" Frustrated Lewis Pairs(FLP) "

Profile:

2005 Fellow of the Royal Society of Canada; 2005 LeSueur Memorial Award (Society for Chemical Industry); 2004 Ciapetta Lectureship Award (North American Catalysis Society); 2003 Synergy Award (with NOVA Chemicals from NSERC of Canada); 2003 University of Windsor Award for Scholarship, Research (Senior); 2003 Department Head, Chemistry and Biochemistry; 2002 University Professor; 2002 Alexander von Humboldt Senior Research Award; 2001-present NSERC/NOVA Chemicals Industrial Research Chair; 2000-present Director of Centre for Catalysis and Materials Research (CCMR); 2001 CIC Alcan Award; 1995 NSERC/DFG Visiting Professor; 1992 FCIC; 1992 Professor; 1985 Associate Professor; 1982 Assistant Professor; 1980-82 NATO PDF (Harvard); 1980 PhD (UWO); 1976-80 NSERC Scholar (UWO); 1976 BSc (McMaster)

Research

Their research interests span a wide range of inorganic main group and organometallic chemistry. In the more fundamental projects, new reactivity and chemical transformations are targeted with a view to developing new catalysts to either new materials or new processes.

Current fundamental projects are focused in the areas:
- Reactivity of hemilabile ligand complexes
- Catalytic P-H bond activation: new routes to polyphosphine materials and polymers
- Cyclometallation and hydrophosphination routes to P-based materials and polymers
- P-functionallized polyolefins
- High temperature olefin polymerization catalysis
- New approaches to olefin hydrogenation catalysts

Representative review:
Organometallics (2005), 24(11), 2548-2560.
Coordination Chemistry Reviews (2002), 233-234 107-129.

- **The reactivity of "sterically frustrated" Lewis acid-base pairs**

Today's Contents

Introduction

Cationic Methyl- and Chlorotitanium Phosphinimide Complexes

Lourdes Cabrera, Emily Hollink, Jeffrey C. Stewart, Pingrong Wei, and Douglas W. Stephan*

Ziegler–Natta Reaction
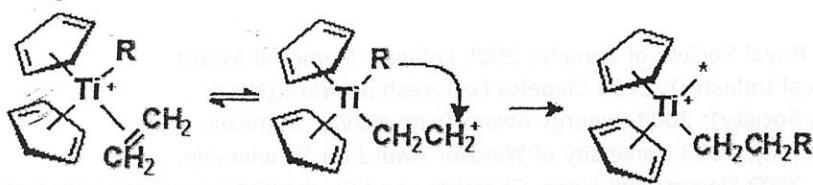
Scheme 1. Synthesis of Complexes 3–20

2→3: Analogous exchange processes have been observed in metallocene systems.

catalyst for polymerization

in the case of PH(2,4,6-MePh)$_2$, target complex was not obtained.

L = THF 4, Py 5, 4-EtPy 6,
4-t-BuPy 7, NC$_5$H$_4$NMe$_2$ 8,
PMe$_3$ 9, Pn-Bu$_3$ 10, PPh$_3$ 11,
P(p-MeC$_6$H$_4$)$_3$ 12

L = Py 13, 4-EtPy 14, 4-t-BuPy 15,
NC$_5$H$_4$NMe$_2$ 16, PMe$_3$ 17,
Pn-Bu$_3$ 18, PPh$_3$ 19,
P(p-MeC$_6$H$_4$)$_3$ 20

$$B(C_6F_5)_3 + \begin{array}{c} PPh_3 \\ NR_3 \end{array} \xrightarrow[\text{30-82\% yield}]{\text{rt., 30 h}} \begin{array}{c} [B(C_6F_5)_3][PPh_3] \\ [B(C_6F_5)_3][NR_3] \end{array}$$

J. Orgnomet. Chem. 1964, **2**, 245.

Arylboron Compounds as Acid Catalysts in Organic Synthetic Transformations

Kazuaki Ishihara[a] and Hisashi Yamamoto*[b]

$$R^1CHO \text{ or other electrophiles} + \begin{array}{c} OSiMe_3 \\ R^2 \diagdown R^4 \\ R^3 \end{array} \xrightarrow[\text{2) HCl or TBAF}]{\text{1) 1 (2-10 mol\%)}} \begin{array}{c} OH \quad O \\ R^1 \diagdown R^4 \\ R^2 R^3 \end{array} \quad \begin{array}{c} Ar \\ B \\ Ar \quad Ar \\ 1 (Ar=C_6F_5) \end{array}$$
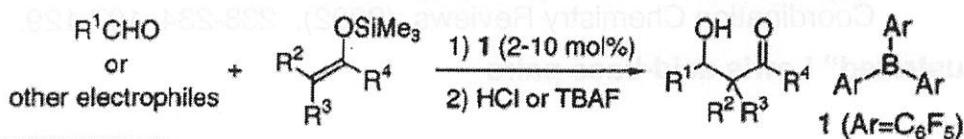
B(C$_6$F$_5$)$_3$-Catalyzed Hydrosilation of Imines via Silyliminium Intermediates

James M. Blackwell, Eric R. Sonmor, Tiziana Scoccitti, and Warren E. Piers*

13 examples

57-97% after purification
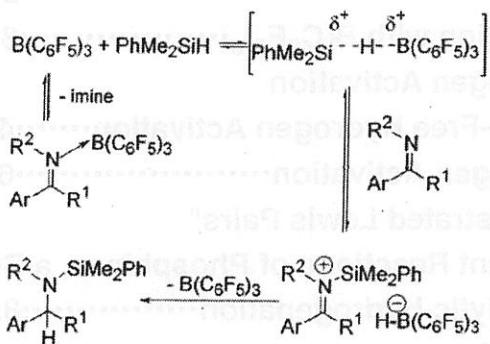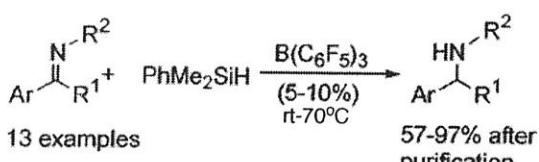
- The role of B(C$_6$F$_5$)$_3$ is to activate the Si reagent rather than imine substarate.
- The reaction proceeds via activation of the imine by "PhMe$_2$Si$^+$" and not by B(C$_6$F$_5$)$_3$

2) Lewis Base Reaction with B(C$_6$F$_5$)$_3$

Phosphonium–Borate Zwitterions, Anionic Phosphines, and Dianionic
Phosphonium–Dialkoxides via Tetrahydrofuran Ring-Opening Reactions

Gregory C. Welch, Jason D. Masuda, and Douglas W. Stephan*
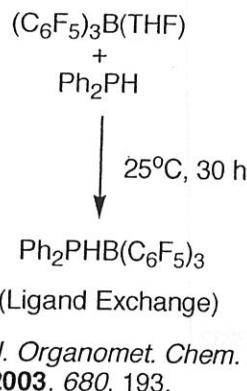
Scheme 1. Ring-Opening Reactions of THF with Sterically
Demanding Phosphines and Phosphides

(C$_6$F$_5$)$_3$B(THF)
+
Ph$_2$PH

↓ 25°C, 30 h

Ph$_2$PHB(C$_6$F$_5$)$_3$

(Ligand Exchange)

J. Organomet. Chem.
2003, *680*, 193.

R$_2$P$^-$Li$^+$

(C$_6$F$_5$)$_3$B(THF) → Mes$_2$P⟶⟶⟶O$^\ominus$–B(C$_6$F$_5$)$_3$

3 ⊕Li(THF)$_2$

R$_2$PH ↓

HR$_2$P$^\oplus$⟶⟶O$^\ominus$–B(C$_6$F$_5$)$_3$

R = Mes **1**, *t*-Bu **2**
1: 79% yield
2: 81% yield

0.5 (*t*-Bu$_2$P$^-$Li$^+$)   80% yield

t-Bu$_2$P$^\oplus$ ... O$^\ominus$ ⊕Li O$^\ominus$
(C$_6$F$_5$)$_3$B   B(C$_6$F$_5$)$_3$

5 89% yield
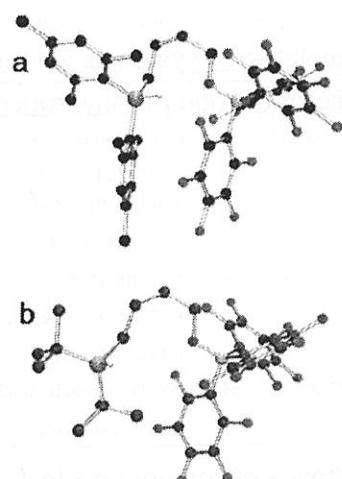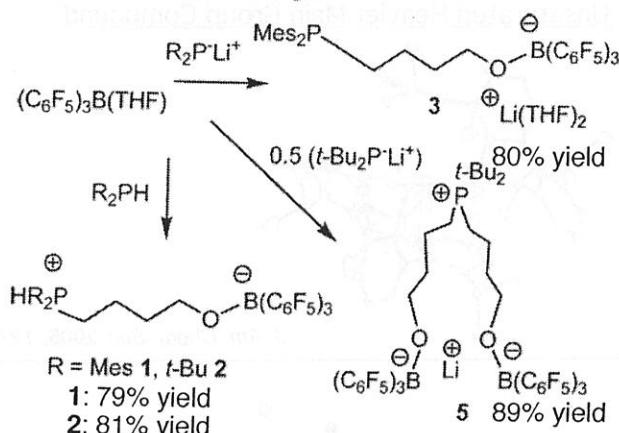
Figure 1. POV-ray depiction of (a) 1 and (b) 2. carbon, black; phosphorus,
orange; fluorine, pink; boron, yellow-green; oxygen, red; hydrogen, light
gray.

• Sterically demanding secondary phosphines and phosphides react with (THF)B(C$_6$F$_5$)$_3$ to give the THF ring–opened compounds.

• These reactions also occur consecutively to give the double THF ring–opened compounds [Mes$_2$P(C$_4$H$_8$OB(C$_6$F$_5$)$_3$)$_2$Li].

Pyridine and phosphine reactions with [CPh$_3$][B(C$_6$F$_5$)$_4$]

Lourdes Cabrera, Gregory C. Welch, Jason D. Masuda, Pingrong Wei, Douglas W. Stephan *

[RC$_5$H$_4$NCPh$_3$][B(C$_6$F$_5$)$_4$]

R = H **1**, *t*Bu **2**,
Et **3**, NMe$_2$ **4**

[CPh$_3$][B(C$_6$F$_5$)$_4$]

L

[R$_3$PCPh$_3$][B(C$_6$F$_5$)$_4$]

R = Me **5** *n*Bu **6**,
Ph **7** MeC$_6$H$_4$ **8**

[R$_3$P⟶⟶CHPh$_2$]

[B(C$_6$F$_5$)$_4$]

R = *i*Pr **9**

[R$_3$P(H)⟶⟶CPh$_2$]

[B(C$_6$F$_5$)$_4$]

R = Cy **10**, *t*Bu **11**
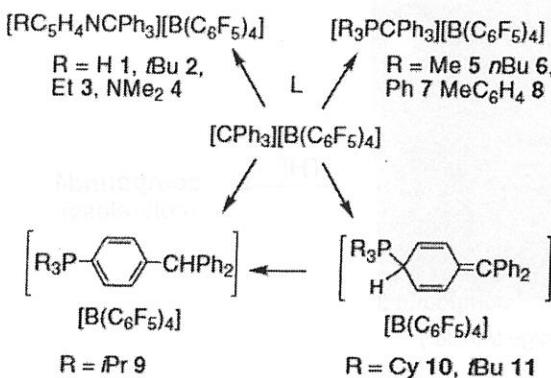
Scheme 1.
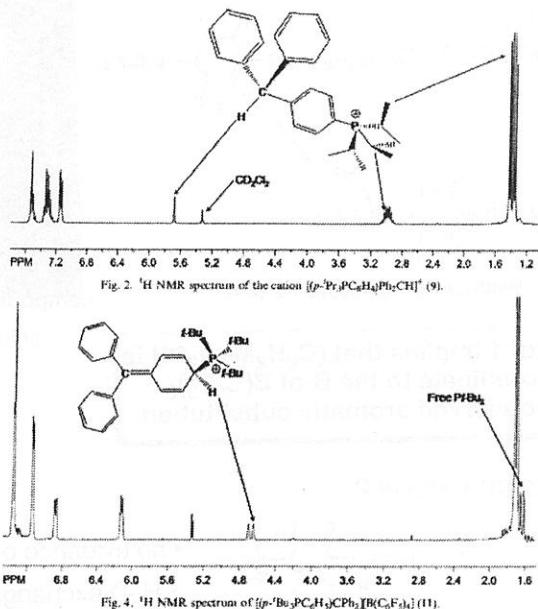
Fig. 2. ^{1}H NMR spectrum of the cation [(*p*-^{i}Pr$_3$PC$_6$H$_4$)Ph$_2$CH]$^+$ (9).
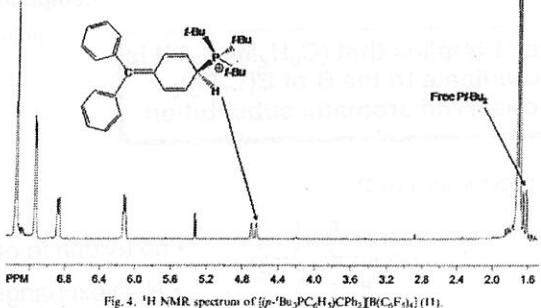

Fig. 4. ^{1}H NMR spectrum of [(*p*-^{t}Bu$_3$PC$_6$H$_4$)CPh$_2$][B(C$_6$F$_5$)$_4$] (11).

• Sterically demanding phosphines are too large to interact with the central carbon of the carbocation and instead effect nucleophilic aromatic substitution at a position *para* to the central trityl carbon involving the conversion of a cyclohexadienyl derivertive to the correspondeing benzylhydryl–phenyl species.

3) Metal–Free Hydrogen Activation

Reversible, Metal-Free Hydrogen Activation

Gregory C. Welch, Ronan R. San Juan, Jason D. Masuda, Douglas W. Stephan*

No metal –free system is yet reported to effect both the clean liberation and addition of H$_2$.

Facile Activation of Dihydrogen by an Unsaturated Heavier Main Group Compound

Ar′GeGeAr′ (**1**) + 1H$_2$ → 60% Ar′GeGeAr′ (**1**)　　　(1)

　　　　+ 21% Ar′HGeGeHAr′ (**2**)

　　　　+ 10% Ar′H$_2$GeGeH$_2$Ar′ (**3**)

　　　　+ 9% Ar′GeH$_3$ (**4**)

Ar′GeGeAr′ (**1**) + 2H$_2$ → 2% Ar′HGeGeHAr′ (**2**)　　　(2)

　　　　+ 85% Ar′H$_2$GeGeH$_2$Ar′ (**3**)

　　　　+ 13% Ar′GeH$_3$ (**4**)

Ar′GeGeAr′ (**1**) + 3H$_2$ → 65% Ar′H$_2$GeGeH$_2$Ar′ (**3**)　　　(3)

　　　　+ 35% Ar′GeH$_3$ (**4**)

Syntheses of compound 1 to 4

compound 2

F$_5$C$_6$-containing structures with (C$_6$H$_2$Me$_3$)$_2$PH

$\xrightarrow{\text{(C}_6\text{H}_2\text{Me}_3)_2\text{PH}}$

(C$_6$H$_2$Me$_3$)$_2$P⁺H···B(C$_6$F$_5$)$_2$ **1** 78% yield

$\xrightarrow{\text{Me}_2\text{SiHCl}}$

2 $\underset{\Delta}{\overset{\text{H}_2}{\rightleftharpoons}}$ **3**

$\xrightarrow{\text{THF}}$ **4**

$\xrightarrow{\text{THF}}$ **compound4** (colorless)

heat $\rightleftharpoons$ **H$_2$**

compound 2　　　compound 3
(internal charge transfer)
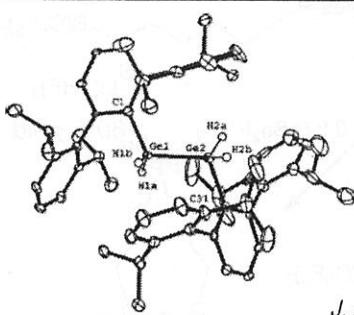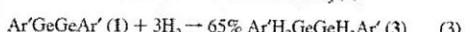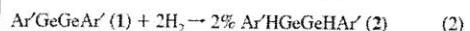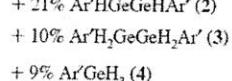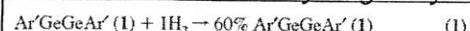
Fig. 1. Syntheses of compounds **1** to **4**.
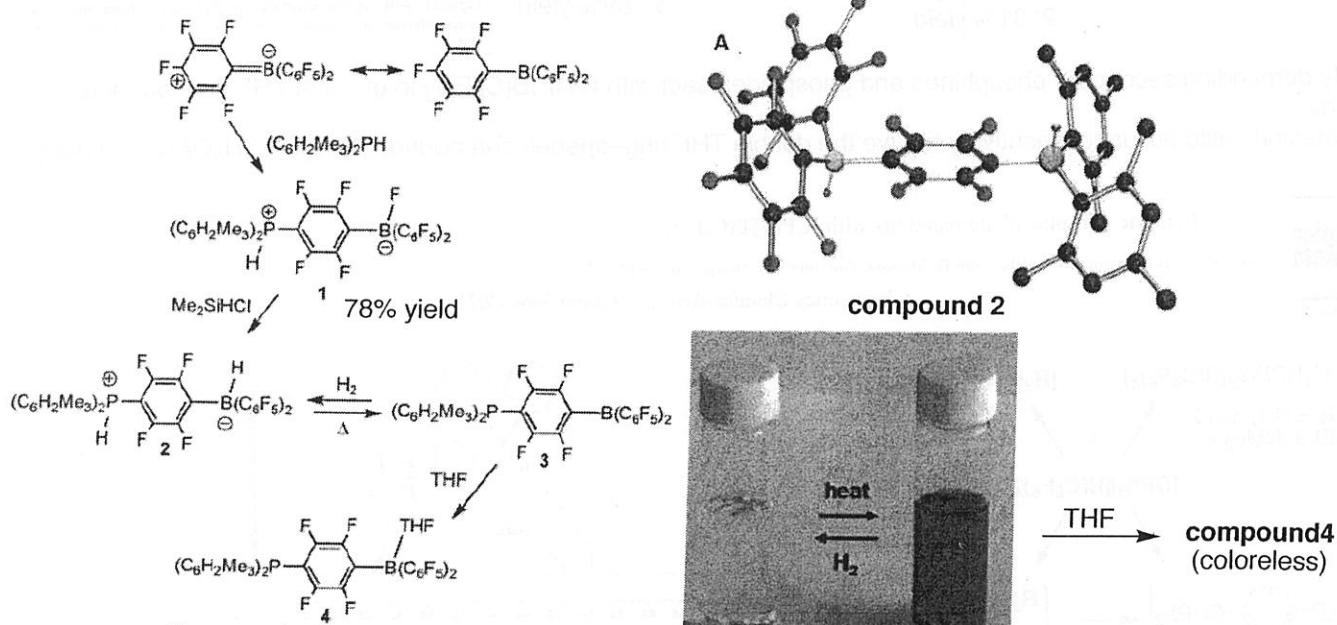
> The formation of **1** implies that (C$_6$H$_2$Me$_3$)$_2$PH is too large to cooordinate to the B of B(C$_6$F$_5$)$_3$, prompting the observed aromatic substitution.

Syntheses of the isotopomers of 2

1 $\xrightarrow{\text{Me}_2\text{SiDCl}}$ **2-d$_B$**

1-d$_P$ $\xrightarrow{\text{Me}_2\text{SiHCl}}$ **2-d$_P$**

3 $\xrightarrow{\text{D}_2}$ **2-d$_2$**
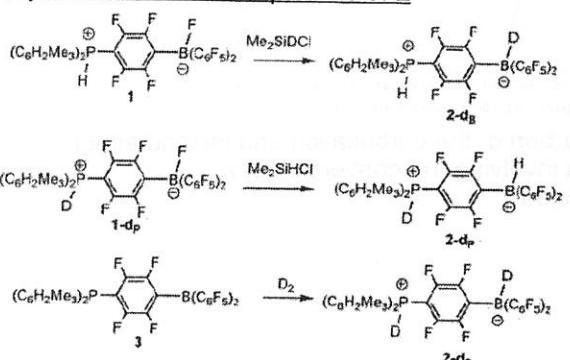
• no evidence of H–D exchange at 25°C

• H–D exchange at 100°C

2-d$_B$ + **2-d$_P$** $\xrightarrow{\Delta\,(>100°C)}$ **2-d$_B$, 2-d$_P$, 2, 2-d$_2$**

⇩
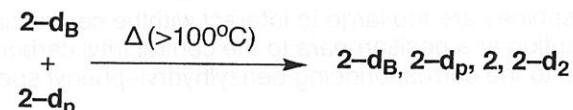
This scrambling of H and D labels suggests the possibility of a high-temperature exchange process.

Figure S2. Example of first order rate plots of the thermal loss of H$_2$ from (C$_6$H$_2$Me$_2$)$_2$PH-C$_6$F$_4$-BH(C$_6$F$_5$)$_2$ (2) at 140°C over 1 hour at varying concentrations.

Figure S3. Eyring plot of the thermal loss of H$_2$ from (C$_6$H$_2$Me$_2$)$_2$PH-C$_6$F$_4$-BH(C$_6$F$_5$)$_2$ (2) over the temperature range 100°C to 150°C. Enthalpy and entropy values extracted from the plot are $\Delta H^{\ddagger} = 90(1)$ kJmol^{-1} and $\Delta S^{\ddagger} = -96(1)$ Jmol^{-1}K^{-1} respectively.
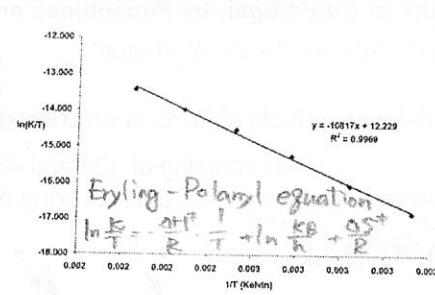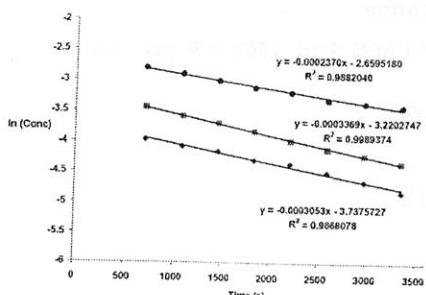
the entropy value, the first order kinetics

⇩

intramolecular process

the enthalpy value

⇩

subtantial bond breakage in the transition state

Eyring-Polanyi equation
$$\ln\frac{k}{T} = -\frac{\Delta H^{\ddagger}}{R}\cdot\frac{1}{T} + \ln\frac{k_B}{h} + \frac{\Delta S^{\ddagger}}{R}$$

Proposed mecanism

Proton Migration

Hydride Migration

1,2 H$_2$ elimination
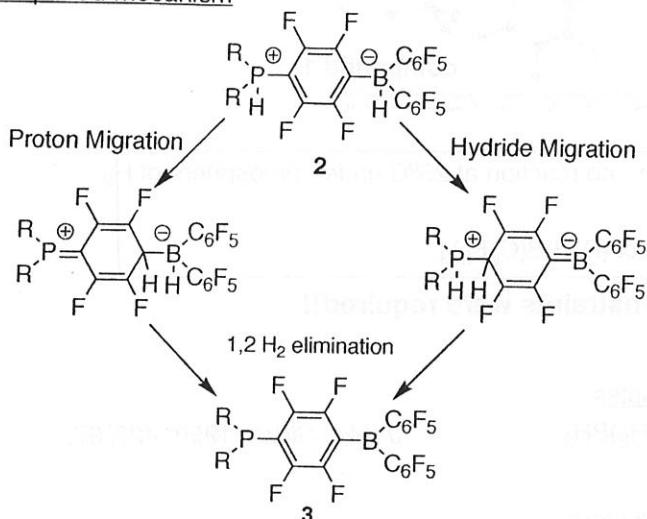
microscopically reverse reaction

4 did not react with H$_2$

⇩

The uptake of H$_2$ by **3** is intuitively thought to be initiated by the interaction of H$_2$ with B, that proton migration is more likely.

> **This reaction system demonstrates that reversible small–molecule activation is achievable in the absence of a transition metal.**

Tuning Lewis acidity using the reactivity of "frustrated Lewis pairs": facile formation of phosphine-boranes and cationic phosphonium-boranes†

Gregory C. Welch, Lourdes Cabrera, Preston A. Chase, Emily Hollink, Jason D. Masuda, Pingrong Wei and Douglas W. Stephan*

(R = R' = i-Pr 1, Cy 2,
R' = H, R = t-Bu 3, C$_6$H$_2$Me$_3$ 4)

(R = t-Bu 13, C$_6$H$_2$Me$_3$ 14)

(R = R' = i-Pr 5, Cy 6,
R' = H, R = t-Bu 7, C$_6$H$_2$Me$_3$ 8)

(R = R' = i-Pr 9, Cy 10,
R' = H, R = t-Bu 11, C$_6$H$_2$Me$_3$ 12)
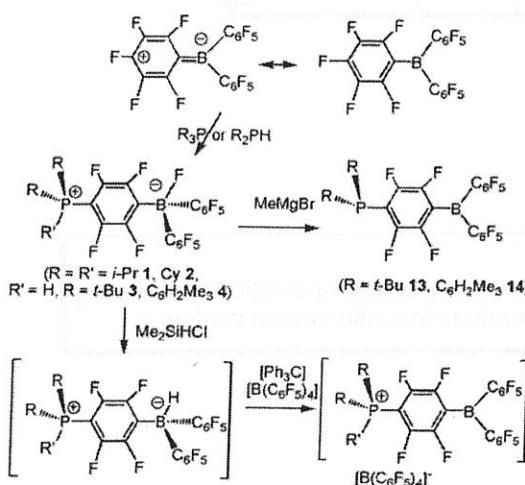
Scheme 2 Synthetic route to 1–14.
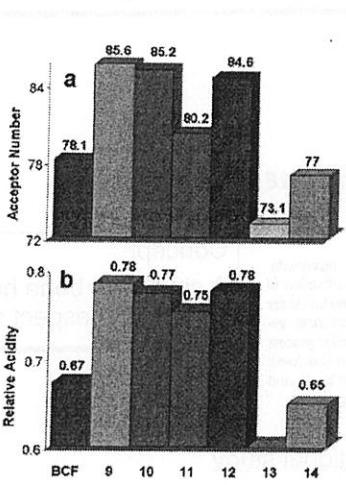
Fig. 4 (a) Plot of the Gutmann acceptor number and (b) relative acidity (to BBr$_3$) as determined by Childs method for BCF(B(C$_6$F$_5$)$_3$), cationic phosphonium boranes 9–12 and phosphine-boranes 13, 14 (NB: in (b) the relative acidity of 13 was not determined).^{77}
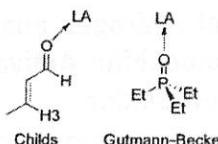
Scheme 3 Basis of Childs and Gutmann–Beckett Lewis acidity tests.

- All cationic complexes **9 –12** were found to be significantly stronger Lewis acids than B(C$_6$F$_5$)$_3$ by both methods.

- Donation of the P–based lone pair into the π–system diminshing the acidity of the B center.

no evidence of the formation of Lewis acid–base adducts at 25°C or on cooling to -50°C.

Scheme 1. Heterolytic Cleavage of H_2 by Phosphine and Borane
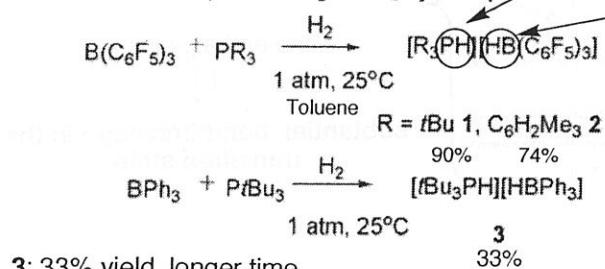
P–H coupling of 454 and 480 Hz

B–H coupling of 100 Hz

$$B(C_6F_5)_3 + PR_3 \xrightarrow[\text{1 atm, 25°C}]{H_2} [R_3PH][HB(C_6F_5)_3]$$

Toluene

R = tBu **1**, $C_6H_2Me_3$ **2**

90%   74%

$$BPh_3 + PtBu_3 \xrightarrow[\text{1 atm, 25°C}]{H_2} [tBu_3PH][HBPh_3]$$

3
33%

3: 33% yield, longer time becaudse of reduced Lewis acidity of B

F

B

P

compound 1
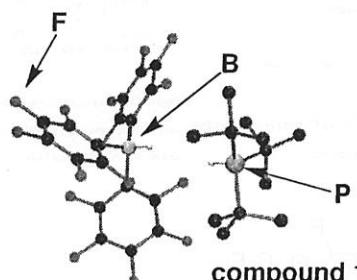
Figure 1. POV-ray drawing of 1 Hydrogen atoms except for BH and PH are omitted for clarity. C, black; P, orange; F, pink; B, yellow-green; H, gray

$(C_6H_2Me_3)_3P + BPh_3$, $(C_6F_5)_3P + B(C_6F_5)_3$, $tBu_3P + BMes_3$ → no reaction at 25°C under atmosphere of H_2

$Ph_3P + B(C_6F_5)_3$, $Me_3P + B(C_6F_5)_3$ → Lewis acid–base adduct $(R_3P)B(C_6F_5)_3$
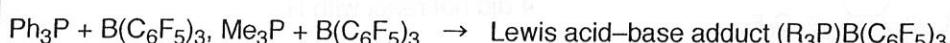
⟹ **Appropriate Lewis acidity/basisity and steric constraints were required!!**

Scheme 2. Possible Mechanisms for Heterolytic Cleavage of H_2 by Phosphine and Borane
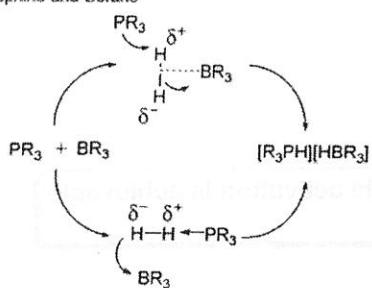
computational studies
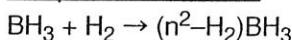
$$BH_3 + H_2 \rightarrow (\eta^2-H_2)BH_3 \qquad \textit{J. Mol. Struct.} \textbf{1999}, 492, 97.$$

Sweany and co-workers

interaction of Lewis bases with H_2

(H_2 interaction involving lone pair donation to the σ^* orbital of H_2)

J. Phys. Chem. Soc. **1990**, *94*, 1352.

Big difference between previous report(*Science*) and this paper:
Heating of 1 and 2 in toluene solutions to 150°C didi not result in the loss of H_2.

The way to split dihydrogen

H

M

H

hornolytic cleavage

$[M——H]^- + H^+$

heterolytic cleavage
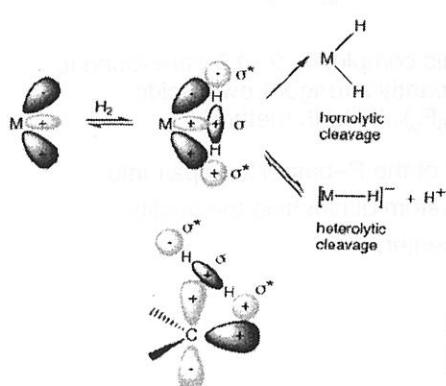
Fig. 1. Schematic representations of modes of activation of H_2 at a transition metal center (top) and a hypothetical extrapolation of a similar process at a carbene carbon (bottom); filled orbitals are in black, and vacant orbitals in gray.

Concept
A singlet carbene has a vacant orbital and afilles nonbonding and in that respect resembles transition metal centers.

computational study

The carbene acts as a base toward H_2.

⇩

Creating a hyderidelike hydrogen that attacks the positively polarlized carbon center.

The cyclicdi(amino)carbenes(NHCs) do not react with H_2
F. E. Hahn, *Angew. Chem. Int. Ed.* **45**, 1348

6/9

Table 1. Calculated energy of the HOMO (E_{HOMO}) and singlet-triplet energy gap [$-(E_S - E_T)$] for the model carbenes shown in Fig. 4, as well as energy changes (ΔE) and activation energies ($\Delta E^{\ddagger}$) for their reactions with H_2 and NH_3 calculated at the B3LYP/6-311 g** level of theory.

	1'	2'	2''	3'	4'	
E_{HOMO} (eV)	−5.0	−5.0	−4.9	−5.2	−5.1	→ slightly higher in energy(1', 2', 2'')
$-(E_S - E_T)$ (kJ/mol)	139.2	193.5	188.9	285.1	214.0	→ significantly smaller in energy(1', 2', 2'')
$\Delta E(H_2)$ (kJ/mol)	−211.8	−189.4	−180.0	−106.3	−121.0	
$\Delta E(H_2)^{\ddagger}$ (kJ/mol)	93.0	99.1	108.3	150.0	147.8	
$\Delta E(NH_3)$ (kJ/mol)	−161.9	−139.3		−70.8	−73.4	exothermic reaction
$\Delta E(NH_3)^{\ddagger}$ (kJ/mol)	87.4	94.5		141.3	137.5	

The Addition of H_2 to Compound 1, 2, 3, 4
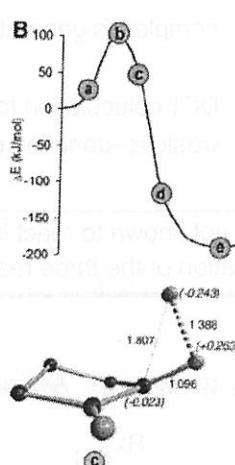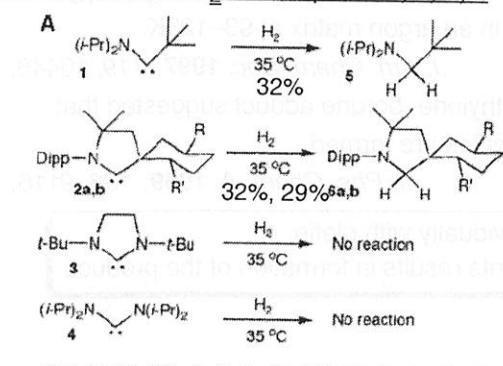
Fig. 2. (A) Under mild conditions, (alkyl)(amino)carbenes 1 and 2 activate H_2, whereas (diamino)carbenes 3 and 4 are inert. **(B)** Some structures along the reaction pathway of the insertion of carbene 2' into H_2, calculated at the B3LYP/6-311 g** level of theory. Bond distances (Å) and charges (in parentheses) are given in the structure drawings, and relative energies are shown in the reaction coordinate diagram.

The Addition of NH_3 to Compound 1, 2, 3, 4
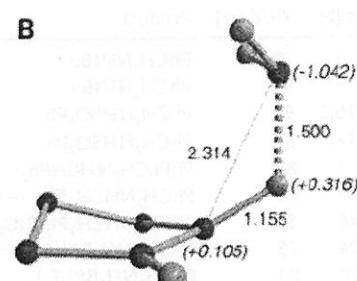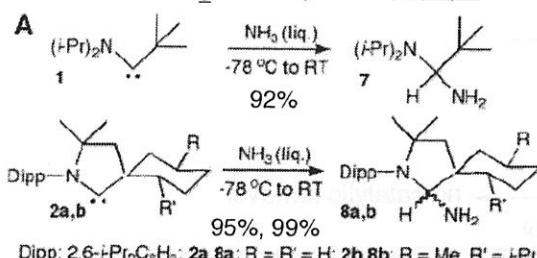
Fig. 3. (A) (Alkyl)(amino)carbenes 1 and 2 split ammonia at subzero temperatures. **(B)** Bond distances (Å) and charges (in parentheses) for the transition state of the reaction of NH_3 with carbene 2', calculated at the B3LYP/6-311 g** level of theory.

4) Reactivity of "Frustrated Lewis Pairs"

Reactivity of "Frustrated Lewis Pairs": Three-Component Reactions of Phosphines, a Borane, and Olefins**

*Jenny S. J. McCahill, Gregory C. Welch, and Douglas W. Stephan* *
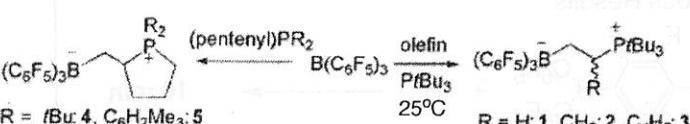
Scheme 1. Inter- and intramolecular addition of frustrated phosphine/borane pairs to olefins.

R = tBu: 4, $C_6H_2Me_3$: 5
94%   52%

R = H: 1, CH_3: 2, C_4H_7: 3
63%   63%   55%

$\delta = -13.3$ ppm

$(C_6F_5)_3\overset{\ominus}{B}$ $\overset{\oplus}{P}tBu_3$

$\delta = 50.1$ ppm

^1H NMR: $\delta = 1.69 - -1.94$ ppm

These data confirm thr presence of phosphonium and borate fragment linked by C_2H_4, thus affirming the formulation of 1 as [$^tBu_3P(C_2H_4)B(C_6H_5)_3$].

c.f.) *J. Chem. Soc. Chem. Commun.* **1990**, 1489.
J. Organomet. Chem. **1993**, 449, 27.

Compound 2, 3 H NMR, F NMR
⇓
having chiral center: inequivalent C_6H_5 group

$$B(C_6F_5)_3 \xrightarrow{\text{(pentenyl)}PR_2} (C_6F_5)_3B^{\ominus}\!-CH_2\!-\!\overset{HR_2}{\underset{\oplus}{P}}$$

Stoichiometric reactions with $B(C_6F_5)_3$ were monitored by ^{31}P NMR.

⇩
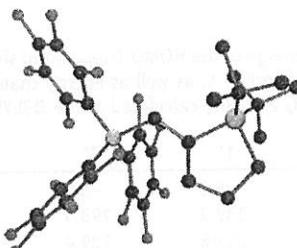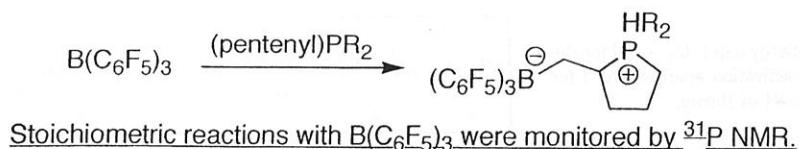
No evidence for the formation of phosphine–borane adducts

An X-ray crystallographic study of **4** confirmed the proposed connectivity

Figure 2. POV-ray drawing of 4. Hydrogen atoms are omitted for clarity. C: black, P: orange, F: pink, B: yellow-green.

Proposed Mechanism

addition of halogen to olefin
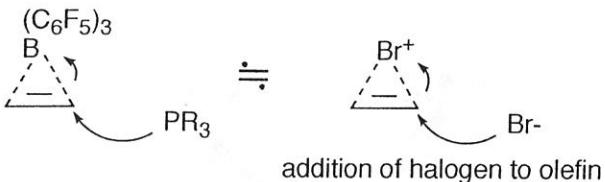
previous observation:

IR data for the van der Waals BF_3–ethylene and BF_3–propylene complexes generated in an argon matrix at 93–123K.

J. Am. Chem. Soc. **1997**, *119*, 10446.

DFT calculation for ethylene–borane adduct suggested that weak π–donation complex are formed.

J. Phs. Chem. A **1999**, *103*, 9116.

> These phosphines and boranes are not known to react individually with olefin.
> Any pair of these reagents do not react, but the combination of the three reagents results in formation of the product.

Metal-Free Catalytic Hydrogenation**

*Preston A. Chase, Gregory C. Welch, Titel Jurca, and Douglas W. Stephan** Angew. Chem. **2007**, 119, 8196–8199*
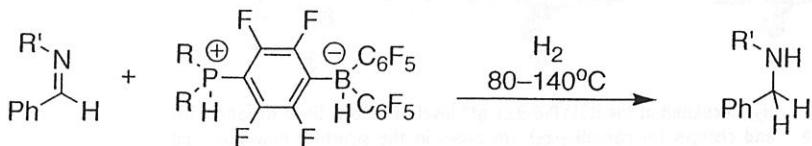
Table 1: Hydrogenations catalyzed by 1 or 2.[a]

| Entry	Substrate	Catalyst	T [°C]	t [h]	Yield [%]	Product	
1	Ph(H)C=NtBu	1[b]	80	1	79	PhCH₂NHtBu	
2	Ph(H)C=NtBu	2[b]	80	1	98	PhCH₂NHtBu	
3	Ph(H)C=NSO₂Ph	1	120	10.5	97	PhCH₂NHSO₂Ph	
4	Ph(H)C=NSO₂Ph	2	120	16	87	PhCH₂NHSO₂Ph	
5	Ph(H)C=NCHPh₂	1	140	1	88	PhPhCH₂NHCHPh₂	
6	Ph(H)C=NCH₂Ph	1	120	48	5[c]	PhCH₂NHCH₂Ph	→ no catalytic turnover
7	Ph(H)C=NCH₂Ph(B(C₆F₅)₃)	1	120	46	57	PhCH₂NHCH₂Ph(B(C₆F₅)₃)	
8	MeCNB(C₆F₅)₃	1	120	24	75	MeCH₂NH₂B(C₆F₅)₃	→ The corresponding imine can not be observed.
9	PhCNB(C₆F₅)₃	1	120	24	84	PhCH₂NH₂B(C₆F₅)₃	
10	(CH₂CH₂CNB(C₆F₅)₃)₂	1[d]	120	48	99	(CH₂CH₂CH₂NH₂B(C₆F₅)₃)₂	
11	PhCHCHPhNPh	1[d]	120	1.5	98	PhCH₂CHPhNHPh	

[a] Standard conditions: 5 mol % catalyst, 4 mL toluene, ca. 5 atm H_2. [b] 1 atm H_2. [c] Determined by ^1H NMR spectroscopy. [d] 10 mol % catalyst.

$Cy_3P(C_6H_4)BH(C_6F_5)_2$ + $^tBuN=CPh(H)$ $\xrightarrow{H_2,\ 120°C}$ **No Reaction (Catalysis is indeed initiated by imine protonation.)**

R = 2,4,6-Me₃C₆H₂ (1)
tBu (2)

R = tBu (5)

R' = CH₂Ph, strong adduct

R' = tBu, weak adduct

R = 2,4,6-Me₃C₆H₂ (3)
tBu (4)

Previous Results

$$R_2P(C_6F_4)B(C_6F_5)_2 + H_2 \longrightarrow \text{10 min}$$

$$PR_3/B(C_6F_5)_3 + H_2 \longrightarrow \text{12 – 24 h}$$
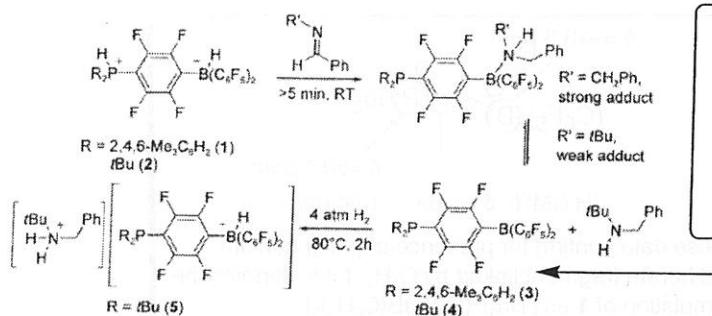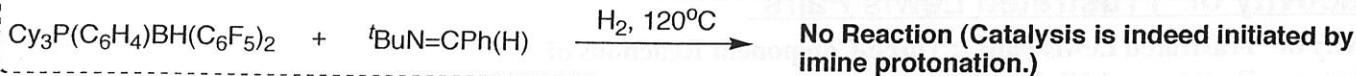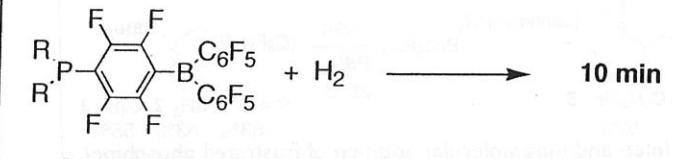
H_2 is cleaved by **4** initially.

Scheme 1. Stoichiometric reaction of imines with 1 or 2 with H_2 in toluene.

**5: 5** act as a living imine reduction catalyst.

Proposed Catalytic Cycle
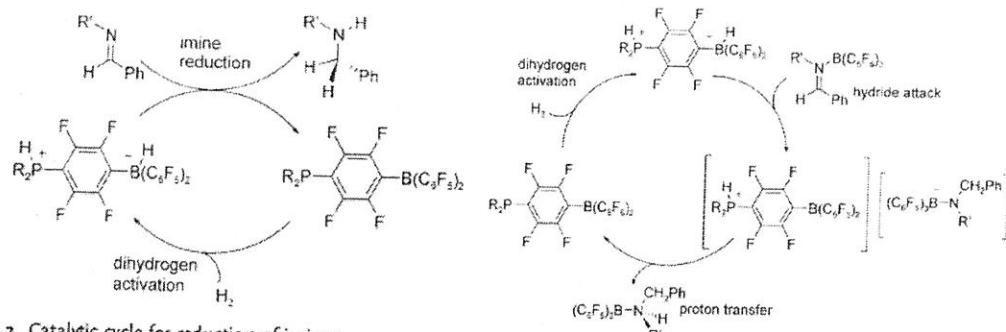
Scheme 2. Catalytic cycle for reduction of imines.

Scheme 3. Catalytic cycle for reduction of B(C₆F₅)₃-protected imines.

R = 2,4,6-Me₃C₆H₂ (1)   R = 2,4,6-Me₃C₆H₂ (6)
tBu (2)   tBu (7)
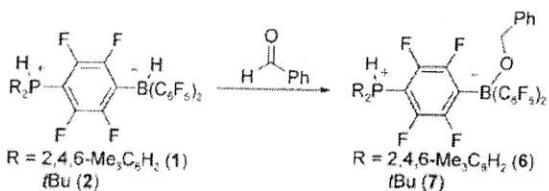
Scheme 4. Stoichiometric reactions of benzaldehyde with 1 or 2 in CH₂Cl₂.

Proton transfer from the phosphonium center to the O atom does not ocur.

⇩

Stoichiometric Reaction

Rapid intramolecular heterolytic dihydrogen activation by a four-membered heterocyclic phosphane–borane adduct†

Patrick Spies,[a] Gerhard Erker,*[a] Gerald Kehr,[a] Klaus Bergander,[a] Roland Fröhlich,‡[a] Stefan Grimme§[a] and Douglas W. Stephan[b]   *Chem. Commun.,* 2007, 5072–5074
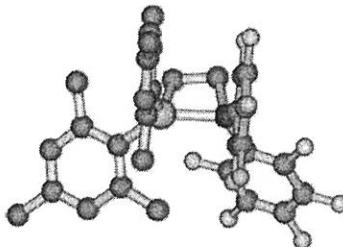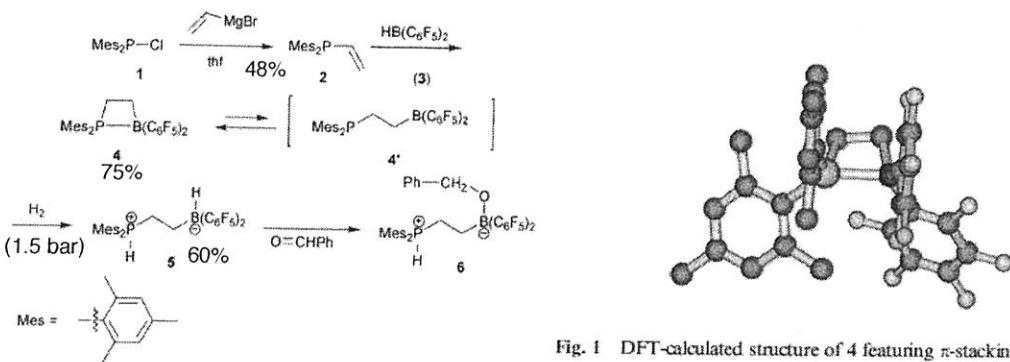

Fig. 1 DFT-calculated structure of 4 featuring π-stacking stabilization.

5) Outlook & Remark

1) Enantioselective Hydrogenation
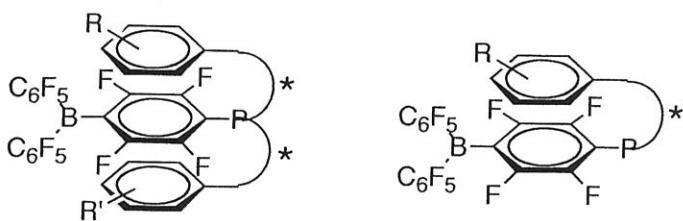
2) Ligand for transition metal
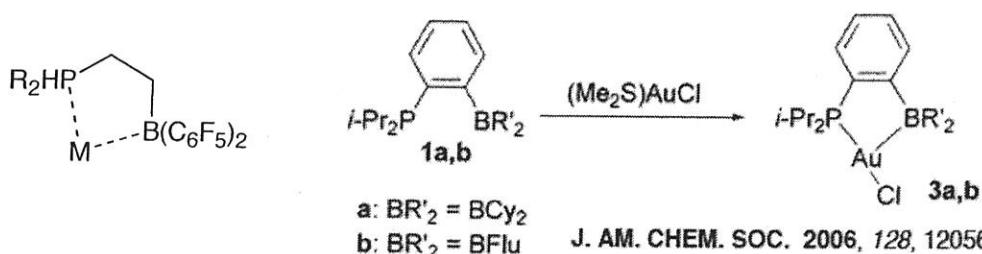
a: BR'₂ = BCy₂
b: BR'₂ = BFlu   **J. AM. CHEM. SOC.** 2006, *128*, 12056−12057