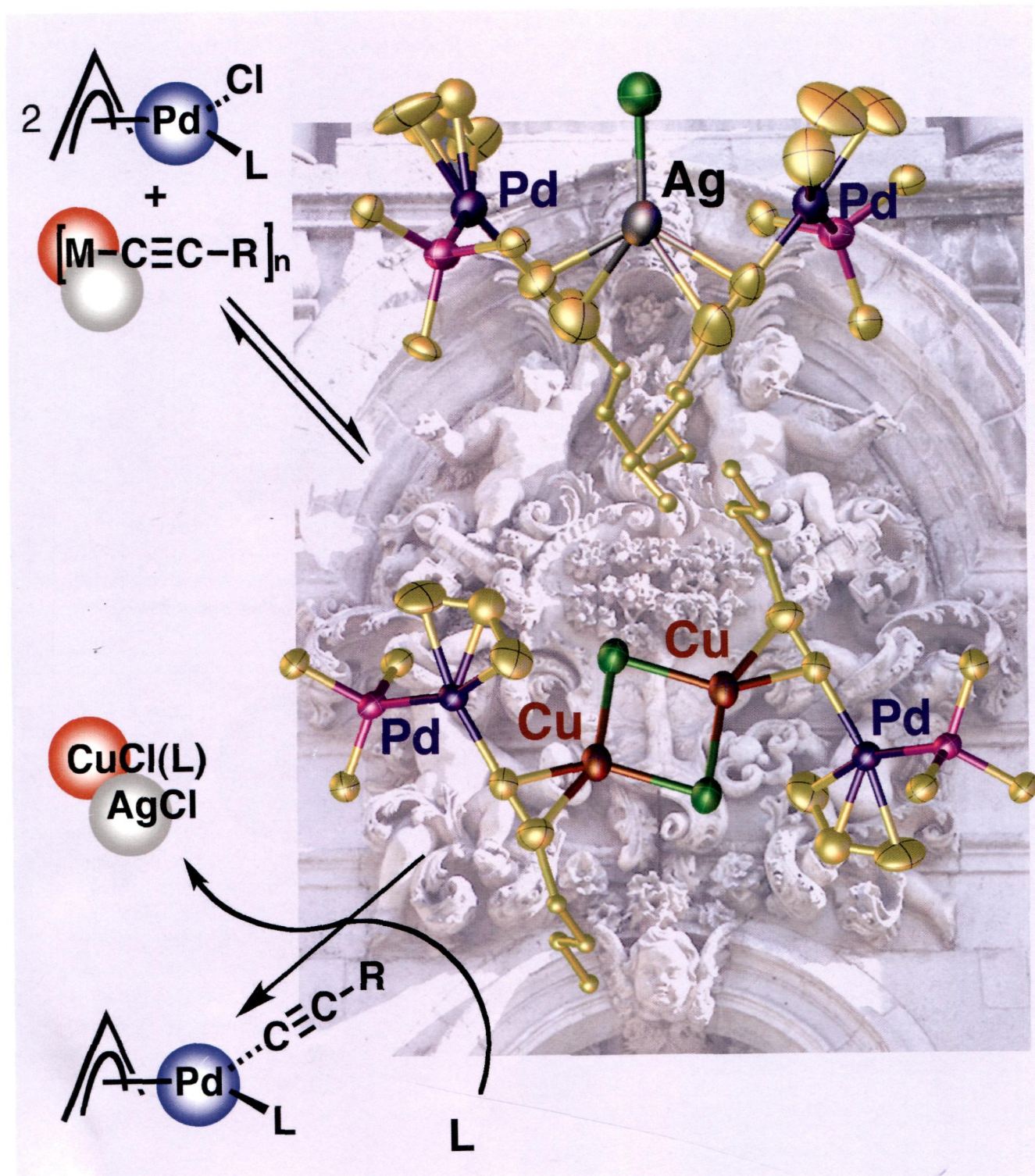


# ORGANOMETALLICS



**ON THE COVER:** The cover shows the simplified structure of the heterometallic Cu-Pd and Ag-Pd complexes formed by alkynyl transmetalation, where the carrier metal stays bound to the alkynyl group. They are shown over the Valladolid University shield carved in the baroque façade of the Old University Building. The silver atom in the complex above is held by two alkynyl groups as the two little angels hold the papal tiara in the shield. The study shows how the transmetalation is completed and alkynyls let the group 11 metals go. See the paper by Albéniz et al. on pages 1-7.

## Articles

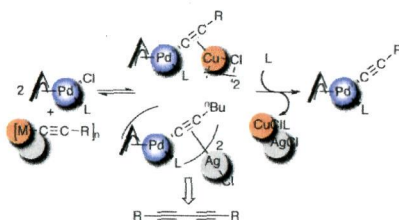
1

S

[dx.doi.org/10.1021/om4005498](https://doi.org/10.1021/om4005498)

### Heterometallic Complexes by Transmetalation of Alkynyl Groups from Copper or Silver to Allyl Palladium Complexes: Demetalation Studies and Alkynyl Homocoupling

Isabel Meana, Pablo Espinet, and Ana C. Albéniz\*



## Communications

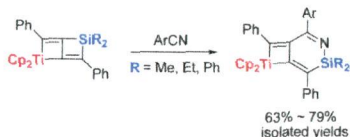
8

S

[dx.doi.org/10.1021/om401065c](https://doi.org/10.1021/om401065c)

### Reaction of Titanacyclobutene–Silacyclobutene Fused-Ring Complexes with Nitriles via Formal Insertion of the C–N Triple Bond of Nitrile into the Silacyclobutene Ring

Jing Zhao, Shaoguang Zhang, Wen-Xiong Zhang,\* and Zhenfeng Xi\*



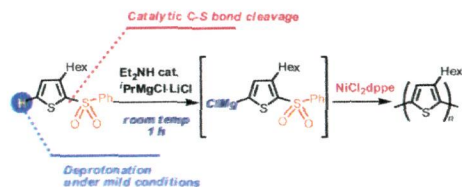
12

5

dx.doi.org/10.1021/om4010737

### Nickel(II)-Catalyzed Cross-Coupling Polycondensation of Thiophenes via C–S Bond Cleavage

Shunsuke Tamba, Kanta Fuji, Karin Nakamura, and Atsunori Mori\*



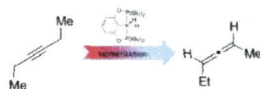
16

5

dx.doi.org/10.1021/om4010934

### Formation of Iridium(III) Allene Complexes via Isomerization of Internal Alkynes

Neha Phadke and Michael Findlater\*



## Articles

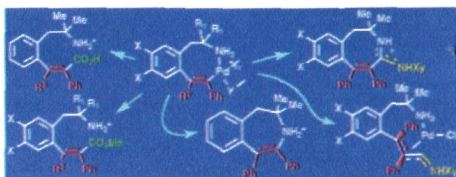
19

5

dx.doi.org/10.1021/om4010059

### Reactivity of Eight-Membered Palladacycles Arising from Monoinsertion of Alkynes into the Pd–C bond of Ortho-Palladated Phenethylamines toward Unsaturated Molecules. Synthesis of Dihydro-3-Benzazocinones, $N^7$ -amino Acids, $N^7$ -amino Esters, and 3-Benzazepines

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



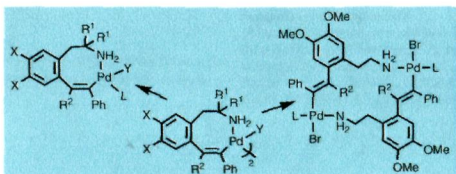
33

5

dx.doi.org/10.1021/om401090b

### Reactivity toward Neutral N- and P-Donor Ligands of Eight-Membered Palladacycles Arising from Monoinsertion of Alkynes into the Pd–C Bond of Orthopalladated Homoveratrylamine and Phentermine. A New Example of the Transphobia Effect

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



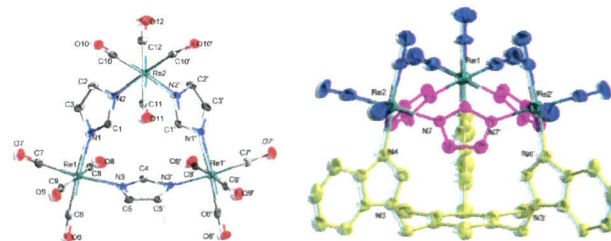
40

5

dx.doi.org/10.1021/om4005065

### A Molecular Triangle as a Precursor Toward the Assembly of a Jar-Shaped Metallasupramolecule

Shih-Ming Lin, Murugesan Velayudham, Chi-Hwe Tsai, Che-Hao Chang, Chung-Chou Lee, Tzuoo-Tsair Luo, Pounraj Thanasekaran, and Kuang-Lieh Lu\*



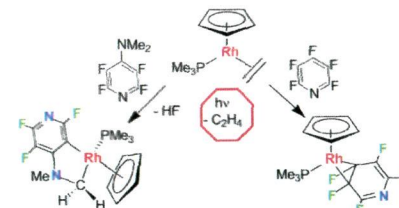
45

5

dx.doi.org/10.1021/om400552r

### Photochemical Reactions of Fluorinated Pyridines at Half-Sandwich Rhodium Complexes: Competing Pathways of Reaction

Barbara Procacci, Robin J. Blagg, Robin N. Perutz,\* Nuria Rendón, and Adrian C. Whitwood



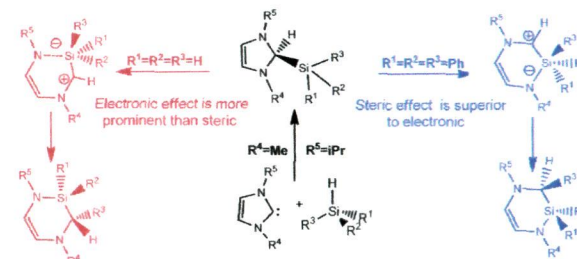
53

5

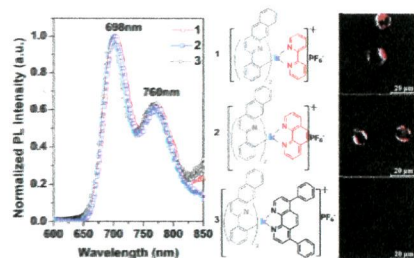
dx.doi.org/10.1021/om400647e

### Mechanism and Regioselectivity of C–N Bond Cleavage and Ring Expansion of N-Heterocyclic Carbenes

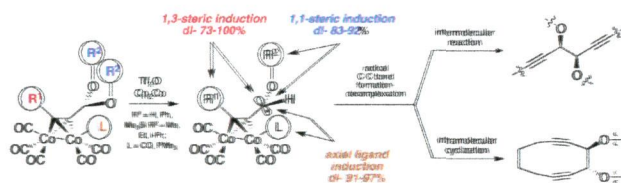
Ran Fang,\* Lizi Yang, and Qiang Wang



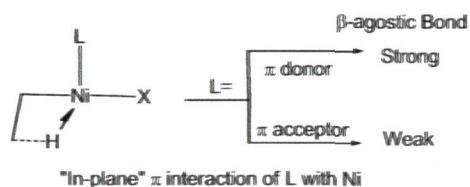
- 61 dx.doi.org/10.1021/om400676h  
**Near-Infrared-Emitting Iridium(III) Complexes as Phosphorescent Dyes for Live Cell Imaging**  
 Guoliang Zhang, Huiyuan Zhang, Yuan Gao, Ran Tao, Lijun Xin, Junyang Yi, Fuyou Li,\* Wanli Liu,\* and Juan Qiao\*



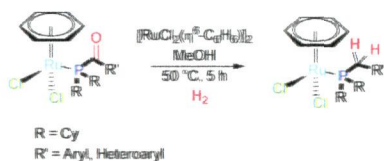
- 69 dx.doi.org/10.1021/om400718w  
**Radical Reactions of the Cobalt-Complexed Propargyl Acetals: Inter- and Intramolecular Variants**  
 Gagik G. Melikyan,\* Erin Voorhees, and Ruth Sepanian



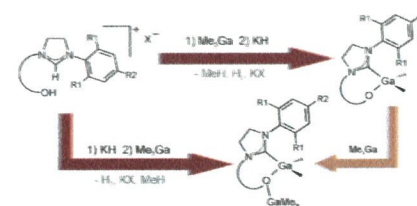
- 84 dx.doi.org/10.1021/om400731j  
**Agostic Interactions in Nickel(II) Complexes: Trans Influence of Ancillary Ligands on the Strength of the Bond**  
 Bimal Pudasaini\* and Benjamin G. Janesko



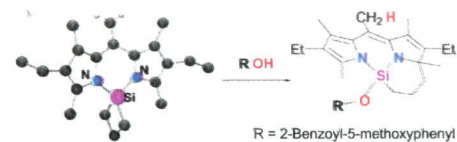
- 94 dx.doi.org/10.1021/om4008086  
**Selective Hydrogenation of Ruthenium Acylphosphine Complexes**  
 Saravanan Gowrisankar, Helfried Neumann, Anke Spannenberg, and Matthias Beller\*



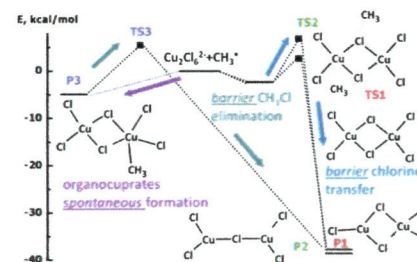
- 100 dx.doi.org/10.1021/om400863y  
**Dialkylgallium Complexes with Alkoxide and Aryloxy Ligands Possessing N-Heterocyclic Carbene Functionalities: Synthesis and Structure**  
 Pawel Horeglad,\* Osman Ablialimov, Grzegorz Szczepaniak, Anna Maria Dąbrowska, Maciej Dranka, and Janusz Zachara



- 112 dx.doi.org/10.1021/om400868w  
**Silicon Compounds of 1,1-Bis(pyrrol-2-yl)ethenes: Molecular Structures and Chemical and Spectroscopic Properties**  
 Alexander Kämpfe, Edwin Kroke, and Jörg Wagler\*



- 121 dx.doi.org/10.1021/om400886e  
**Two Mechanisms of Chlorocuprate Reactions with Alkyl Radicals: Dramatic Role of Nuclearity**  
 Ekaterina M. Zubanova,\* Elena N. Golubeva, and Georgii M. Zhidomirov

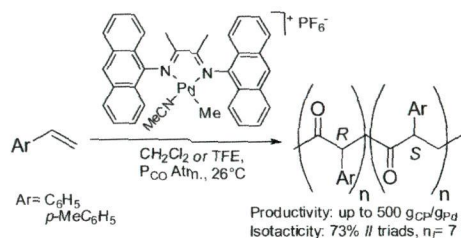


129 **S**

dx.doi.org/10.1021/om400887x

**New Aryl  $\alpha$ -Diimine Palladium(II) Catalysts in Stereocontrolled CO/Vinyl Arene Copolymerization**

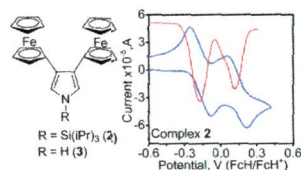
Carla Carfagna,\* Giuseppe Gatti, Paola Paoli, Barbara Binotti, Francesco Fini, Alessandra Passeri, Patrizia Rossi, and Bartolo Gabriele

145 **S**

dx.doi.org/10.1021/om400901w

**Electron-Transfer Processes in 3,4-Diferrocenylpyrroles: Insight into a Missing Piece of the Polyferrocenyl-Containing Pyrroles Family**

Wil R. Goetsch, Pavlo V. Solntsev, Casey Van Stappen, Anatolii A. Purchel, Semen V. Dudkin, and Victor N. Nemykin\*

158 **S**

dx.doi.org/10.1021/om400907s

**Chelation and Stereodynamic Equilibria in Neutral Hypercoordinate Organosilicon Complexes of 1-Hydroxy-2-pyridinone**

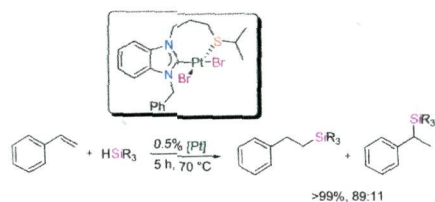
Bradley M. Kraft\* and William W. Brennessel

172 **S**

dx.doi.org/10.1021/om400929t

**Platinum(II) Complexes with Thioether-Functionalized Benzimidazolin-2-ylidene Ligands: Synthesis, Structural Characterization, and Application in Hydroelementation Reactions**

Jan C. Bernhammer and Han Vinh Huynh\*



10A

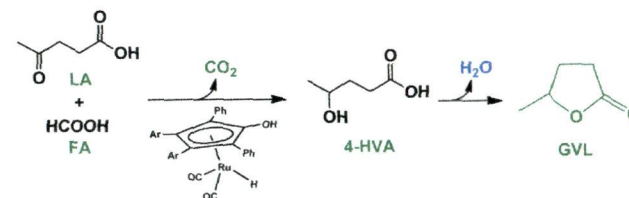
Organometallics, Volume 33, Issue 1

181

dx.doi.org/10.1021/om400938h

**Selective Conversion of Levulinic and Formic Acids to  $\gamma$ -Valerolactone with the Shvo Catalyst**

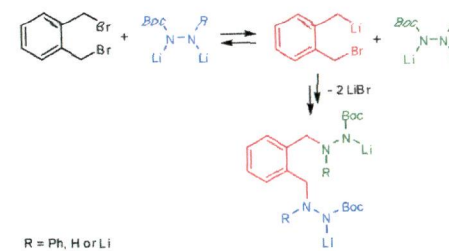
Viktória Fábos, László T. Mika, and István T. Horváth\*

188 **S**

dx.doi.org/10.1021/om4009394

**Metal-Halogen Exchange between Hydrazine Polyanions and  $\alpha,\alpha'$ -Dibromo-*o*-xylene**

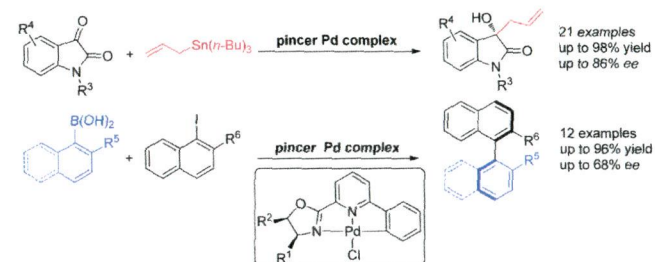
Oleg Lebedev and Uno Mæroerg\*

194 **S**

dx.doi.org/10.1021/om400945d

**Chiral CNN Pincer Palladium(II) Complexes with 2-Aryl-6-(oxazoliny)pyridine Ligands: Synthesis, Characterization, and Application to Enantioselective Allylation of Isatins and Suzuki-Miyaura Coupling Reaction**

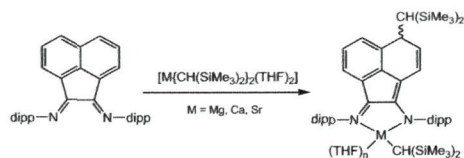
Tao Wang, Xin-Qi Hao, Juan-Juan Huang, Kai Wang, Jun-Fang Gong,\* and Mao-Ping Song\*



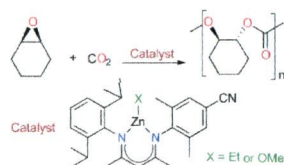
11A

Organometallics, Volume 33, Issue 1

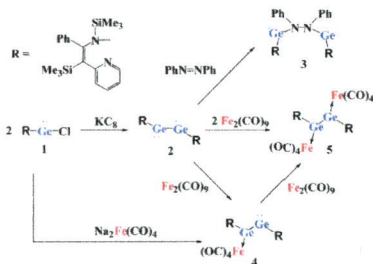
Dearomatized BIAN Alkaline-Earth Alkyl Catalysts for the Intramolecular Hydroamination of Hindered Aminoalkenes  
Merle Arrowsmith, Michael S. Hill,\* and Gabriele Kociok-Köhn



Copolymerization of CO<sub>2</sub> and Cyclohexene Oxide:  $\beta$ -Diketiminato-Supported Zn(II)OMe and Zn(II)Et Complexes as Initiators  
N. M. Rajendran, A. Haleel, and N. Dastagiri Reddy\*

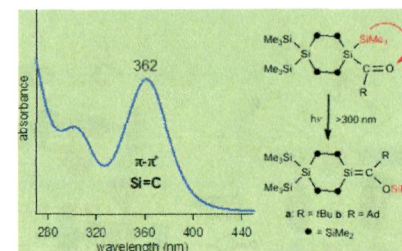


Reactivity of Pyridyl-1-azaallyl Germanium(II) Dimer: Synthesis of a Digermahydrazone Derivative and an Iron-Coordinated Germanium(II) Dimer  
Wing-Por Leung,\* Wang-Kin Chiu, and Thomas C. W. Mak



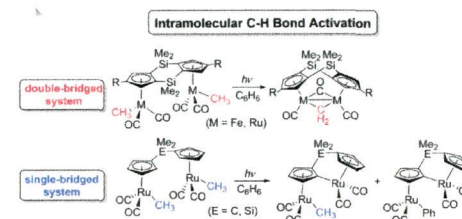
Photoinduced Brook-Type Rearrangement of Acylcyclopolysilanes

Harald Stueger,\* Bernd Hasken, Michael Haas, Martin Rausch, Roland Fischer, and Ana Torvisco



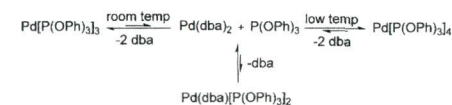
Intramolecular C–H Bond Activation in Bridged Dicyclopentadienyl Dimethyl Dinuclear Complexes

Bolin Zhu,\* Xiaoting Hao, and Yunfei Chen



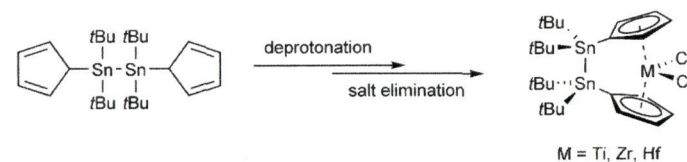
Equilibrium Study of Pd(dba)<sub>2</sub> and P(OPh)<sub>3</sub> in the Pd-Catalyzed Allylation of Aniline by Allyl Alcohol

Supaporn Sawadjoon, Andreas Orthaber, Per J. R. Sjöberg, Lars Eriksson, and Joseph S. M. Samec\*



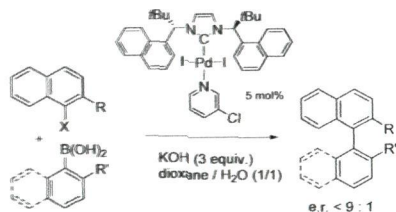
Synthesis and Structure of Group IV Distanna[2]metallocenophanes

Thomas Arnold, Holger Braunschweig,\* Alexander Damme, Ivo Kruppenacher, and Krzysztof Radacki



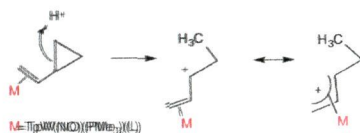
### Chiral PEPPSI Complexes: Synthesis, Characterization, and Application in Asymmetric Suzuki–Miyaura Coupling Reactions

Laure Benhamou, Céline Besnard, and E. Peter Kündig\*



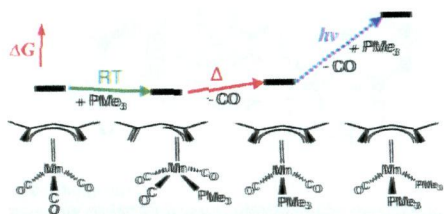
### Tungsten-Mediated Selective Ring Opening of Vinylocyclopropanes

Jared A. Pienkos, Anne T. Knisely, Benjamin K. Liebow, Victor Teran, Victor E. Zottig, Michal Sabat, William H. Myers, and W. Deam Hamman\*



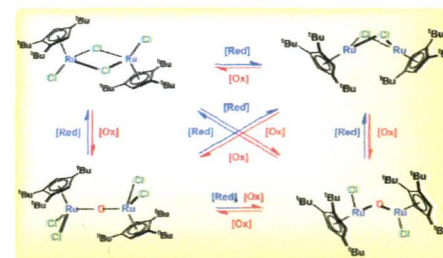
### Phosphine-Substituted ( $\eta^3$ -Pentadienyl) Manganese Carbonyl Complexes: Geometric Structures, Electronic Structures, and Energetic Properties of the Associative Substitution Mechanism, Including Isolation of the Slipped $\eta^3$ -Pentadienyl Associative Intermediate

José Ignacio de la Cruz Cruz, Patricia Juárez-Saavedra, Brenda Paz-Michel, Marco Antonio Leyva-Ramírez, Asha Rajapakshe, Aaron K. Vannucci, Dennis L. Lichtenberger,\* and M. Angeles Paz-Samckovall\*



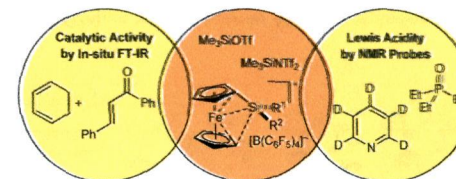
### Synthesis, Characterization, and Reactions of Ruthenium(II), -(III), and -(IV) Complexes with Sterically Demanding 1,2,4-Tri-*tert*-butylcyclopentadienyl Ligands

Ryuichi Shimogawa, Toshiro Takao, and Hiroharu Suzuki\*



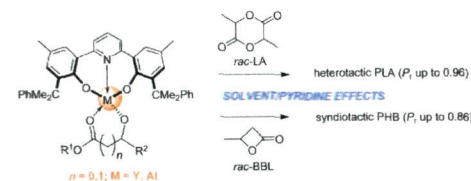
### Ferrocene-Stabilized Silicon Cations as Catalysts for Diels–Alder Reactions: Attempted Experimental Quantification of Lewis Acidity and ReactIR Kinetic Analysis

Alexander R. Nödling, Kristine Mütter, Volker H. G. Rohde, Gerhard Hilt,\* and Martin Oestreich\*



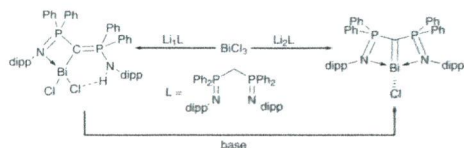
### Yttrium- and Aluminum-Bis(phenolate)pyridine Complexes: Catalysts and Model Compounds of the Intermediates for the Stereoselective Ring-Opening Polymerization of Racemic Lactide and $\beta$ -Butyrolactone

Joice S. Klitzke, Thierry Roisnel, Evgeny Kirillov,\* Osvaldo de L. Casagrande Jr.,\* and Jean-François Carpentier\*



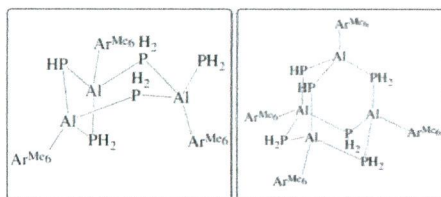
### Heavy Group 15 Element Compounds of a Sterically Demanding Bis(iminophosphorane)methanide and -methanediide

Christian P. Sindlinger, Andreas Stasch, and Lars Wesemann\*



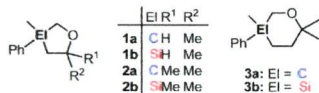
### Synthesis and Characterization of Primary Aluminum Parent Amides and Phosphides

Christopher E. Melton, Jonathan W. Dube, Paul J. Ragogna,\* James C. Fetting, and Philip P. Power\*



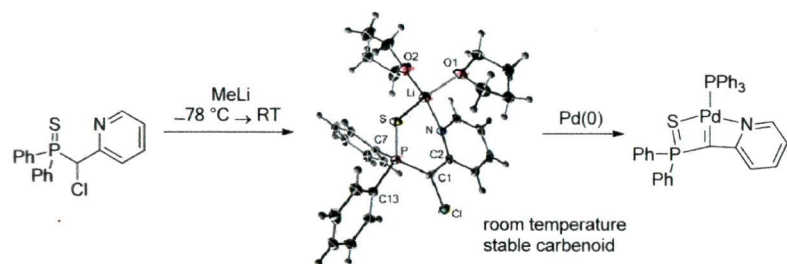
### Sila-rhubafuran and Derivatives: Synthesis and Olfactory Characterization of Novel Silicon-Containing Odorants

Bettina Förster, Rüdiger Bertermann, Philip Kraft, and Reinhold Tacke\*



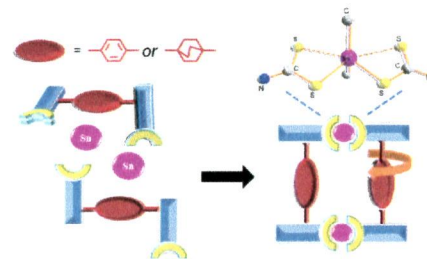
### Structure, Bonding, and Reactivity of Room-Temperature-Stable Lithium Chloride Carbenoids

Claudia Kupper, Sebastian Molitor, and Viktoria H. Gessner\*



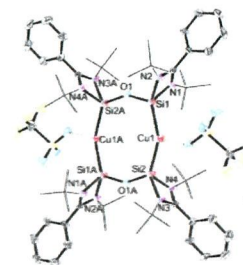
### Synthesis and Solid-State Characterization of Self-Assembled Macrocyclic Molecular Rotors of Bis(dithiocarbamate) Ligands with Diorganotin(IV)

Aarón Torres-Huerta, Braulio Rodríguez-Molina, Herbert Höpfl,\* and Miguel A. García-Garibay\*



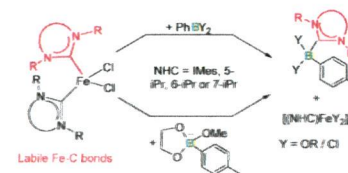
### Facile Access to Mono- and Dinuclear Heteroleptic N-Heterocyclic Silylene Copper Complexes

Gengwen Tan, Burgert Blom, Daniel Gallego, and Matthias Driess\*



### Reactivity of (NHC)<sub>2</sub>FeX<sub>2</sub> Complexes toward Arylborane Lewis Acids and Arylboronates

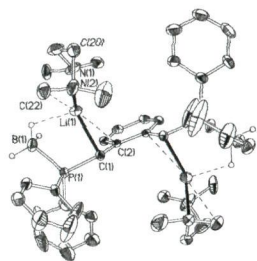
Jay J. Dunsford, Ian A. Cade, Kathlyn L. Fillman, Michael L. Neidig, and Michael J. Ingleson\*





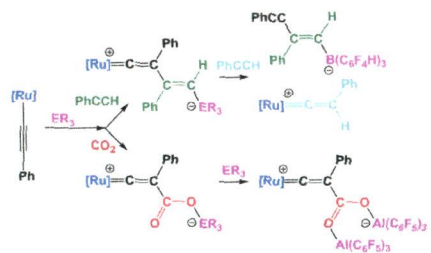
### Synthesis and Structural Characterization of Phosphine–Borane-Stabilized Dicarbanions with either Rigid or Flexible Spacers

Keith Izod,\* Casey M. Dixon, Emma McMeekin, Lee Rodgers, Ross W. Harrington, and Ulrich Baisch



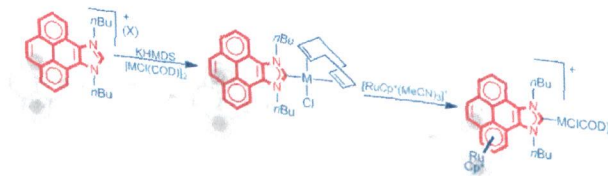
### Ancillary Metal Centers in Frustrated Lewis Pair Chemistry: Ruthenium Acetylide as a Lewis Base in the Activation of CO<sub>2</sub>, Aldehyde, and Alkyne

Michael P. Boone and Douglas W. Stephan\*



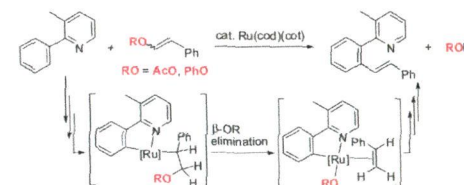
### A Pyrene-Based N-Heterocyclic Carbene: Study of Its Coordination Chemistry and Stereoelectronic Properties

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



### Ruthenium-Catalyzed Ortho-Selective C–H Alkenylation of Aromatic Compounds with Alkenyl Esters and Ethers

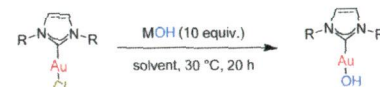
Yohei Ogiwara, Masaru Tamura, Takuya Kochi, Yusuke Matsuura, Naoto Chatani, and Fumitoshi Kakiuchi\*



## Notes

### New [Au(NHC)(OH)] Complexes for Silver-Free Protocols

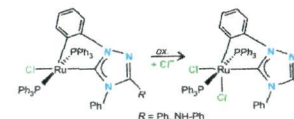
Scott R. Patrick, Adrián Gómez-Suárez, Alexandra M. Z. Sławin, and Steven P. Nolan\*



NHC = IPr, SiPr, IPr<sup>Cl</sup>, IPr<sup>Me</sup>, IPr<sup>+</sup>, IPr<sup>+</sup>TOI, IMes, SiMes, I<sup>t</sup>Bu, IAd, ICy, IDD  
M = K, Cs

### Reactions of [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] with Nitron and with the “Enders Carbene”: Access to Ruthenium(III) NHC Complexes

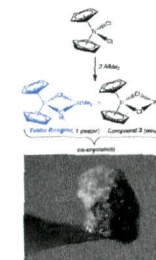
Sandra Hitzel, Christian Färber, Clemens Bruhn, and Ulrich Siemeling\*



R = Ph, NH-Ph

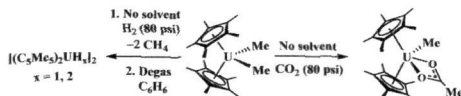
### Structural Elucidation of the Illustrious Tebbe Reagent

Rick Thompson, Eiko Nakamaru-Ogiso, Chun-Hsing Chen,\* Maren Pink,\* and Daniel J. Mindiola\*



Solvent-Free Organometallic Reactivity: Synthesis of Hydride and Carboxylate Complexes of Uranium and Yttrium from Gas/Solid Reactions

Christopher L. Webster, Joseph W. Ziller, and William J. Evans\*



## Additions and Corrections

Correction to Award-Winning Organometallic Chemistry:<sup>1</sup> The 2013 Yao Zeng Award in Organometallic Chemistry

John A. Gladysz