

# ORGANOMETALLICS

LB:  $e^-$

A<sup>-</sup> D:

4 <b>Be</b> Beryllium 9.01	5 <b>B</b> Boron 10.81	6 <b>C</b> Carbon 12.01	7 <b>N</b> Nitrogen 14.01	8 <b>O</b> Oxygen 16.00
12 <b>Mg</b> Magnesium 24.31	13 <b>Al</b> Aluminum 26.98	14 <b>Si</b> Silicon 28.09	15 <b>P</b> Phosphorus 30.97	16 <b>S</b> Sulfur 32.07
20 <b>Ca</b> Calcium 40.08	31 <b>Ga</b> Gallium 69.72	32 <b>Ge</b> Germanium 72.61	33 <b>As</b> Arsenic 74.92	34 <b>Se</b> Selenium 78.96
38	49 <b>In</b> Indium 114.82	50 <b>Sn</b> Tin 118.71	51 <b>Sb</b> Antimony 121.76	52 <b>Te</b> Tellurium 127.60

$E^{n+}$   $E^{n+}$

$M^{n+}$   $M^{n+}$   $M^{n+}$   $M^{n+}$

## APPLICATIONS OF ELECTROPHILIC MAIN GROUP ORGANOMETALLIC MOLECULES



**ON THE COVER:** An artistic rendition illustrating the affinity that electrophilic main group molecules display toward electron-rich species: Investigations into the fascinating chemistry of electron-deficient, Lewis acidic organo-main group compounds have gained renewed prominence in recent years as novel applications for this class of molecules have emerged. This special issue provides a current snapshot of the field, highlighting these exciting developments in a series of experimental and computational reports on the syntheses, structures, and properties of main group organometallics from groups 2, 13, 14, and 15. This collection also underscores the potential that these electrophilic main group species hold for applications in materials science, small molecule activation, and catalysis.

## SPECIAL ISSUE: APPLICATIONS OF ELECTROPHILIC MAIN GROUP ORGANOMETALLIC MOLECULES

### Editor's Page

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Introduction to the "Applications of Electrophilic Main Group Organometallic Molecules" Special Issue of *Organometallics*  
 François P. Gabbaï and Warren E. Piers\*

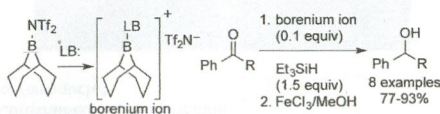
### Communications

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[dx.doi.org/10.1021/om400582k](http://dx.doi.org/10.1021/om400582k)

Lewis Base Activation of Lewis Acids: Group 13. In Situ Generation and Reaction of Borenium Ions

Scott E. Denmark\* and Yusuke Ueki

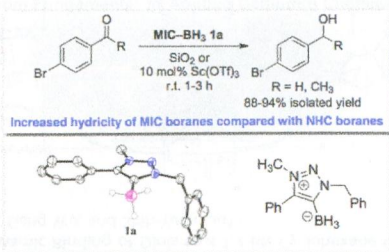


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[dx.doi.org/10.1021/om400743c](http://dx.doi.org/10.1021/om400743c)

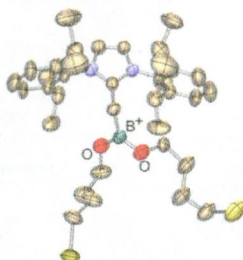
Mesoionic Carbene–Boranes

Luiza Baptista de Oliveira Freitas, Patrick Eisenberger, and Cathleen M. Crudden\*

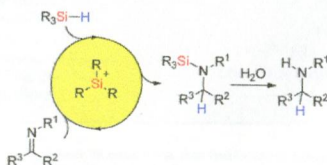


**N-Heterocyclic Olefin Stabilized Borenium Cations**

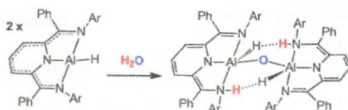
Yuzhong Wang, Mariham Y. Abraham, Robert J. Gilliard Jr., Daniel R. Sexton, Pingrong Wei, and Gregory H. Robinson\*

**Silylium Ion Promoted Reduction of Imines with Hydrosilanes**

Kristine Mütter, Jens Mohr, and Martin Oestreich\*

**Aluminum–Amido-Mediated Heterolytic Addition of Water Affords an Alumoxane**

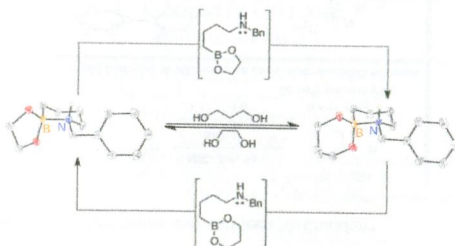

Thomas W. Myers and Louise A. Berben\*

*Heterolytic Addition of Water Affords Alumoxane*

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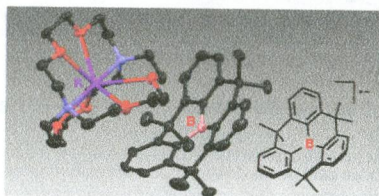
dx.doi.org/10.1021/om400697r

**Thermodynamically Controlled, Dynamic Binding of Diols to a 1,2-BN Cyclohexane Derivative**  
 Gregory P. Harlow, Lev N. Zakharov, Gang Wu, and Shih-Yuan Liu\*

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dx.doi.org/10.1021/om400560u

**A Radical Anion of Structurally Constrained Triphenylborane**  
 Tomokatsu Kushida and Shigehiro Yamaguchi\*



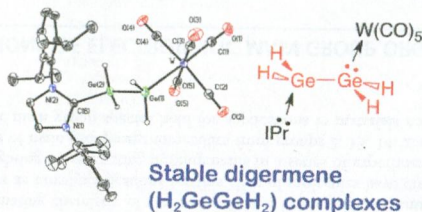
## Articles

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dx.doi.org/10.1021/om400361n

**Stable Complexes of Parent Digermene: An Inorganic Analogue of Ethylene**

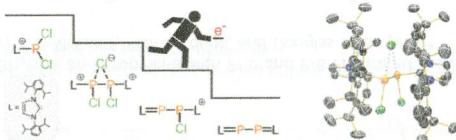
S. M. Ibrahim Al-Rafia, Mohammad R. Momeni, Michael J. Ferguson, Robert McDonald, Alex Brown,\* and Eric Rivard\*



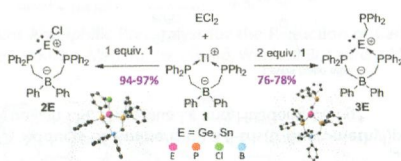
Reaction Pathways for Addition of H<sub>2</sub> to Amido-Diteterylnes R<sub>2</sub>N–EE–NR<sub>2</sub> (E = Si, Ge, Sn). A Theoretical Study  
Markus Hermann, Catharina Goedecke, Cameron Jones,\* and Gernot Frenking\*



Observation of a Chloride-Bridged P–P Bond in the Phosphorus Cation [L(Cl)P(μ-Cl)P(Cl)L]<sup>+</sup> (L = NHC)  
Florian D. Henne, Eva-Maria Schnöckelborg, Kai-Oliver Feldmann, Jörg Grunenberg, Robert Wolf,\* and Jan J. Weigand\*

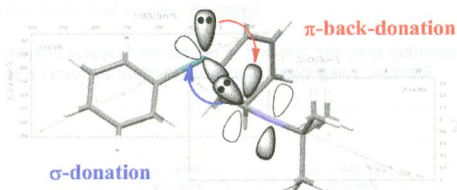


Synthesis of Zwitterionic Group 14 Centered Complexes: Traditional Coordination and Unusual Insertion Chemistry  
Sarah A. Weicker, Jonathan W. Dube, and Paul J. Ragogna\*



Computational Analysis of n→π\* Back-Bonding in Metallylene–Isocyanide Complexes R<sub>2</sub>MCNR' (M = Si, Ge, Sn; R = tBu, Ph; R' = Me, tBu, Ph)

Akseli Mansikkamäki, Philip P. Power,\* and Heikki M. Tuononen\*



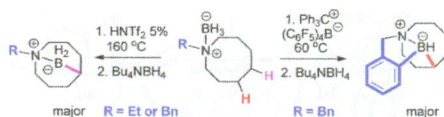
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## Electrophilic C–H Borylation and Related Reactions of B–H Boron Cations

Aleksandrs Prokofjevs, Janis Jermaks, Alina Borovika, Jeff W. Kampf, and Edwin Vedejš\*

dx.doi.org/10.1021/om400651p



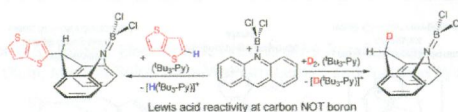
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[[acridine]BCl<sub>2</sub>]<sup>+</sup>: A Borenium Cation That Is a Strong Boron- and Carbon-Based Lewis Acid

Ewan R. Clark and Michael J. Ingleson\*

dx.doi.org/10.1021/om400463r



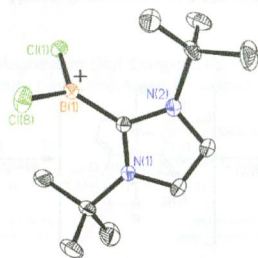
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## Counterion Dependence on the Synthetic Viability of NHC-stabilized Dichloroborenium Cations

Senthilkumar Muthaiah, Dinh Cao Huan Do, Rakesh Ganguly, and Dragoslav Vidović\*

dx.doi.org/10.1021/om400541q



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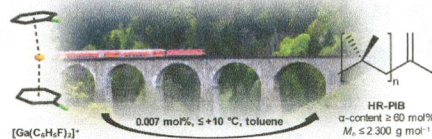
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## Univalent Gallium Salts of Weakly Coordinating Anions: Effective Initiators/Catalysts for the Synthesis of Highly Reactive Polyisobutylene

Martin R. Lichtenhaler, Alexander Higelin, Anne Kraft, Sarah Hughes, Alberto Steffani, Dietmar A. Plattner, John M. Slattery, and Ingo Krossing\*

dx.doi.org/10.1021/om400551e

## From Fundamental to Applied Gallium(I) Chemistry



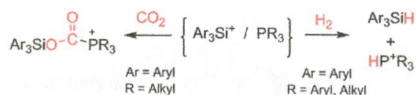
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dx.doi.org/10.1021/om400559x

## Silylium Ion/Phosphane Lewis Pairs

Matti Reißmann, André Schäfer, Sebastian Jung, and Thomas Müller\*



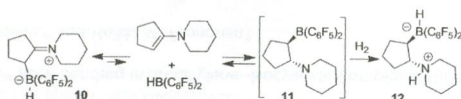
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dx.doi.org/10.1021/om4004225

An Enamine/HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> Adduct as a Dormant State in Frustrated Lewis Pair Chemistry

Bao-Hua Xu, Kathrin Bussmann, Roland Fröhlich, Constantin G. Daniliuc, Jan Gerit Brandenburg, Stefan Grimme, Gerald Kehr, and Gerhard Erker\*



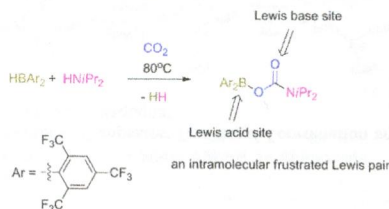
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dx.doi.org/10.1021/om4007246

Synthesis and Reactivity of the CO<sub>2</sub> Adducts of Amine/Bis(2,4,6-tris(trifluoromethyl)phenyl)borane Pairs

Zhenpin Lu, Yuwen Wang, Jia Liu, Yue-jian Lin, Zhen Hua Li, and Huadong Wang\*



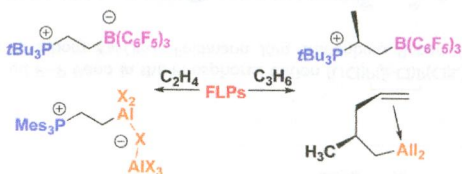
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dx.doi.org/10.1021/om400222w

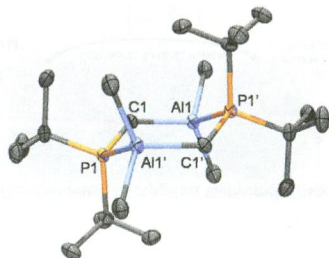
## Contrasting the Reactivity of Ethylene and Propylene with P/Al and P/B Frustrated Lewis Pairs

Gabriel Ménard, Lina Tran, Jenny S. J. McCahill, Alan J. Lough, and Douglas W. Stephan\*

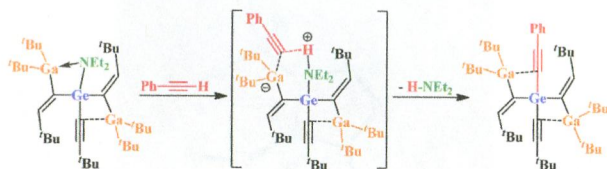


Reactivity of Dimeric P/Al-Based Lewis Pairs toward Carbon Dioxide and *tert*-Butyl Isocyanate

Federica Bertini, Frank Hoffmann, Christian Appelt, Werner Uhl,\* Andreas W. Ehlers, J. Chris Sloatweg, and Koop Lammertsma\*

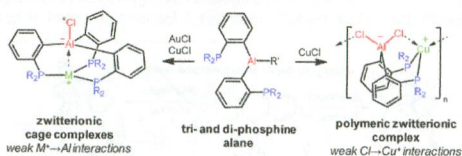
Cooperative Ge–N Bond Activation in Hydrogallation Products of Alkynyl(diethylamino)germanes  $(Et_2N)_nGe(C\equiv C^tBu)_{4-n}$ 

Werner Uhl,\* Jens Tannert, Marcus Layh, Alexander Hepp, Stefan Grimme, and Tobias Risthaus



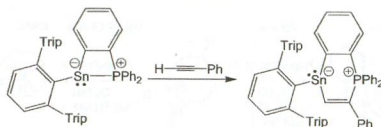
## Activation of M–Cl Bonds with Phosphine–Alanes: Preparation and Characterization of Zwitterionic Gold and Copper Complexes

Marie Sircoglou, Nathalie Saffon, Karinne Miqueu,\* Ghenwa Bouhadir,\* and Didier Bourissou\*



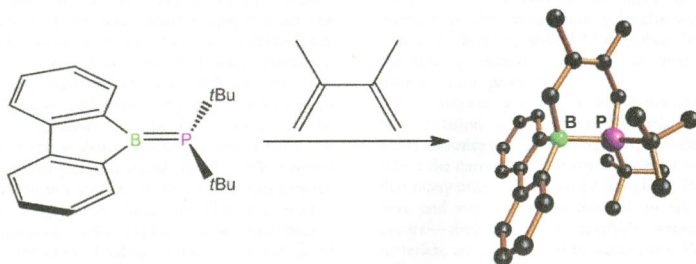
## Stannylene-Based Lewis Pairs

Sarah Freitag, Kilian M. Krebs, Jens Henning, Janina Hirdler, Hartmut Schubert, and Lars Wesemann\*



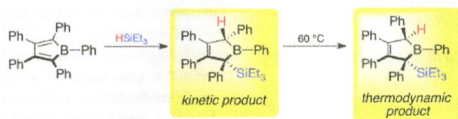


Reactivity of Phosphoradibenzofulvene toward Hydrogen, Acetonitrile, Benzophenone, and 2,3-Dimethylbutadiene  
 Jens Michael Breunig, Alexander Hübner, Michael Bolte, Matthias Wagner, and Hans-Wolfram Lerner\*



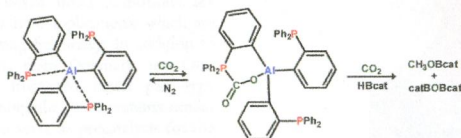
Si–H Bond Activation at the Boron Center of Pentaphenylborane

Holger Braunschweig,\* Alexander Damme, Christian Hörl, Thomas Kupfer, and Johannes Wahler



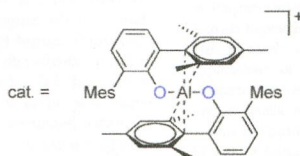
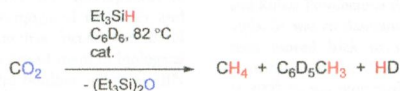
A Tris(triphenylphosphine)aluminum Ambiphilic Precatalyst for the Reduction of Carbon Dioxide with Catecholborane

Marc-André Courtemanche, Jérémie Larouche, Marc-André Légaré, Wenhua Bi, Laurent Maron, and Frédéric-Georges Fontaine\*



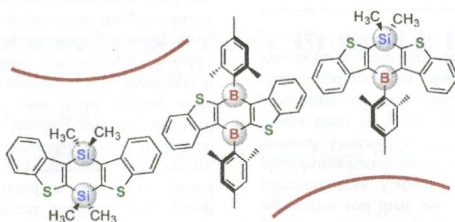
CO<sub>2</sub> Activation with Bulky Neutral and Cationic Phenoxyalanes

Rudolf J. Wehmschulte,\* Mahmoud Saleh, and Douglas R. Powell

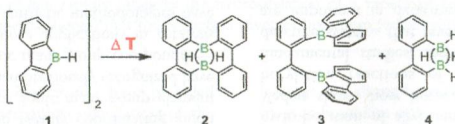


Benzo[*b*]thiophene-Fused Boron and Silicon Ladder Acenes

Lauren G. Mercier, Warren E. Piers,\* Ross W. Harrington, and William Clegg

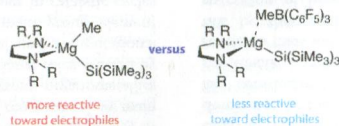
High-Temperature Reactivity of the Strongly Electrophilic Pristine 9*H*-9-Borafluorene

Alexander Hübner, Andreas M. Diehl, Michael Bolte, Hans-Wolfram Lerner, and Matthias Wagner\*



## Nucleophilicity of Neutral versus Cationic Magnesium Silyl Compounds

KaKing Yan, Brianna M. Upton, Jing Zhu, Arkady Ellern, and Aaron D. Sadow\*



## Potential Protecting Group Strategy for Disila Analogues of Vinylolithium: Synthesis and Reactivity of a 2,4,6-Trimethoxyphenyl-Substituted Disilene

Antje Meltzer, Mounita Majumdar, Andrew J. P. White, Volker Huch, and David Schesckewitz\*

