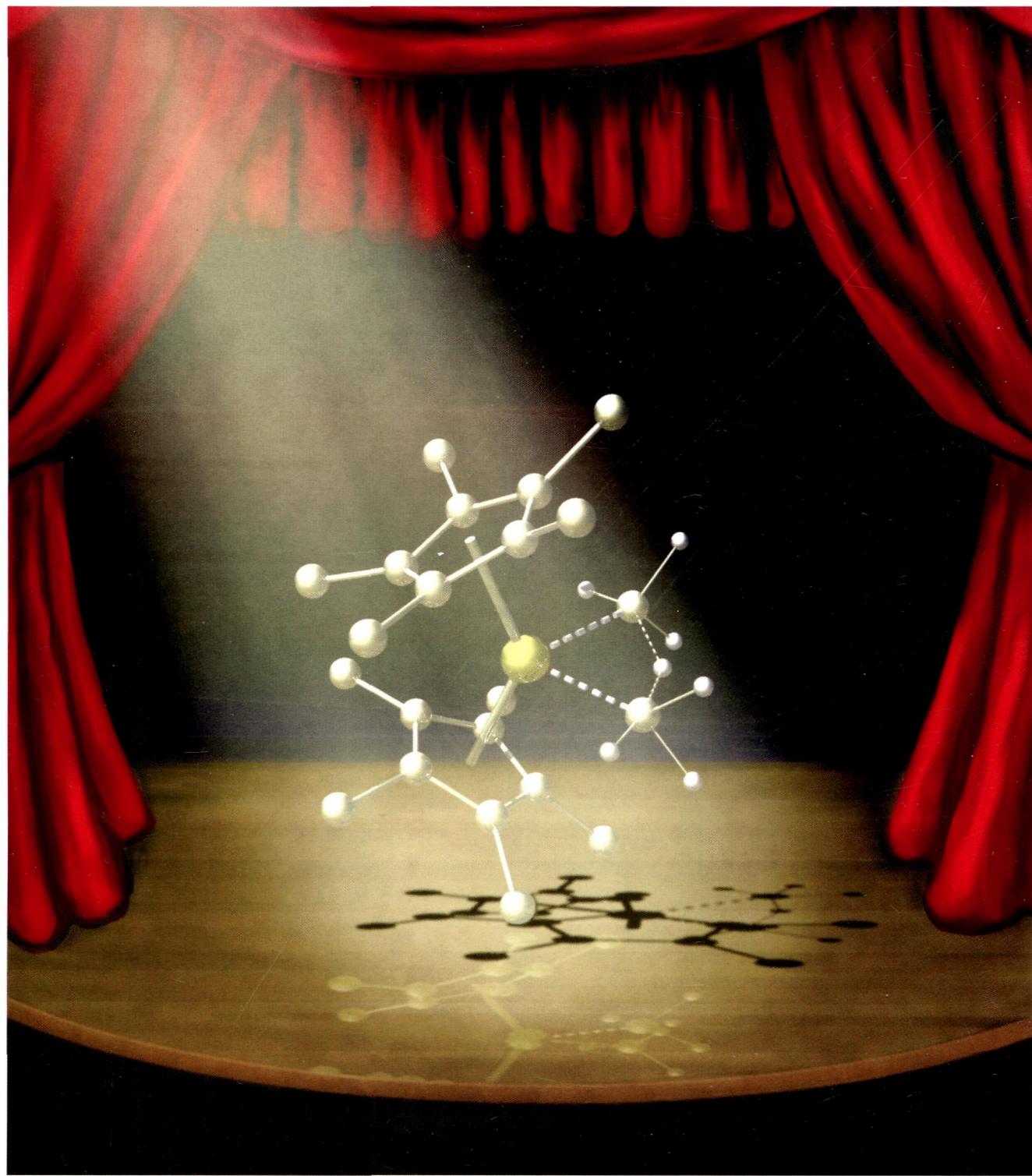


organometallics

DECEMBER 23, 2013 VOL. 32 • ISSUE 24

# ORGANOMETALLICS



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**ON THE COVER:**  $\sigma$ -Bond metathesis takes center stage! A workhorse reaction type for high oxidation state metals,  $\sigma$ -bond metathesis, is re-examined on the 30th anniversary of Watson's discovery of degenerative methyl ligand exchange at  $d^0$  metallocenes (depicted). A discussion of the main features of the reaction is provided to then explore several highlighted exploits of  $\sigma$ -bond metathesis in catalysis. See the paper by Waterman on pages 7250–7264.

## Reviews

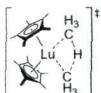
### Cover Paper

7249

#### $\sigma$ -Bond Metathesis: A 30-Year Retrospective

Rory Waterman\*

[dx.doi.org/10.1021/om400760k](https://doi.org/10.1021/om400760k)



## Communications

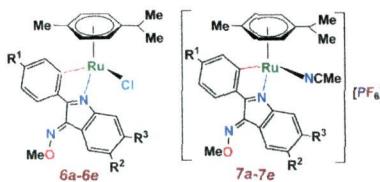
7264



[dx.doi.org/10.1021/om400941b](https://doi.org/10.1021/om400941b)

#### Neutral and Ionic Cycloruthenated 2-Phenylindoles as Cytotoxic Agents

Lluís Belsa, Concepción López,\* Asensio González, Mercè Font-Bardia, Teresa Calvet, Carmen Calvís, and Ramon Messeguer



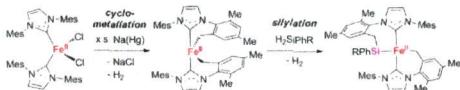
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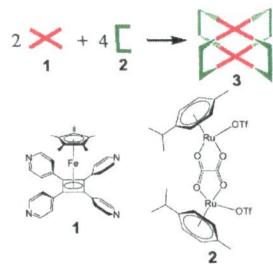


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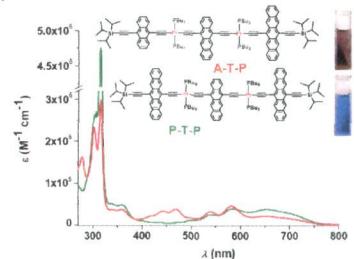
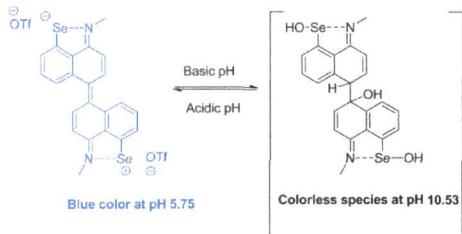
#### Iron(II) Complexes Featuring Bidentate N-Heterocyclic Carbene–Silyl Ligands: Synthesis and Characterization

Zhenwu Ouyang and Liang Deng\*

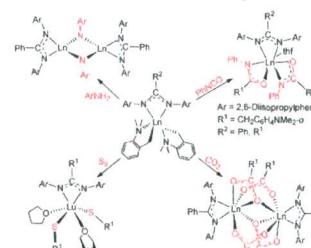
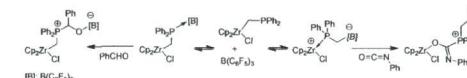
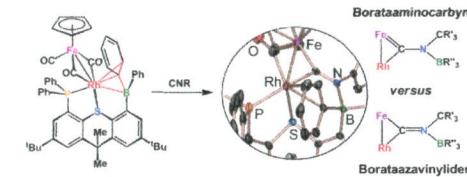
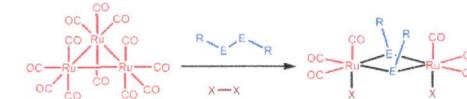




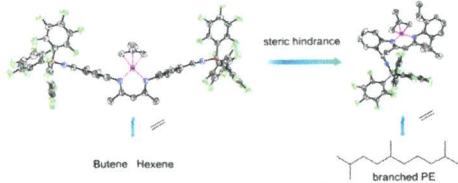
## Articles



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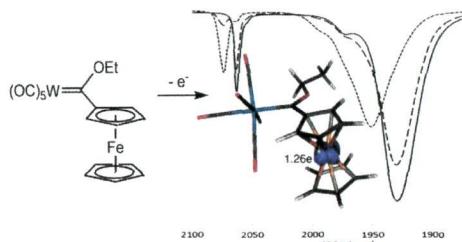
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*N*-Arylcyno- $\beta$ -diketiminato Methallyl Nickel Complexes: Synthesis, Adduct Formation, and Reactivity toward Ethylene  
Oleksandra S. Trofymchuk, Dmitry V. Gutsulyak, Celso Quintero, Masood Parvez, Constantin G. Daniliuc, Warren E. Piers,\* and Rene S. Rojas\*



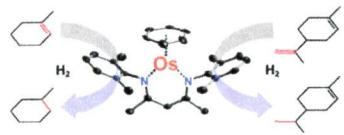
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Electrochemical and Computational Study of Tungsten(0) Ferrocene Complexes: Observation of the Mono-Oxidized Tungsten(0) Ferrocenium Species and Intramolecular Electronic Interactions  
Daniela I. Bezuidenhout,\* Israel Fernández,\* Belinda van der Westhuizen, Pieter J. Swarts, and Jannie C. Swarts\*



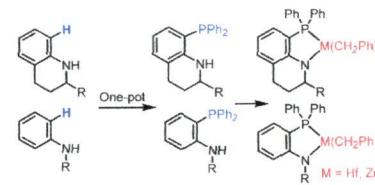
dx.doi.org/10.1021/om400865m

Synthesis, Characterization, and Reactivity of the First Osmium  $\beta$ -Diketiminato Complexes and Application in Catalysis  
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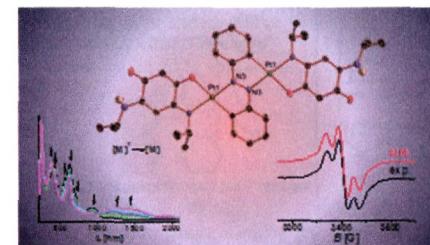
dx.doi.org/10.1021/om400875r

Preparation of Phosphine-Amido Hafnium and Zirconium Complexes for Olefin Polymerization  
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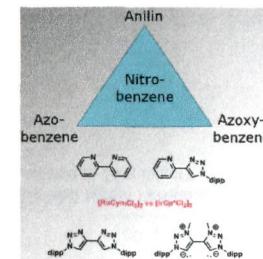
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Electrochromic Platinum(II) Complexes Derived from Azobenzene and Zwitterionic Quinonoid Ligands: Electronic and Geometric Structures  
Naina Deibel, Stephan Hohloch, Michael G. Sommer, David Schweinfurth, Fabian Ehret, Pierre Braunstein, and Biprajit Sarkar\*



dx.doi.org/10.1021/om4009179

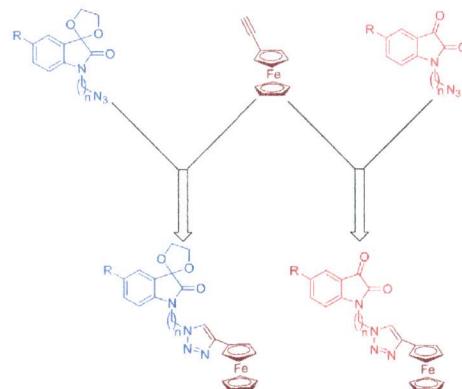
Arene–Ruthenium(II) and –Iridium(III) Complexes with “Click”-Based Pyridyl-triazoles, Bis-triazoles, and Chelating Abnormal Carbenes: Applications in Catalytic Transfer Hydrogenation of Nitrobenzene  
Stephan Hohloch, Lisa Suntrup, and Biprajit Sarkar\*



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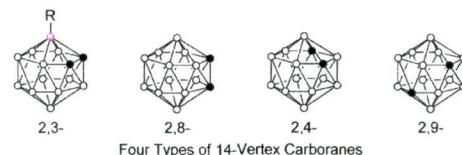
**Base-Promoted Expedient Access to Spiroisatins: Synthesis and Antitubercular Evaluation of 1*H*-1,2,3-Triazole-Tethered Spiroisatin–Ferrocene and Isatin–Ferrocene Conjugates**

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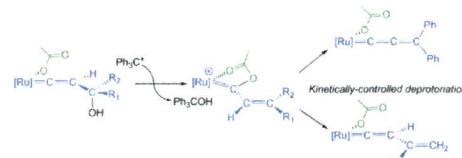
**Synthesis and Characterization of 14-Vertex Carboranes**

Jian Zhang, Fangrui Zheng, and Zuowei Xie\*



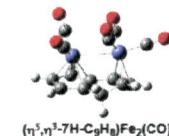
**Mapping the Elimination of Water from Hydroxyvinylidene Complexes of Ruthenium(II): Access to Allenylidene and Vinylvinylidene Complexes in a Stepwise Fashion**

Elizabeth J. Smith, David G. Johnson, Robert J. Thatcher, Adrian C. Whitwood, and Jason M. Lynam\*



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Rong Jin, Xiaohong Chen, Quan Du, Hao Feng,\* Yaoming Xie, and R. Bruce King\*



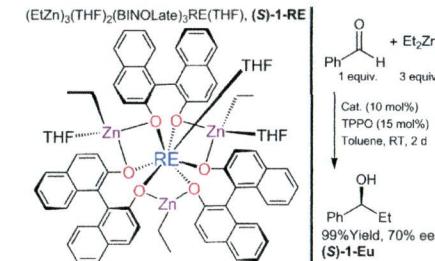
**Activation of C–F and Ni–C Bonds of [P,S]-Ligated Nickel Perfluorometallacycles**

Kaitie A. Giffin, Daniel J. Harrison, Ilia Korobkov, and R. Tom Baker\*



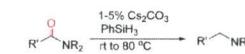
**Synthesis and Catalytic Activity of Heterobimetallic Rare Earth–Zinc Ethyl BINOLate Analogues of Shibasaki’s Catalysts**

Ismael Nieto, Alfred J. Wooten, Jerome R. Robinson, Patrick J. Carroll, Eric J. Schelter,\* and Patrick J. Walsh\*



**Cesium Carbonate-Catalyzed Reduction of Amides with Hydrosilanes**

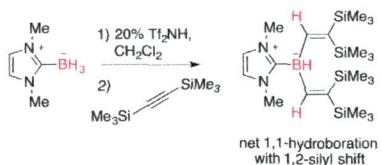
Weilong Xie, Mengdi Zhao, and Chunming Cui\*



Borenium-Catalyzed Hydroborations of Silyl-Substituted Alkenes and Alkynes with a Readily Available N-Heterocyclic Carbene–Borane

Anne Boussonnière, Xiangcheng Pan, Steven J. Geib, and Dennis P. Curran\*

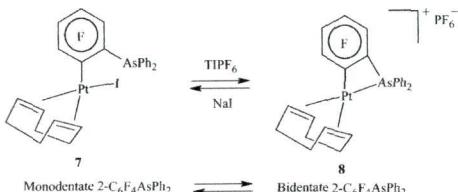
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Divalent Platinum Complexes of the Carbanion  $2\text{-C}_6\text{F}_4\text{AsPh}_2$ : Monodentate or Bidentate Coordination?

Nedaossadat Mirzadeh, Steven H. Privér, Martin A. Bennett, Jörg Wagler, and Suresh K. Bhargava\*

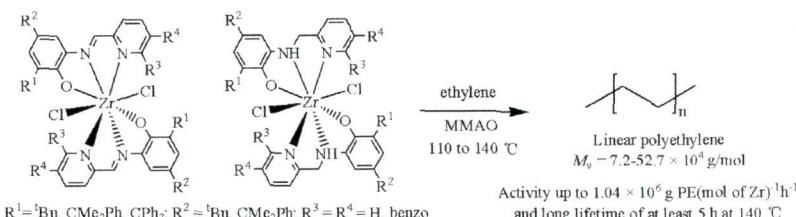
[dx.doi.org/10.1021/om400961z](https://doi.org/10.1021/om400961z)



Highly Thermally Stable Eight-Coordinate Dichloride Zirconium Complexes Supported by Tridentate [ONN] Ligands: Syntheses, Characterization, and Ethylene Polymerization Behavior

Aike Li, Haiyan Ma,\* and Jiling Huang\*

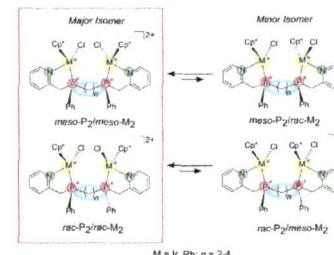
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Configurational Isomerization of Dinuclear Iridium and Rhodium Complexes with a Series of NPPN Ligands,  $2\text{-PyCH}_2(\text{Ph})\text{P}(\text{CH}_2)_n\text{P}(\text{Ph})\text{CH}_2\text{-2-Py}$  ( $\text{Py} = \text{Pyridyl, } n = 2\text{--}4$ )

Takayuki Nakajima,\* Yuki Fukushima, Minoru Tsuji, Naoko Hamada, Bunsho Kure, and Tomoaki Tanase\*

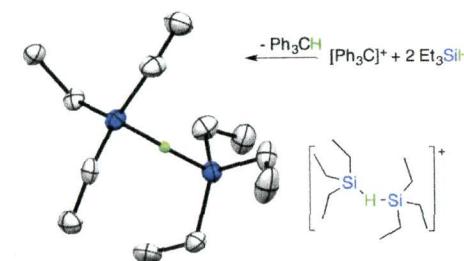
[dx.doi.org/10.1021/om400965g](https://doi.org/10.1021/om400965g)



Structure and Solution Reactivity of (Triethylsilylum)triethylsilane Cations

Samantha J. Connolly, Werner Kaminsky, and D. Michael Heinekey\*

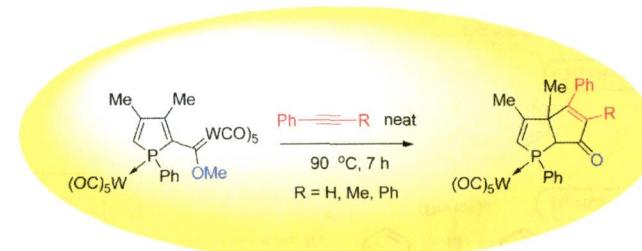
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Annelation of Phosphole-Substituted Fischer Carbene Complexes by Alkynes

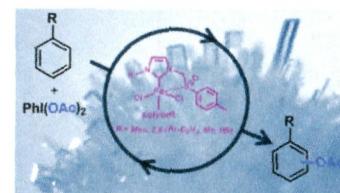
Kim Hong Ng, Yongxin Li, Rakesh Ganguly, and Francois Mathey\*

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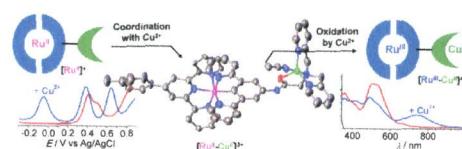


Palladium-Catalyzed Acetoxylation of Arenes by Novel Sulfinyl N-Heterocyclic Carbene Ligand Complexes  
Francisco Tato, Andrés García-Domínguez, and Diego J. Cárdenas\*

dx.doi.org/10.1021/om400981x



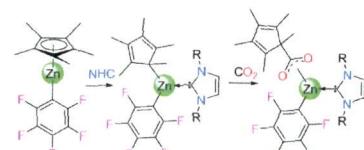
Stepwise Coordination Followed by Oxidation Mechanism for the Multichannel Detection of Cu<sup>2+</sup> in an Aqueous Environment  
Zhong-Liang Gong and Yu-Wu Zhong\*



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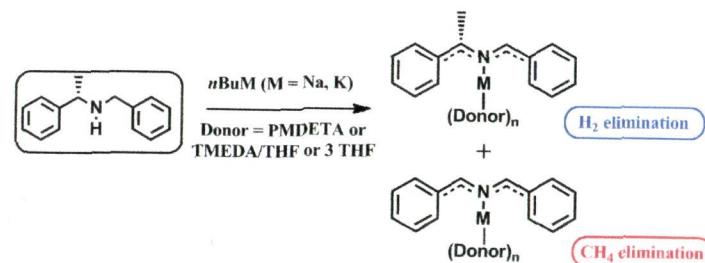
Reactions of CO<sub>2</sub> with Heteroleptic Zinc and Zinc–NHC Complexes  
Phillip Jochmann and Douglas W. Stephan\*

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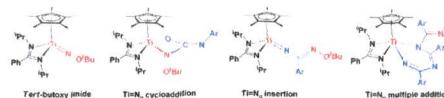
Alkali-Metal-Induced C–C Bond Cleavage and CH<sub>4</sub> Elimination in the Amido → Aza-Allyl Transformation of the (S)-N- $\alpha$ -(Methylbenzyl)benzylamido Anion  
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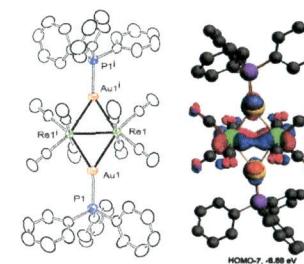
Synthesis and Reactions of a Cyclopentadienyl-Amidinate Titanium *tert*-Butoxymido Compound  
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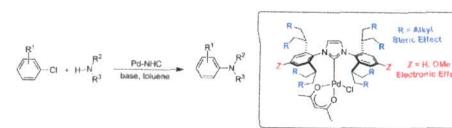
Studies of the Structures and Bonding of Gold-Bridged Dirhenium Carbonyl Cluster Complexes  
Richard D. Adams,\* Yuen Onn Wong, and Qiang Zhang

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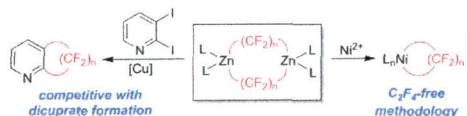


Effect of Electronic Enrichment of NHCs on the Catalytic Activity of [Pd(NHC)(acac)Cl] in Buchwald–Hartwig Coupling  
Gaétan Le Duc, Sébastien Meiries, and Steven P. Nolan\*

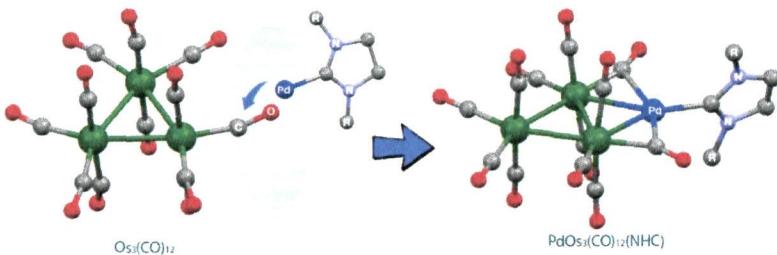
dx.doi.org/10.1021/om401014s



**Mild, Safe, and Versatile Reagents for  $(CF_3)_n$  Transfer and the Construction of Fluoroalkyl-Containing Rings**  
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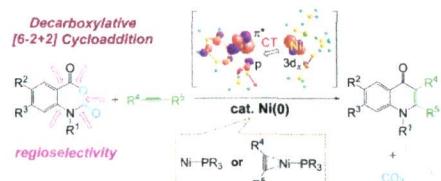


**Palladium–Osmium Heterometallic Clusters Containing N-Heterocyclic Carbene Ligands**  
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**Theoretical Mechanistic Study of Novel Ni(0)-Catalyzed [6 – 2 + 2] Cycloaddition Reactions of Isatoic Anhydrides with Alkynes: Origin of Facile Decarboxylation**

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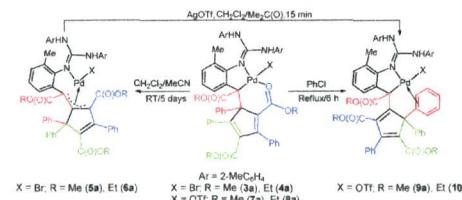


**Enantioselective Desymmetrization of Bicyclic Hydrazines using a  $C_2$ -Symmetric N-Heterocyclic Carbene (NHC) Palladium Complex as Catalyst**  
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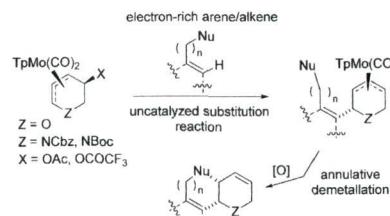
**Insertion Reactions of Six-Membered Cyclopalladated  $N,N',N''$ -Triarylguanidine,  $[Pd(\mu^2(C,N)-C_6H_3Me-3(NHC(NHAr)(=NAr))-\text{2}](\mu\text{-Br})_2$  ( $\text{Ar} = 2\text{-MeC}_6\text{H}_4$ ) with  $\text{PhC}\equiv\text{C}-\text{C}(=\text{O})\text{OR}$  ( $\text{R} = \text{Me}$  and  $\text{Et}$ ): A Gateway to Second Orthopalladation through Novel Rearrangements**

Priya Saxena, Natesan Thirupathi,\* and Munirathinam Nethaji



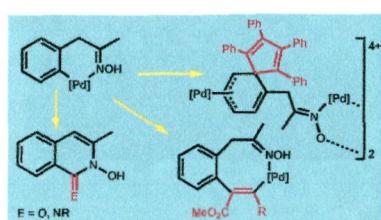
**Regio- and Stereospecific Uncatalyzed Reactions of Electron-Rich Arenes and Olefins at Organomolybdenum Enantiomeric Scaffolds**

Wenyong Chen, Kasinath Sana, Yi Jiang, Esmerelda V. S. Meyer, Stacey Lapp, Mary R. Galinski, and Lanny S. Liebeskind\*



**Cyclopalladated Complexes Derived from Phenylacetone Oxime. Insertion Reactions of Carbon Monoxide, Isocyanides, and Alkynes. Novel Amidines of the Isoquinoline Series**

Antonio Abellán-López, María-Teresa Chicote, Delia Bautista, and José Vicente\*

**Notes****Synthesis and Properties of a Dicationic  $\pi$ -Extended Dithieno[3,2-c:2',3'-e]2,7-diketophosphhepin**

Xiaoming He and Thomas Baumgartner\*

