Ligand Complexes as Catalysts of Hydrogenation and Redox Isomerization**

Henrietta Horváth,\* Ágnes Kathó,\* Antal Udvardy, Gábor Papp, Dorina Szikszai, and Ferenc Joó



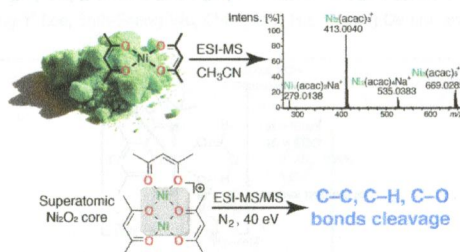
**Photochemical Reactivity of Ru<sup>II</sup>(η<sup>6</sup>-p-cymene) Flavonolato Compounds**

Sushma L. Saraf, Trevor J. Fish, Abby D. Benninghoff, Ashley A. Buel, Rhett C. Smith, and Lisa M. Berreau\*



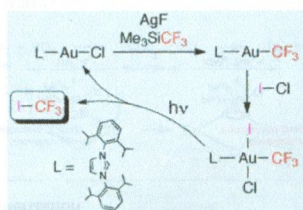
**Exceptional Behavior of Ni<sub>2</sub>O<sub>2</sub> Species Revealed by ESI-MS and MS/MS Studies in Solution. Application of Superatomic Core To Facilitate New Chemical Transformations**

Dmitry B. Eremin and Valentine P. Ananikov\*

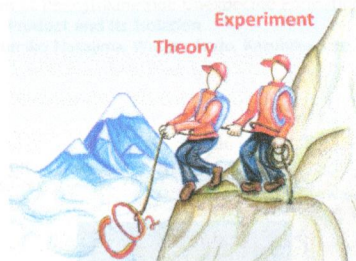


**Synthesis of Au(I) Trifluoromethyl Complexes. Oxidation to Au(III) and Reductive Elimination of Halotrifluoromethanes**

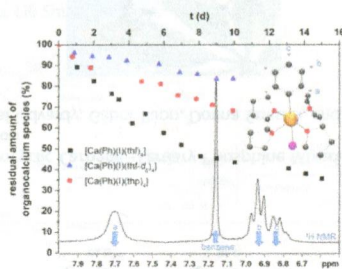
María Blaya, Delia Bautista, Juan Gil-Rubio,\* and José Vicente\*



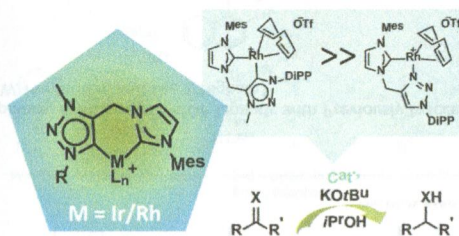
Formation of Acrylates from Ethylene and CO<sub>2</sub> on Ni Complexes: A Mechanistic Viewpoint from a Hybrid DFT Approach  
Wenping Guo, Carine Michel, Renate Schwiedemoch, Raphael Wischert, Xin Xu,\* and Philippe Sautet\*



Solution Stability of Organocalcium Compounds in Ethereal Media  
Mathias Köhler, Jens Langer, Helmar Görls, and Matthias Westerhausen\*



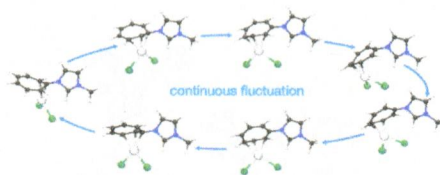
Synthesis and Reactivity of Heteroditopic Dicarbene Rhodium(I) and Iridium(I) Complexes Bearing Chelating 1,2,3-Triazolylidene–Imidazolylidene Ligands  
Soraya N. Sluijter and Cornelis J. Elsevier\*





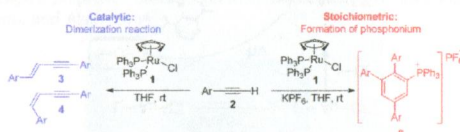
Structure and Dynamics of Imidazolium- and Pyridinium-Substituted  $\eta^3$ -Cycloheptatrienide-Pd Complexes

Christian Jandl, Karl Öfele, Fritz E. Kühn, Wolfgang A. Hermann, and Alexander Pöthig\*

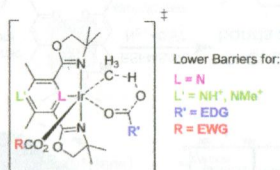


## Synthesis of Arylphosphonium Salts from Cyclotrimerization of Terminal Aryl Alkynes by a Ruthenium Pentadienyl Complex and Revisiting the Catalytic Dimerization

Chi-Ren Chen and Ying-Chih Lin\*

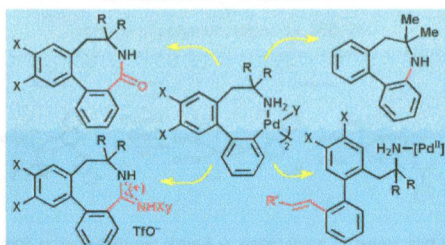
Understanding the Effect of Ancillary Ligands on Concerted Metalation–Deprotonation by  $(^{dm}\text{Phebox})\text{Ir}(\text{OAc})_2(\text{H}_2\text{O})$  Complexes: A DFT Study

Dale R. Pahls, Kate E. Allen, Karen I. Goldberg, and Thomas R. Cundari\*



## Insertion Reactions on Carbopalladated Benzynes: From Eight- to Nine- and Ten-Membered Palladacycles. Applications to the Synthesis of N-Heterocycles

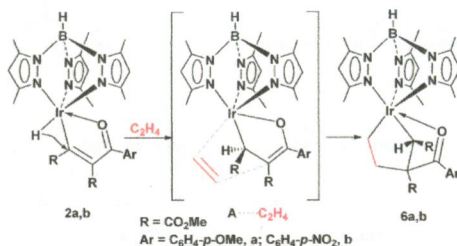
María-José Oliva-Madrid, José-Antonio García-López, Isabel Saura-Llamas,\* Delia Bautista, and José Vicente\*



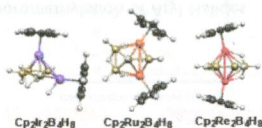


**Reactivity of  $Tp^{Me_2}$ -Containing Hydride-Iridafurans with Alkenes, Alkynes, and  $H_2$** 

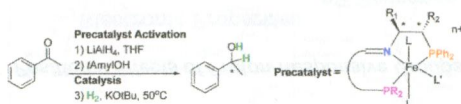
Ángela Vivancos, Cristina M. Posadas, Yohar A. Hernández, Nuria Rendón, Silvia García-Rubín, Eleuterio Álvarez, Margarita Paneque,\* and Manuel L. Poveda\*


**Six-Vertex Hydrogen-Rich  $Cp_2M_2B_4H_8$  Dimetallaboranes of the Second- and Third-Row Transition Metals: Effects of Skeletal Electron Count on Preferred Polyhedra**

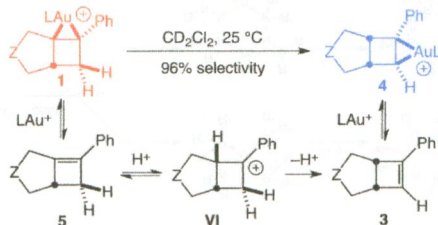
Adrian M. V. Brânzanic, Alexandru Lupan,\* and R. Bruce King\*


**Synthesis of Iron P-N-P' and P-NH-P' Asymmetric Hydrogenation Catalysts**

Jessica F. Sonnenberg, Alan J. Lough, and Robert H. Morris\*

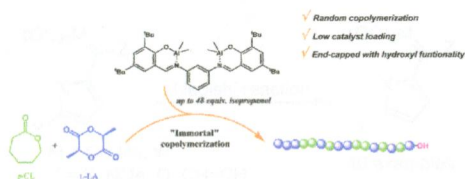

**Mechanism of 1,3-Hydrogen Migration in a Gold Bicyclo[3.2.0]heptene Complex: The Role of Brønsted Acid in the Gold-Catalyzed Cycloisomerization of 7-Aryl-1,6-Enynes**

Rachel E. M. Brooner, Bradley D. Robertson, and Ross A. Widenhoefer\*



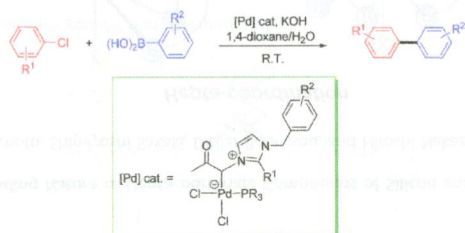
### Copolymerization of $\epsilon$ -Caprolactone and L-Lactide Catalyzed by Multinuclear Aluminum Complexes: An Immortal Approach

Lei Li, Bo Liu, Dongtao Liu, Chunji Wu, Shihui Li,\* Bo Liu,\* and Dongmei Cui\*



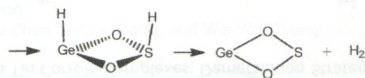
### Zwitterionic Palladium Complexes: Room-Temperature Suzuki–Miyaura Cross-Coupling of Sterically Hindered Substrates in an Aqueous Medium

Jhen-Yi Lee, Dabalina Ghosh, Jing-Yi Lee, Shih-Sheng Wu, Ching-Han Hu, Shuang-De Liu, and Hon Man Lee\*



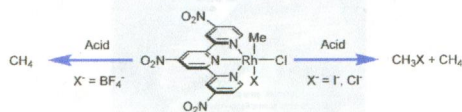
### Reaction of Germylene with Sulfur Dioxide: Gas-Phase Kinetic and Theoretical Studies

Rosa Becerra,\* J. Pat Cannady, and Robin Walsh\*



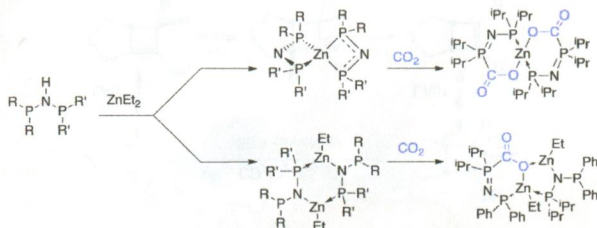
### Reductive Functionalization of a Rhodium(III)–Methyl Bond in Acidic Media: Key Step in the Electrophilic Functionalization of Methane

Matthew E. O'Reilly, Dale R. Pahls, Thomas R. Cundari,\* and T. Brent Gunnoe\*



Structures and CO<sub>2</sub> Reactivity of Zinc Complexes of Bis(diisopropyl-) and Bis(diphenylphosphino)amines

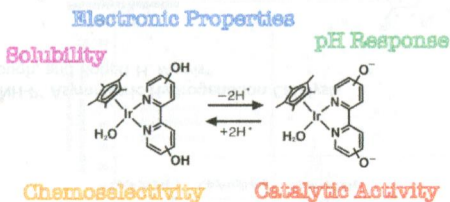
Diane A. Dickie and Richard A. Kemp\*



## Positional Effects of Hydroxy Groups on Catalytic Activity of Proton-Responsive Half-Sandwich Cp\*Iridium(III) Complexes

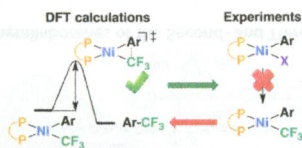
Yuki Suna, Mehmed Z. Ertem, Wan-Hui Wang, Hide Kambayashi, Yuichi Manaka, James T. Muckerman, Etsuko Fujita,\* and Yuichiro Himeda\*

## Positional Effects of Proton-Responsive Groups



## On the Feasibility of Nickel-Catalyzed Trifluoromethylation of Aryl Halides

Jesús Jover, Fedor M. Miloserdov, Jordi Benet-Buchholz, Vladimir V. Grushin,\* and Felü Maseras\*

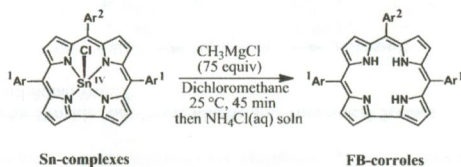




**Support-Free Palladium–NHC Catalyst for Highly Recyclable Heterogeneous Suzuki–Miyaura Coupling in Neat Water**  
 Mathieu Charbonneau, George Addoumieh, Paul Oguadinma, and Andreea R. Schmitzer\*

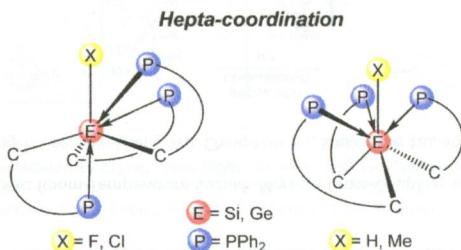


**Reactions of Grignard Reagents with Tin–Corrole Complexes: Demetalation Strategy and  $\sigma$ -Methyl/Phenyl Complexes**  
 Woomileela Sinha and Sanjib Kar\*

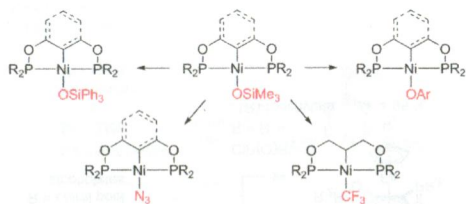


**Synthesis, Geometry, and Bonding Nature of Heptacoordinate Compounds of Silicon and Germanium Featuring Three Phosphine Donors**

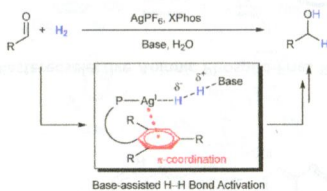
Hajime Kameo,\* Tatsuya Kawamoto, Shigeyoshi Sakaki, Didier Bourissou, and Hiroshi Nakazawa\*



**POCOP-Ligated Nickel Siloxide Complexes: Syntheses, Characterization, and Reactivities**  
Jingjun Hao, Boris Vabre, and Davit Zargarian\*

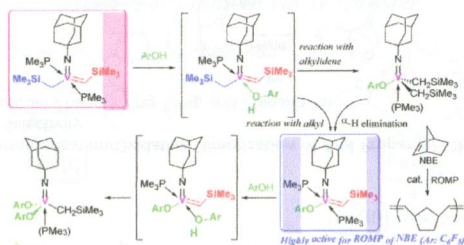


**Theoretical Study on Homogeneous Hydrogen Activation Catalyzed by Cationic Ag(I) Complex**  
Yuan-Ye Jiang, Hai-Zhu Yu, and Yao Fu\*



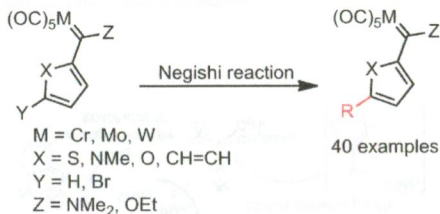
**Synthesis of (Adamantylmido)vanadium(V)-Alkyl, Alkylidene Complex Trapped with  $\text{PMe}_3$ : Reactions of the Alkylidene Complexes with Phenols**

Kohei Hatagami and Kotohiro Nomura\*



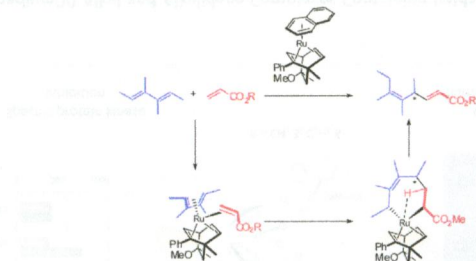
Negishi Cross-Coupling Reaction as a Simple and Efficient Route to Functionalized Amino and Alkoxy Carbene Complexes of Chromium, Molybdenum, and Tungsten

Tomáš Tobrman, Ivana Jurásková, and Dalimil Dvořák\*



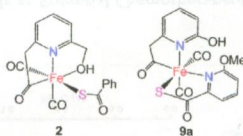
Regio- and Enantioselective Linear Cross-Dimerizations between Conjugated Dienes and Acrylates Catalyzed by New Ru(0) Complexes

Yuki Hiroi, Nobuyuki Komine, Sanshiro Komiya, and Masafumi Hirano\*



Several New [Fe]Hydrogenase Model Complexes with a Single Fe Center Ligated to an Acylmethyl(hydroxymethyl)pyridine or Acylmethyl(hydroxy)pyridine Ligand

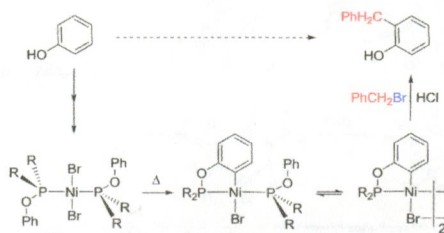
Li-Cheng Song,\* Fu-Qiang Hu, Gao-Yu Zhao, Ji-Wei Zhang, and Wei-Wei Zhang





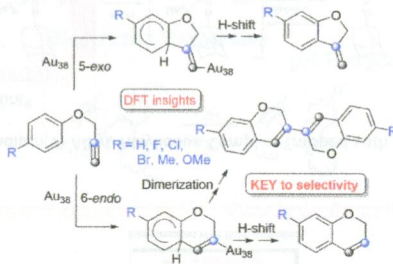
### Ortho Derivatization of Phenols through C–H Nickelation: Synthesis, Characterization, and Reactivities of Ortho-Nickelated Phosphinite Complexes

Boris Vabre, Félix Deschamps, and Davit Zargarian\*



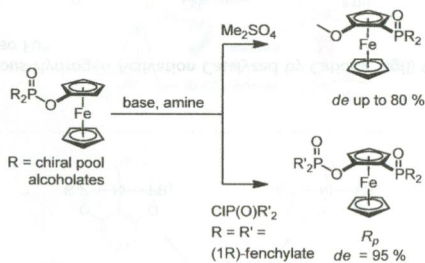
### Computational Study on Cycloisomerization/Oxidative Dimerization of Aryl Propargyl Ethers Catalyzed by Gold Nanoclusters: Mechanism and Selectivity

Dianyong Tang,\* Zhongzhu Chen, Jin Zhang,\* Ying Tang, and Zhigang Xu



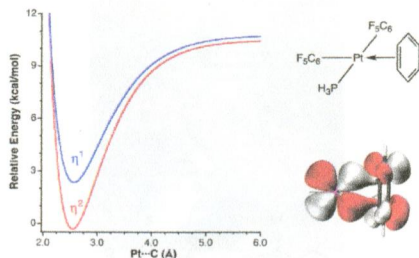
### Planar Chirality from the Chiral Pool: Diastereoselective Anionic Phospho-Fries Rearrangements at Ferrocene

Marcus Korb and Heinrich Lang\*



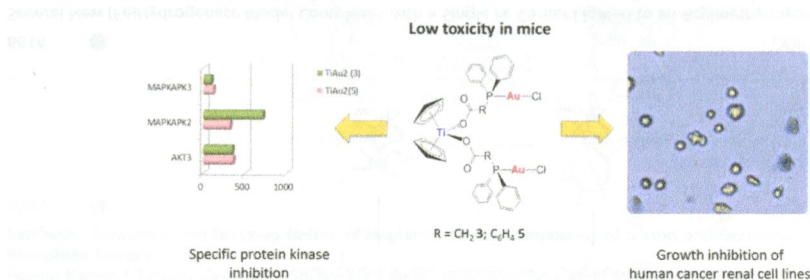
### Electronic and Structural Effects of Low-Hapticity Coordination of Arene Rings to Transition Metals

Andrés Falceto, Ernesto Carmona, and Santiago Alvarez\*



### Organometallic Titanocene–Gold Compounds as Potential Chemotherapeutics in Renal Cancer. Study of their Protein Kinase Inhibitory Properties

Jacob Fernández-Gallardo, Benelita T. Elie, Florian J. Sulzmaier, Mercedes Sanaú, Joe W. Ramos,\* and María Contel\*



### Synthesis of (Imido)vanadium(V) Alkyl and Alkylidene Complexes Containing Imidazolidin-2-iminato Ligands: Effect of Imido Ligand on ROMP and 1,2-C–H Bond Activation of Benzene

Kotohiro Nomura,\* Bijal Kottukkal Bahuleyan, Ken Tsutsumi, and Atsushi Igarashi

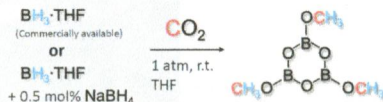


6692 **S**

DOI: 10.1021/om5008488

Reduction of CO<sub>2</sub> to Trimethoxyboroxine with BH<sub>3</sub> in THF

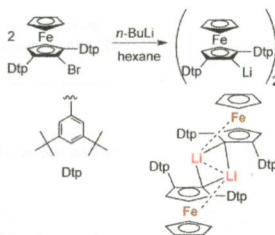
Koji Fujiwara, Shogo Yasuda, and Tsutomu Mizuta\*

6696 **S**

DOI: 10.1021/om500898v

## Isolation and Structural Characterization of a Lewis Base-Free Monolithioferrocene

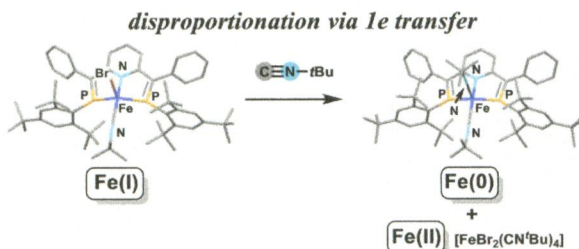
Takahiro Sasamori,\* Yuko Suzuki, and Norihiro Tokitoh

6700 **S**

DOI: 10.1021/om500901a

## Disproportionation of Bis(phosphaethenyl)pyridine Iron(I) Bromide Induced by tBuNC

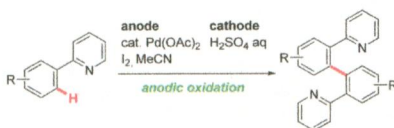
Ya-Fan Lin, Nobuko Ichihara, Yumiko Nakajima,\* and Fumiyuki Ozawa\*

6704 **S**

DOI: 10.1021/om500957a

## Palladium-Catalyzed Regioselective Homocoupling of Arenes Using Anodic Oxidation: Formal Electrolysis of Aromatic Carbon–Hydrogen Bonds

Fumito Saito, Hiroko Aiso, Takuya Kochi, and Fumitoshi Kakiuchi\*





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DOI: 10.1021/om501104z

Corrections to Isomerization of an Enantiomerically Pure Phosphorus-Bridged [1]Ferrocenophane  
Elaheh Khozeimeh Sarbisheh, Jennifer C. Green, and Jens Müller\*