

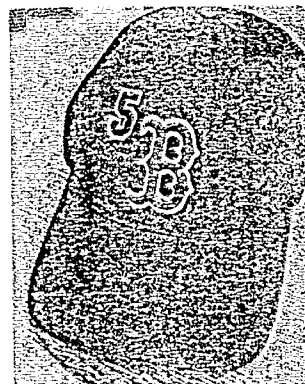
Literature Seminar (M2)

2005. 09. 14. D. Tomita

Regio- and stereoselective synthesis of boryl-substituted allylsilanes via transition metal-catalyzed silaboration



Michinori Suginome was born in 1966. He graduated from Kyoto University, where he received his Doctor Degree of Engineering under the supervision of Professor Y. Ito in 1993 with his thesis titled *Bis-Silylation of Unsaturated Compounds Catalyzed by Palladium-Isonitrile Complex*. Since 1993 he has worked as Assistant Professor of the Department of Synthetic Chemistry and Biological Chemistry, Kyoto University. Afterward, he carried out postdoctoral work in the United States with Professor Gregory C. Fu at Massachusetts Institute of Technology during 1998–1999. He has been the recipient of the Chemical Society of Japan Award for Young Chemists (1999). His research interests are currently in the catalytic, stereoselective synthesis of organic molecules, including organosilicon compounds and stereoregular macromolecules, by means of transition-metal catalysts.



Introduction

Transition metal-catalyzed additions of boron-containing α -bonds across carbon-carbon multiple bonds have gained increasing attention in organic chemistry.

The possibility of highly efficient and selective introduction of boron functionalities to organic molecules makes the α -bond addition reactions highly attractive for the synthesis of organoboron compounds not otherwise readily available.

Today's Contents

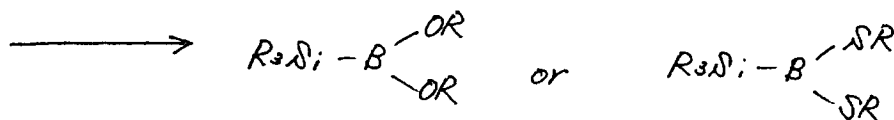
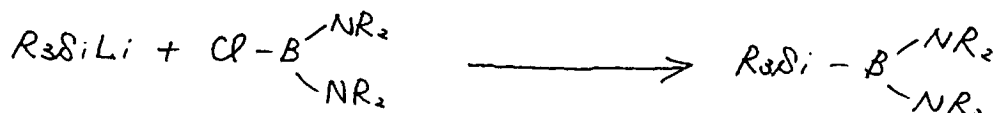
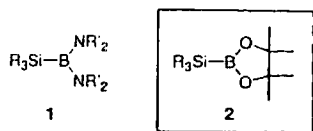
1. Convenient Preparation of Silyl boranes
2. Silicon-Boron Bonds
 - (A) Addition to Alkynes (including mechanism)
 - (B) Addition to Alkenes
 - (C) Addition to 1,3-Dienes
 - (D) Addition to Allenes
3. Palladium- and Nickel-Catalyzed Cyanoboration of Alkynes

Convenient Preparation of Silylboranes

Michinori Suginome,* Takanori Matsuda, and Yoshihiko Ito*

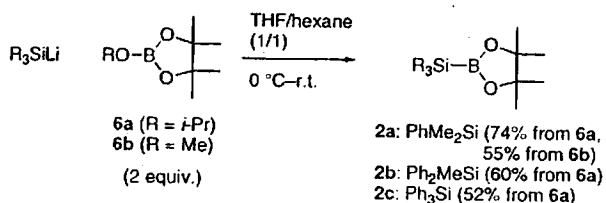
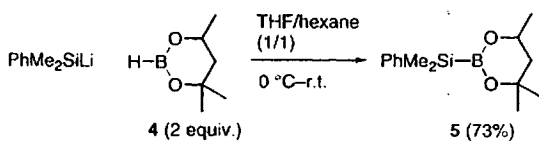
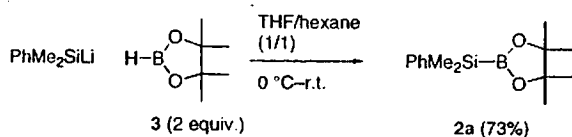
Organometallics 2000, 19, 4647-4649

+ JACS, 1960, 82, 501



The preparation of chlorobis(dialkylamino) boranes can be difficult, especially due to their high moisture sensitivity.

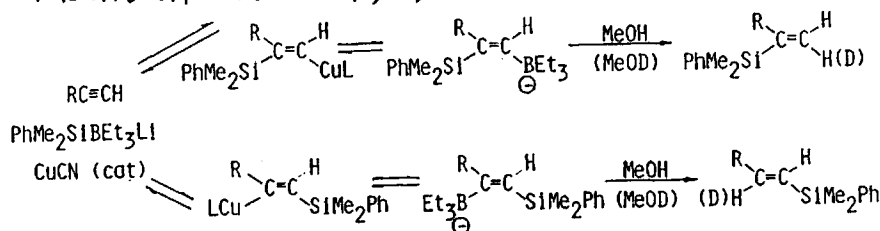
↓ ↓
New Method



In contrast with the silylborane synthesis with hydroboranes, the use of alkoxy-pinacolboranes was applicable to the synthesis of other silylborane derivatives.

Silicon - Boron Bonds

(A) Addition to Alkynes.



Nozaki, K.; Wakamatsu, K.; Nonaka, W.; Tückmantel, W.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* 1986, 27, 2007.

Regio- and stereo-selective silaboration of alkynes catalysed by palladium and platinum complexes

Michinori Suginome, Hiroshi Nakamura and Yoshihiko Ito* *Chem. Commun.*, 1996, 2777

The use of palladium(0)-tert-alkylisocyanide complex is crucial for promoting the bis-silylation reaction effectively.

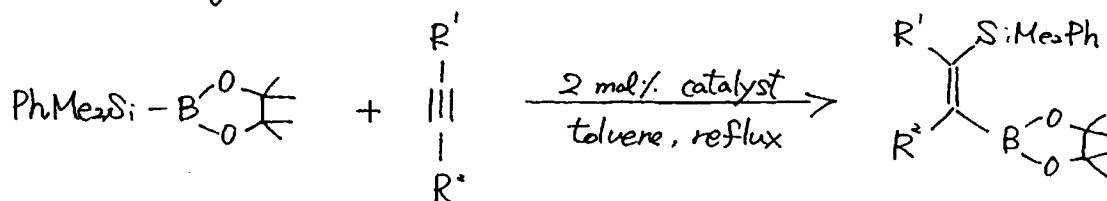


Table 1 Transition metal catalysed reactions of silylborane 2 with oct-1-yne ($\text{R}^1 = \text{C}_6\text{H}_{11}$, $\text{R}^2 = \text{H}$)^a

Entry	Catalyst (equiv.)	T/°C	t/h	Yield of 3a (%)	Regioselectivity ^b
1	Pd(OAc) ₂ (0.02) + Bu ^c CH ₂ CMe ₂ NC (0.3)	110	1	92	>99:1
2	Pd(OAc) ₂ (0.02) + Bu ^c CH ₂ CMe ₂ NC (0.3)	50	3	89	>99:1
3	Pd(PPh ₃) ₄ (0.02)	110	1	<20 ^c	>99:1
4	RhCl(PPh ₃) ₃ (0.02)	110	1	0	—
5	Pt(PPh ₃) ₄ (0.02)	110	1	80	90:10
6	Pt(PPh ₃) ₄ (0.02)	50	3	24	95:5 ^d

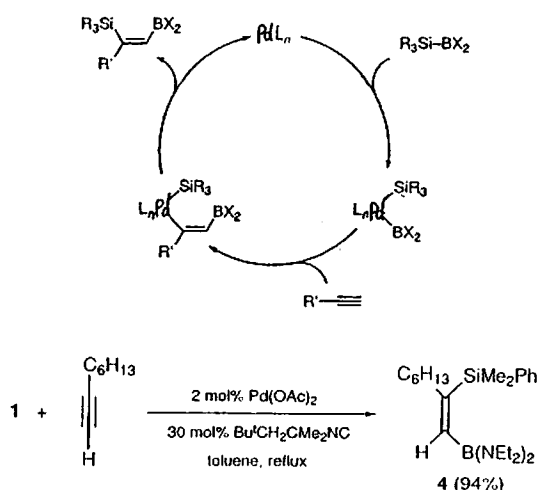
^a Silylborane 2 (1.0 equiv.), oct-1-yne (1.5 equiv.) and catalyst were heated with stirring in toluene under nitrogen. ^b Ratios of the regioisomers (1-boryl:2-boryl) determined by ¹H NMR. ^c Determined by ¹H NMR. ^d (Z)-1,2-Bis(dimethylphenylsilyl)oct-1-ene was also obtained (5%).

An NOE experiment revealed that the silyl and boryl groups had added to the carbon-carbon triple bond in a cis fashion.

Table 2 Silaboration of alkynes ($\text{R}^1\text{C}\equiv\text{CR}^2$) with 2 in the presence of the palladium(0)-isonitrile complex catalyst^a

Entry	R ¹	R ²	T/°C	t/h	Product	Yield (%) ^b
1	Ph	H	110	2	3b	82
2	THPO(CH ₂) ₂	H	110	2	3c	88
3	MEMO(CH ₂) ₃	H	110	2	3d	85
4	c-Hex-1-enyl	H	110	2	3e	82
5 ^c	Me ₃ Si	H	110	2	3f	73 ^d
6	Ph	Ph	110	4	3g	74
7	Bu	Bu	110	4	3h	24

^a Silylborane 2 (1.0 equiv.), alkynes (1.5 equiv.), Pd(OAc)₂ (0.02 equiv.) and 1,1,3,3-tetramethylbutyl isocyanide (0.30 equiv.) were heated with stirring in toluene under nitrogen unless otherwise noted. ^b Isolated yield. ^c 2.0 equiv. of alkyne were used. ^d A mixture of the regio-adducts was formed in a ratio of 94:6, with the terminal alkenylboron predominating.



Nickel-Catalyzed Silaborative Dimerization of Alkynes

Michinori Suginome, Takanori Matsuda, and Yoshihiko Ito*

Organometallics 1998, 17, 5233–5235

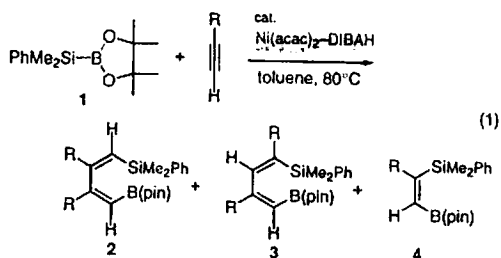
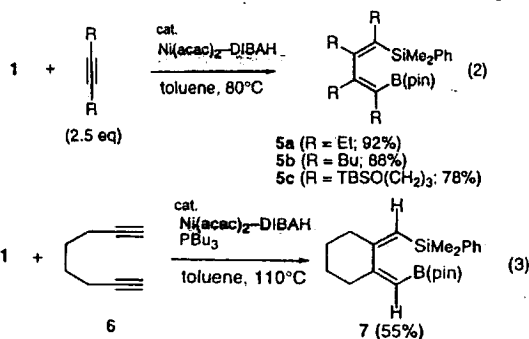
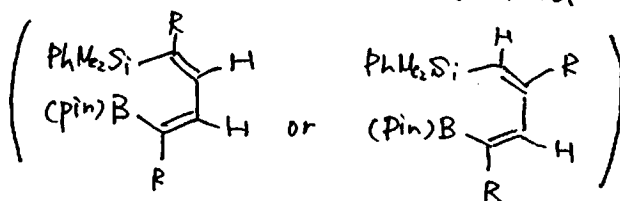


Table 1. Reactions of Silylborane 1 with Terminal Alkynes in the Presence of Nickel Catalysts^a

entry	alkyne R (equiv)	additive	selectivity ^{b,c} (2 + 3)/4	yield ^d % of 2 + 3	regio ^b 2/3
1	Bu (2.5)	none	94/6	50	76/24
2	Bu (4.0)	none	92/8	64	74/26
3	Bu (6.0)	none	96/4	78	75/25
4 ^e	Bu (4.0)	none	93/7	52	75/25
5	Bu (4.0)	PBu ₃	96/4	68	75/25
6	c-Pen (4.0)	none	87/13	39	59/41

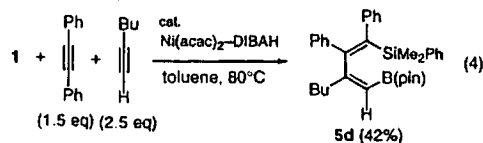
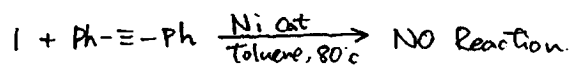
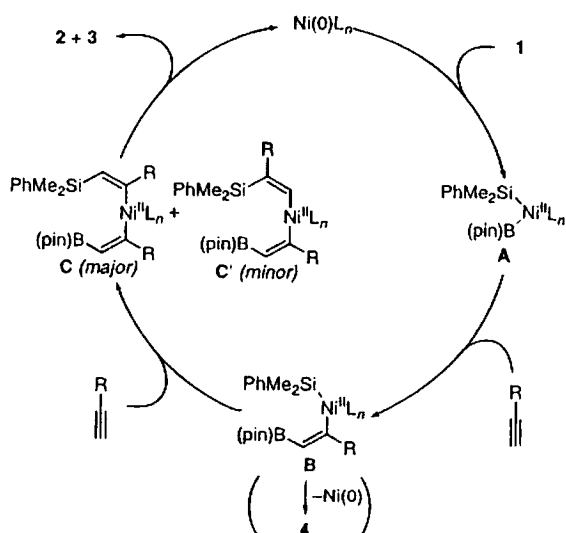
^a Ni(acac)₂ (5 mol %) and DIBAH (10 mol %) were used unless otherwise noted. ^b Determined by ¹H NMR of the reaction mixtures. ^c Isolated yields. ^d In all cases, the compounds 4 were obtained as single isomers. ^e Ni(acac)₂ (2 mol %) and DIBAH (4 mol %) were used.

No products derived from tail-to-tail or tail-to-head dimerization compound.



Internal alkynes also afforded the silaborative dimerization products in high yield.

Scheme 1. Possible Mechanism for Nickel-Catalyzed Silaborative Dimerization of Alkynes

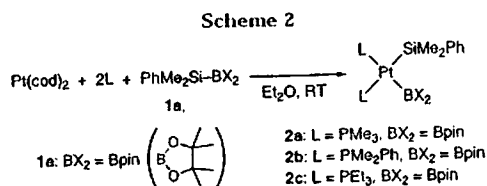
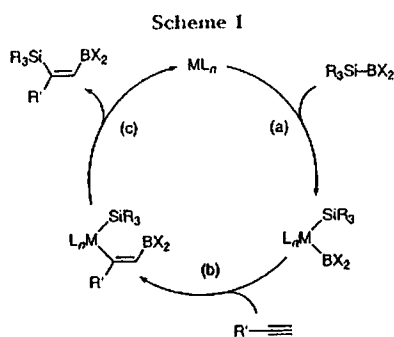


The insertion of alkyne into the Si-Ni bond of B may be much faster than the insertion into the B-Ni bond of A.

Synthesis and Reactions of *cis*-Silyl(boryl)platinum(II) Complexes

Takashi Sagawa, Yasuaki Asano, and Fumiyouki Ozawa*

Organometallics 2002, 21, 5879-5886



1a rapidly reacted with PMe_3 , PMe_2Ph and PEt_3 at room temp. to give 2a-2c.

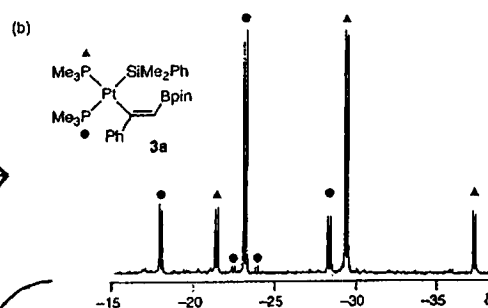
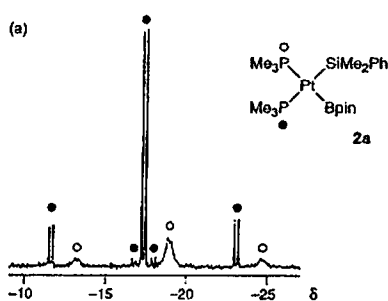


Table 1. ^{31}P (^1H) NMR Data for 2a-2d in CD_2Cl_2 at -50°C

complex	δ	assignment	$^1J_{\text{PtP}}$ (Hz)	$^2J_{\text{SiP}}$ (Hz)	$^2J_{\text{BP}}$ (Hz)
2a	-17.4 (d)	trans to Si	1374	148	29
	-19.0 (br)	trans to B	1375	0	
2b	-5.2 (br)	trans to B	1391	0	
	-6.4 (d)	trans to Si	1404	139	30
2c	+14.8 (br)	(overlap) ¹	1468	b	

almost same value

There is no broadening peak.

||
the selective insertion of phenylacetylene into the Pt-B bond.

サテライト [satellite] 【1】スペクトルや回折図形において主要なピークに伴ってその近傍に現れる随伴的な弱いピークをいう。たとえば、少量の同位体が原因でサテライトが現れる場合などがある。
 【2】衛星反射ともいう。X線や粒子線の回折でブラッグ(Bragg)反射の位置の付近に現れる反射。結晶の基本周期に対し、長周期の変調構造があるときに現れる。長周期変調構造には、合金などに見られる反位相ドメインの形成、磁性体その他の電荷分布の変調によるものなどがある。また中性子回折の場合には、らせん磁気構造などの磁気モメントについての変調構造によるサテライトが観測される。

化学辞典

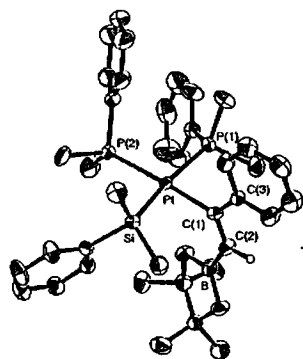
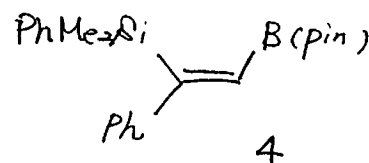


Figure 2. Molecular structure of 3b. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (deg): Pt-C(1) = 2.062(7), C(1)-C(2) = 1.366(9), C(1)-C(3) = 1.501(9), C(2)-B = 1.54(1), Pt-Si = 2.371(2), Pt-P(1) = 2.383(2), Pt-P(2) = 2.299(2), Pt-C(1)-C(2) = 122.0(5), Pt-C(1)-C(3) = 118.8(4), C(2)-C(1)-C(3) = 119.2(6), C(1)-C(2)-B = 129.7(6), Si-Pt-C(1) = 83.9(2), P(1)-Pt-C(1) = 87.5(2), P(1)-Pt-P(2) = 95.90(6), P(2)-Pt-Si = 92.79(6).

$\text{Pt-P}(1) = 2.383(2)\text{Å} > \text{Pt-P}(2) = 2.299(2)\text{Å}$
 : reflecting the greater trans influence of the silyl ligand than the alkenyl ligand.

60°C



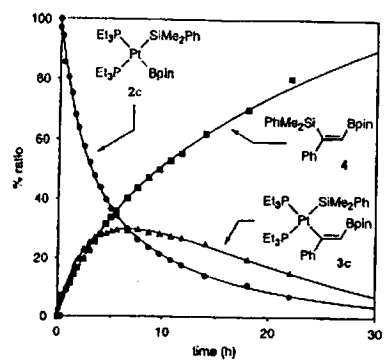
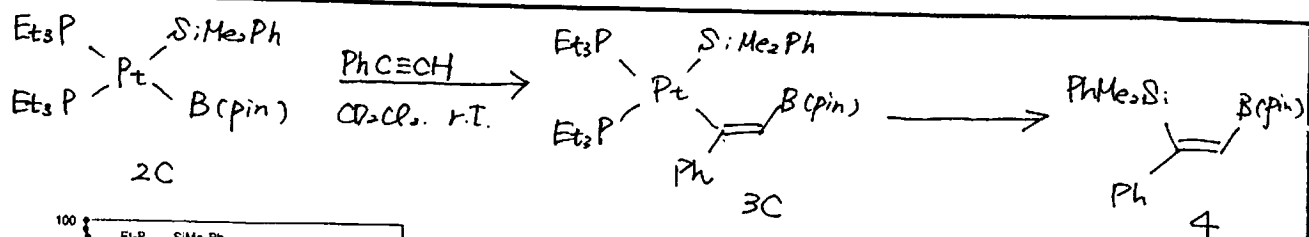


Figure 3. Time course of the reaction of 2c with phenylacetylene (10 molar quantity) at 20 °C in CD₂Cl₂. The amount of each component at time t was determined by ¹H NMR spectroscopy.

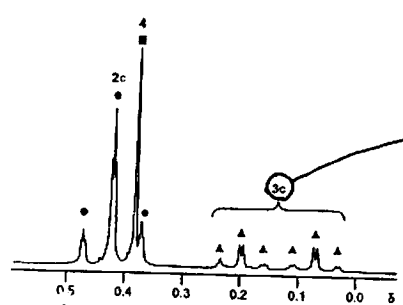


Figure 4. ¹H NMR spectrum of the reaction solution of 2c and phenylacetylene (10 molar quantity) in CD₂Cl₂ at 20 °C. The solution consists of a 44:28:28 ratio of 2c, 3c, and 4. Only the SiMe proton region is shown for clarity.

Kinetic Study on the Insertion of Phenylacetylene

Table 2. Pseudo-First-Order Rate Constants for the Insertion of Phenylacetylene into 2a*

run	[PhC≡CH] (M)	10 ³ [PMe ₃] (M)	10 ⁴ k _{obsd} (s ⁻¹)
1	0.15	4.0	2.38(5)
2	0.25	4.0	3.8(1)
3	0.40	4.0	5.4(1)
4	0.60	4.0	6.5(3)
5	0.25	6.3	2.6(1)
6	0.25	11	1.49(3)
7	0.25	16	1.09(3)
8	0.25	25	0.71(4)

* In CD₂Cl₂ at 20 °C. [2a]₀ = 0.025 M.

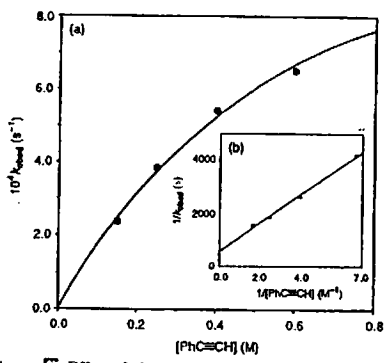


Figure 5. Effect of phenylacetylene concentration on the insertion rate of phenylacetylene into 2a in CD₂Cl₂ in the presence of added PMe₃ at 20 °C. Initial concentration: [2a] = 25 mM, [PMe₃] = 4.0 mM.

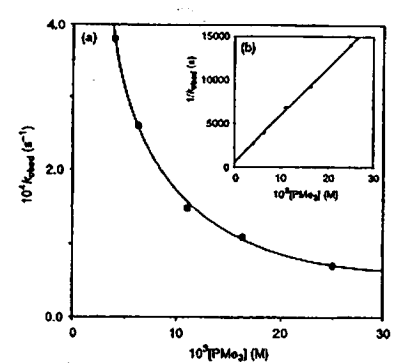
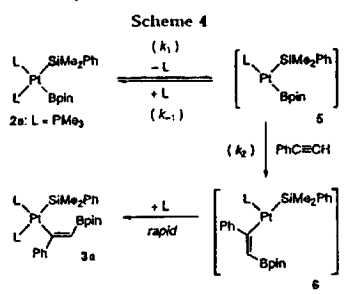


Figure 6. Effect of added PMe₃ on the insertion rate of phenylacetylene into 2a in CD₂Cl₂ at 20 °C. Initial concentration: [2a] = 25 mM, [PhC≡CH] = 0.25 M.

their proposed mechanism



Steady-state approximation for the concentration 5:

$$\begin{aligned}
 \frac{d[5]}{dt} &= k_1[2a] - k_{-1}[PMe_3][5] - k_2[PhC\equiv CH][5] = 0 & (1) \\
 [5] &= \frac{k_1[2a]}{k_{-1}[PMe_3] + k_2[PhC\equiv CH]} & (2) \\
 \frac{d[3a]}{dt} &= -\frac{d[2a]}{dt} = k_2[PhC\equiv CH][5] & (3) \\
 \frac{d[2a]}{dt} &= \frac{k_1 k_2 [PhC\equiv CH]}{k_{-1}[PMe_3] + k_2[PhC\equiv CH]} [2a] & (4) \\
 \frac{1}{k_{obsd}} &= \frac{k_{-1}[PMe_3]}{k_1 k_2 [PhC\equiv CH]} + \frac{1}{k_1} & (5)
 \end{aligned}$$

Figure 5:

$$k_1 = 3.27 \times 10^{-3} \text{ (s}^{-1}\text{)}$$

$$k_1/k_2 k_2 = 1.03 \times 10^5 \text{ (s)}$$

Figure 6:

$$k_1 = 2.71 \times 10^{-3} \text{ (s}^{-1}\text{)}$$

$$k_1/k_2 k_2 = 1.43 \times 10^5 \text{ (s)}$$

Sakai, D.; Sugimoto, M. *J. Organomet. Chem.* 2000, 611, 288

Pt-E	Bond Energy (kcal/mol)	C-E	Bond Energy (kcal/mol)
Pt-B(OH) ₂	64.4	C-B(OH) ₂	109.7
Pt-SiH ₃	54.2	C-SiH ₃	86.0
Pt-SnH ₃	46.3	C-SnH ₃	73.6

late transition model

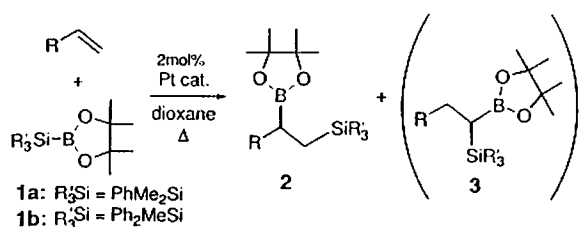
(B) Addition to alkene

Platinum-Catalyzed Regioselective Silaboration of Alkenes**

Michinori Suginome, Hiroshi Nakamura, and Yoshihiko Ito*

Angew. Chem. Int. Ed. Engl. 1997, 36, 2516

Bis-metallation of alkenes with heterometallic compounds has not been reported.



Scheme 1. Platinum-catalyzed silaboration of alkenes.

This result is interesting because silaboration of terminal alkenes proceeds with opposite regiochemistry.

Table 1. Platinum-catalyzed silaboration of 1-octene [a].

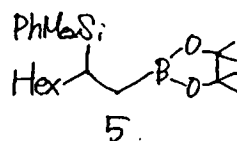
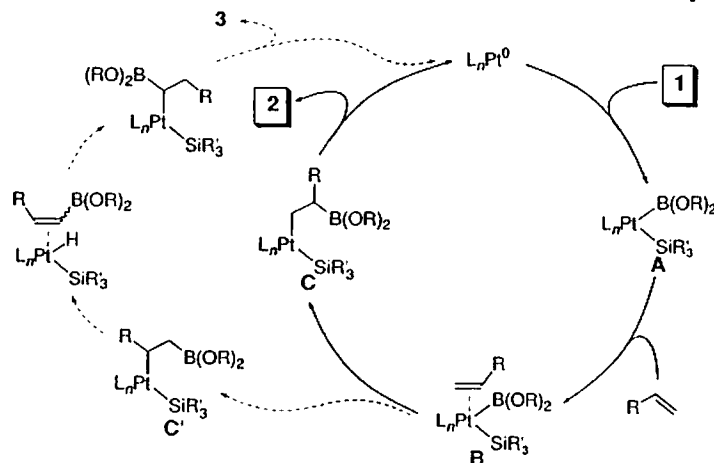
Entry	1	Catalyst	Product	Yield [%]	Ratio 2:3
1	a	$[Pt(PPh_3)_4]$	2a	45	85:15
2	a	$[Pt(CH_2=CH_2)(PPh_3)_2]$	2a	53	87:13
3	b	$[Pt(CH_2=CH_2)(PPh_3)_2]$	2a'	65	93:7
4	a	$[Pt(PMePh_2)_4]$	2a	7	74:26

[a] Silylborane (1 equiv), 1-octene (1.5 equiv), and catalyst (0.02 equiv) were heated at reflux in dioxane for 2 h.

Table 2. Platinum-catalyzed silaboration of alkenes with 1a [a].

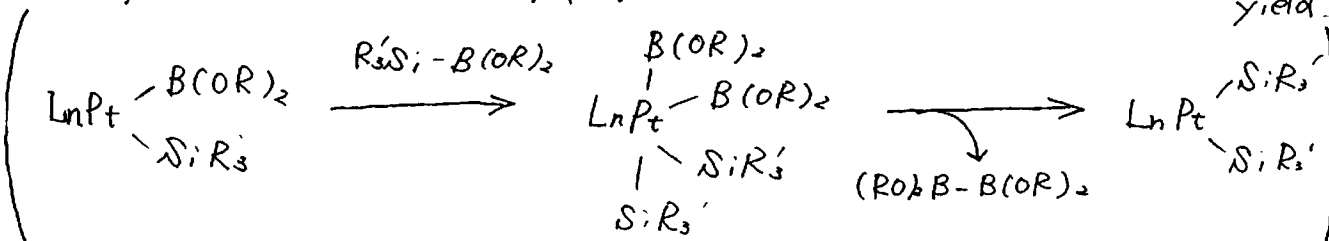
Entry	R	Product	Yield [%]	Ratio 2:3
1	$AcOCH_2CH_2$	2b	46	84:16
2	$CH_3COCH_2CH_2$	2c	46	85:15
3	Ph	2d	51	>99:1
4	4-MeOC ₆ H ₄	2e	53	>99:1
5	4-CF ₃ C ₆ H ₄	2f	46	>99:1
6[b]	H	2g	73[c]	>99:1
7[b,d]	H	2g	74	>99:1

[a] Borane 1a (1 equiv), alkene (1.5 equiv), and $[Pt(CH_2=CH_2)(PPh_3)_2]$ (0.02 equiv) were heated to reflux in dioxane for 2 h, unless otherwise noted. [b] Reaction under an ethylene pressure of 60 atm in toluene. [c] 1,2-Bis(dimethylphenylsilyl)ethane was also isolated (10%). [d] $[Pt(PPh_3)_4]$ (0.02 equiv) was used as a catalyst.



compound 5 was not obtained.

In entry 6, 1,2-bis(dimethylphenylsilyl)ethane was obtained in 10% yield.



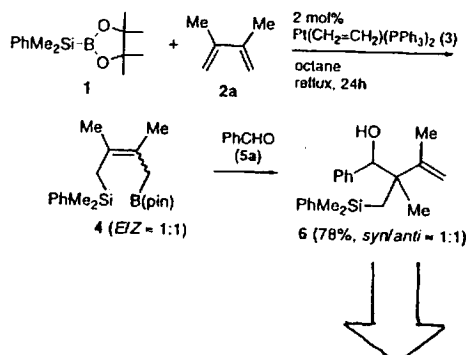
(c) Addition to 1,3-diene

JACS, 1998, 120, 4248

Platinum-Catalyzed Silaborative Coupling of 1,3-Dienes to Aldehydes: Regio- and Stereoselective Allylation with Dienes through Allylic Platinum Intermediates

Michinori Suginome, Hiroshi Nakanura, Takanori Matsuda, and Yoshihiko Ito*

Scheme 1. Silaboration of 2,3-Dimethyl-1,3-butadiene Followed by Reaction with Benzaldehyde



The lack of stereoselectivity was presumed to be due to isomerization of the primarily formed *E* or *Z* alkenes **4** under the reaction conditions.

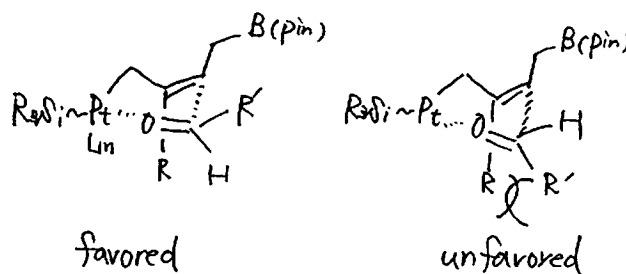
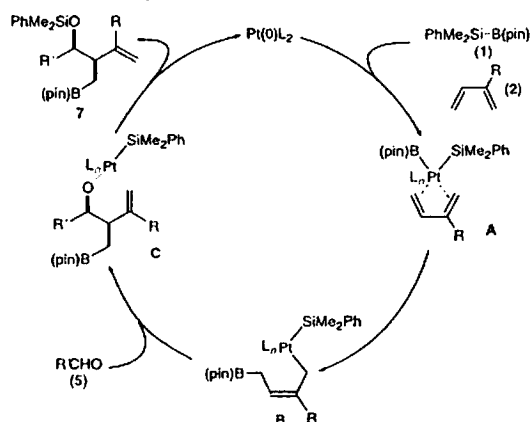
Table 2. Reaction of Dienes (**2**), Aldehydes (**5**), and Silylborane **1** in the Presence of Platinum Catalyst **3**^a

entry	dienes (R ¹ , R ²)	aldehydes (R')	temp (°C) ^b	products 7 yield (%)	ratio
1	2b (H, Ph)	5a (Ph)	120	b (79)	99:1
2	2b	5b (<i>p</i> -MeOPh)	120	c (77)	99:1
3	2b	5c (<i>o</i> -MeOPh)	120	d (83)	99:1
4	2b	5d (<i>p</i> -NCPH)	120	e (80)	99:1
5	2b	5e (<i>n</i> -Hex)	120	f (71)	93:7
6	2b	5f (<i>c</i> -Hex)	120	g (60)	96:4
7 ^{c,d}	2c (H, H)	5a (Ph)	50	h (63)	95:5
8 ^c	2d (-(CH ₂) ₄ -)	5a (Ph)	80	i (60)	99:1

^a All reactions were carried out in octane using 1.5 equiv of aldehyde unless otherwise noted. ^b Bath temp. ^c 3.0 equiv of aldehydes. ^d A reaction in hexane under atmospheric pressure of 1,3-butadiene.

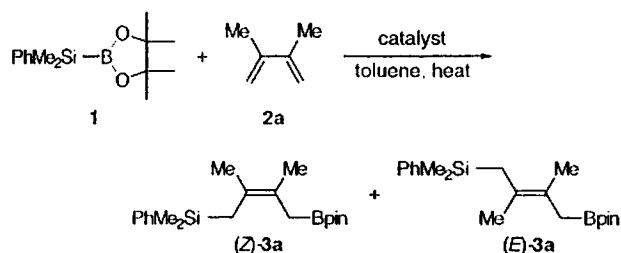
The finding that the platinum-catalyzed reaction did not take place with silylborane reagent and aldehyde in the absence of diene suggests that some reactive platinum intermediate may be formed from silylborane and dienes in the presence of the platinum catalyst.

Scheme 2. Possible Mechanism for the Silaborative Coupling of Dienes to Aldehydes



Stereoselective 1,4-Silaboration of
1,3-Dienes Catalyzed by Nickel
Complexes

Michinori Suginome, Takanori Matsuda, Takaya Yoshimoto, and Yoshihiko Ito*

Table 1. Reaction of Silylborane 1 with
2,3-Dimethyl-1,3-butadiene (2a) in the Presence of Nickel,
Palladium, and Platinum Complexes^a

entry	catalyst ^b	temp/°C	yield/% ^c	Z/E ^d
1	Ni(acac) ₂ -DIBAH	80	90	>99/1
2	Pd(OAc) ₂ - <i>t</i> -OcNC	110	0	
3	Pt(CH ₂ =CH ₂)(PPH ₃) ₂	110	95	48/52

^a Silylborane 1 (1 equiv) and 2a (2 equiv) were heated in the presence of Ni (0.05 equiv), Pd (0.02 equiv), or Pt (0.02 equiv) catalyst in toluene for 24 h. ^b Ni/DIBAH = 1/2; Pd/isocyanide = 1/15. ^c Isolated yield by bulb-to-bulb distillation. ^d Determined by ¹H NMR.

Table 2. Nickel-Catalyzed 1,4-Silaboration of 1,3-Dienes
2b-d^a

Entry	Diene 2	yield/%	product(s) 3,4 ^b
1		92	 3b/4b = 72/28
2		84	 3c/4c = 67/33
3 ^c		90	

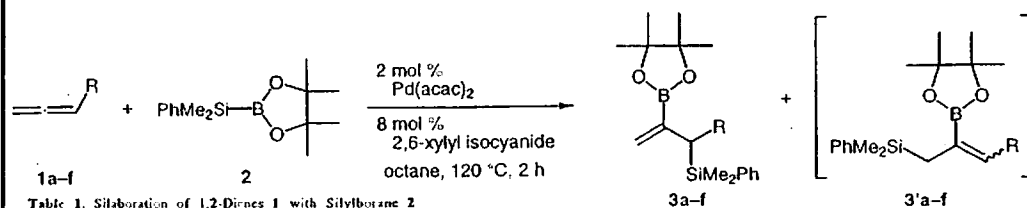
^a Silylborane 1 (1 equiv) and 2b-d (2 equiv) were reacted in the presence of Ni(acac)₂ (0.05 equiv) and DIBAH (0.10 equiv) in toluene at 80 °C for 24 h unless otherwise noted. ^b Ratios of 3 and 4 were determined by ¹H NMR. ^c The reaction was carried out under 1 atm of 1,3-butadiene.

Neither the 1,2-addition product nor the silaborative dimerization product was detected in the reaction.

(D) Addition to alleneHighly Regioselective Silaboration of 3-Substituted 1,2-Dienes Catalyzed by
Palladium/2,6-Xylyl Isocyanide

Michinori Suginome, Yutaka Ohmori, Yoshihiko Ito*

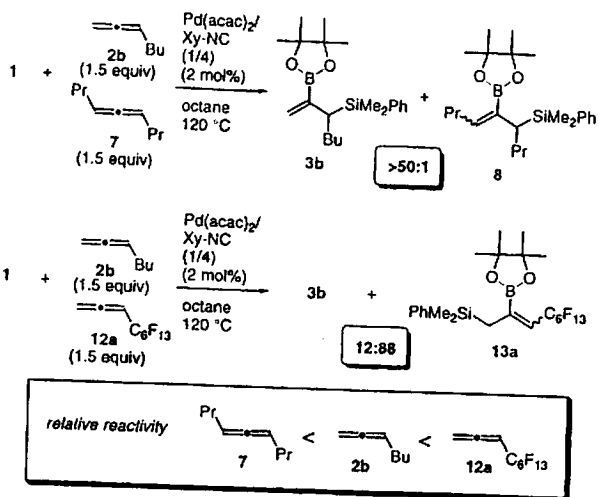
Synlett 1999, No. 10, 1567-1568

Table 1. Silaboration of 1,2-Dienes 1 with Silylborane 2
Catalyzed by Palladium/2,6-Xylyl Isocyanide Complex^a

1,2-diene (1)	yield (%)	3/3'
	99	>99/1
	91	>99/1
	88	94/6
	95	86/14
	92	>99/1
	79	-
	88	-

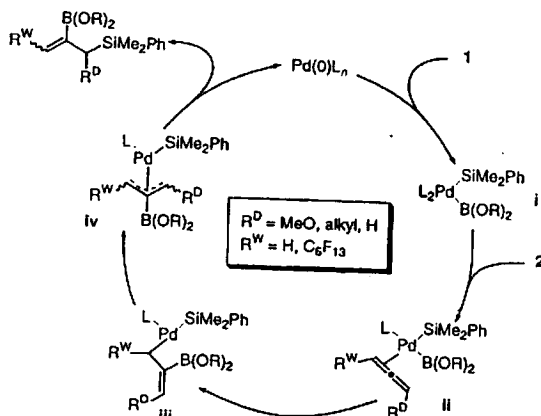
Ligand
2,6-xylyl isocyanide > tert-alkyl isocyanide
better

Palladium-catalyzed regioselective silaboration of 1,2-dienes

Michinori Suginome*¹, Yutaka Ohmori, Yoshihiko Ito*² *Journal of Organometallic Chemistry* 611 (2000) 403-413

• The presence of the terminal C=C bond enhanced the reactivity.

• The silaboration of C=C bond bearing electron-withdrawing group was accelerated.

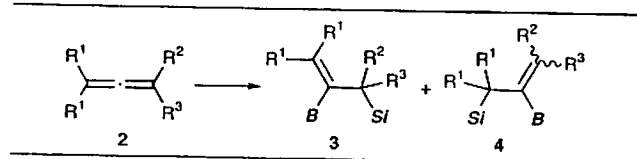


• The boryl group is generally attached to the central (sp) carbon of the allenes.

• The silyl group is preferentially attached to more electron-rich sp² carbon of the allenes.

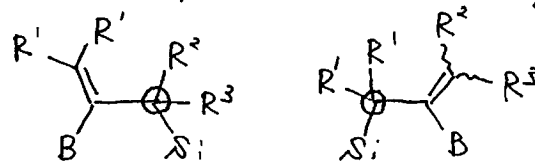
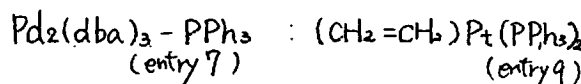
Palladium-catalysed borylsilylation and borylstannylation dimerization of 1,2-dienes

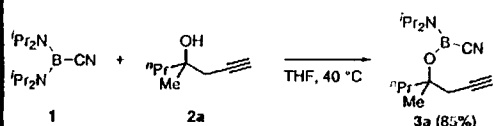
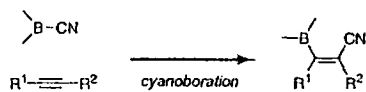
Shun-ya Onozawa, Yasuo Hatanaka and Masato Tanaka*

Chem. Commun., 1999, 1863-1864Table 1 Borylsilylation of 1,2-dienes^{a,b}

Entry	1,2-Diene				Yield (%) ^c	3:4 ^d
	2	R ¹	R ²	R ³		
1	2a	H	Me	H	88 (98)	100:0
2	2b	H	OMe	H	86 (93)	100:0
3 ^e	2c	H	H	H	91 (96)	—
4	2d	Me	Me	Me	92 (94)	—
5	2e	H	Ph	Ph	94	0:100
6	2f	H	Me	Me	84 (85)	52:48
7 ^f	2f	H	Me	Me	(90)	100:0
8 ^e	2f	H	Me	Me	(90)	71:29
9 ^e	2f	H	Me	Me	87 (94)	0:100

^a Reaction conditions: borylsilane 1 (0.33 mmol), 1,2-dienes (1.0 mmol), catalyst $\text{Pd}_2(\text{dba})_3$ (2.5 mol%)– ctpo (10.0 mol%), THF (1 ml), 80 °C, 9 h unless otherwise noted. ^b Si = SiMe₂Ph. B = B(OCMe₂)₂. ^c Isolated yields based on the amount of the borylsilane 1. Figures in parentheses are GC yields. ^d Determined by ¹H NMR spectroscopy. ^e A large excess of 1,2-diene was used. ^f $\text{Pd}_2(\text{dba})_3$ (2.5 mol%)– PPh_3 (10.0 mol%) was used as catalyst. ^g $\text{Pd}_2(\text{dba})_3$ (2.5 mol%)– PMe_3 (10.0 mol%) was used as catalyst. ^h Run in the presence of $(\text{CH}_2=\text{CH}_2)\text{Pt}(\text{PPh}_3)_2$ (5 mol%) at 80 °C for 3 h.





The selective substitution of one of the two amino groups by the alcohol took place without any loss of the cyano group from the boron atom.

Table 1. Catalyst Screening for Intramolecular Cyanoboration of 3a^a

catalyst	% yield (reaction time) ^b		
	at 50 °C	at 80 °C	at 110 °C
Pd(acac) ₂	nr	nr	86 (8 h)
PdCl ₂	nr	nr	83 (8 h)
PdCl ₂ (MeCN) ₂	nr	94 (5 h)	—
PdCl ₂ -pyridine	nr	71 (3 h)	—
Pd(PPh ₃) ₄	38 (96 h)	70 (14 h)	74 (1 h)
Pd ₂ (dba) ₃	94 (18 h)	98 (2 h)	—
Ni(COD) ₂	13 (96 h)	80 (96 h)	93 (2 h)

^a Cyanoborane 3a (0.30 mmol) in toluene-*d*₈ (0.5 mL) was heated in the presence of the palladium or nickel complexes (5 mol % Pd or Ni). ^b NMR yield (1,3-dimethoxybenzene as an internal standard). Abbreviations: nr = no reaction in 3 h; — = reactions not carried out.

The cyclization proceeded via the cis-addition of the B-CN bond in a regioselective 5-exo fashion.

< Possible Mechanism >

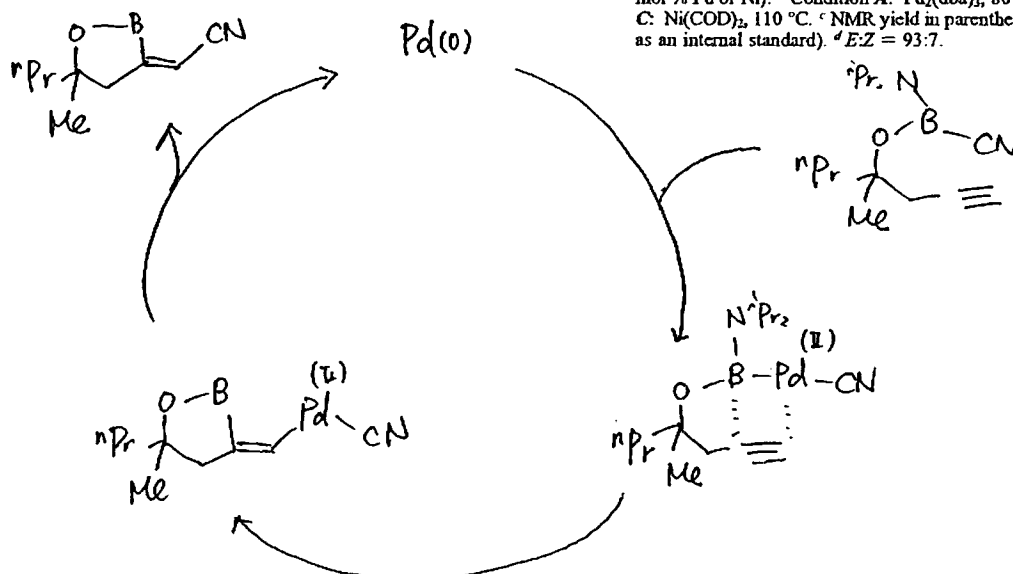


Table 2. Intramolecular Cyanoboration of Homopropargylic Ethers^a

entry	substrate	conditions, ^b time/h	product	% yield ^c
1		A, 2		88 (99)
2		A, 2		84 (97)
3		A, 7		92 (98)
4		B, 5		88 (99)
5		C, 10		63 (83)
6		B, 43		94
7		B, 20		86 ^d (99)

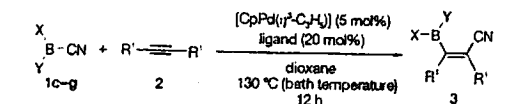
^a Cyanoborane 3 in toluene was heated in the presence of the catalyst (5 mol % Pd or Ni). ^b Condition A: Pd₂(dba)₃, 80 °C. B: Pd(PPh₃)₄, 110 °C. C: Ni(COD)₂, 110 °C. ^c NMR yield in parentheses (1,3-dimethoxybenzene as an internal standard). ^d E:Z = 93:7.

Cyanoboration

Palladium-Catalyzed Addition of Cyanoboranes to Alkynes: Regio- and Stereoselective Synthesis of α,β -Unsaturated β -Boryl Nitriles

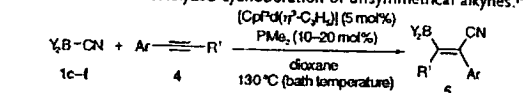
Michinori Suginome,* Akihiko Yamamoto, and Masahiro Murakami*

Angew. Chem. Int. Ed. 2005, 44, 2380.

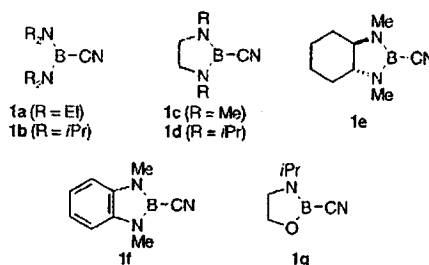
Table 1: Palladium-catalyzed reaction of symmetrical alkynes with cyanoboranes.^[a]

Entry	1	Alkyne (R')	Ligand	Yield [%]
1	1c	2a (Pr)	PMe ₃	47 ^[b]
2	1d	2a (Pr)	PMe ₃	49 ^[d]
3	1e	2a (Pr)	PMe ₃	81 ^[b]
4	1e	2a (Pr)	PCy ₃	66 ^[b]
5	1e	2a (Pr)	PMe ₃ , Ph	8 ^[b]
6	1e	2a (Pr)	PPh ₃	0
7	1f	2a (Pr)	PMe ₃	97 ^[b] (87 ^[d])
8	1g	2a (Pr)	PMe ₃	0
9	1f	2b (Ph)	PMe ₃	99 ^[d] (82 ^[b])

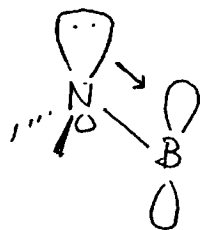
[a] The corresponding cyanoborane 1 (0.5 mmol) and alkyne 2 (0.6 mmol) were heated in dioxane (0.5 mL) in the presence of [CpPd(η^5 -C₅H₅)] (0.025 mmol; Cp is cyclopentadiene) and PMe₃ (0.1 mmol). [b] Yield determined by GC. [c] Yield determined by NMR spectroscopy. [d] Yield of isolated product.

Table 2: Palladium-catalyzed cyanoboration of unsymmetrical alkynes.^[a]

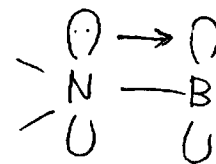
Entry	1	Alkyne (Ar, R')	Yield [%] ^[b]	Product ratio ^[c]
1	1c	4a (Ph, Me)	77	85:15
2	1d	4a (Ph, Me)	94	95:5
3	1e	4a (Ph, Me)	97	83:17
4	1f	4a (Ph, Me)	96	83:17
5	1d	4b (Ph, Bu)	89	95:5
6	1d	4c (<i>p</i> -EtO ₂ CC ₆ H ₄ , Bu)	72	88:12
7	1d	4d (<i>p</i> -CF ₃ C ₆ H ₄ , Me)	81	93:7
8	1d	4e (<i>o</i> -CH ₃ C ₆ H ₄ , Bu)	59	98:2
9	1d	4f (<i>o</i> -MOMOC ₆ H ₄ , Bu)	80	99:1
10	1d	4g (1-Naph, Me)	72	99:1
11	1d	4h (2-Naph, Bu)	61	91:9



The steric factor bring high reactivity!?



weak donation



strong donation.

ChemComm

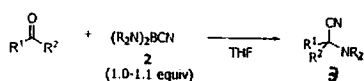
www.rsc.org/chemcomm

Bis(dialkylamino)cyanoboranes: highly efficient reagents for the Strecker-type aminative cyanation of aldehydes and ketones†

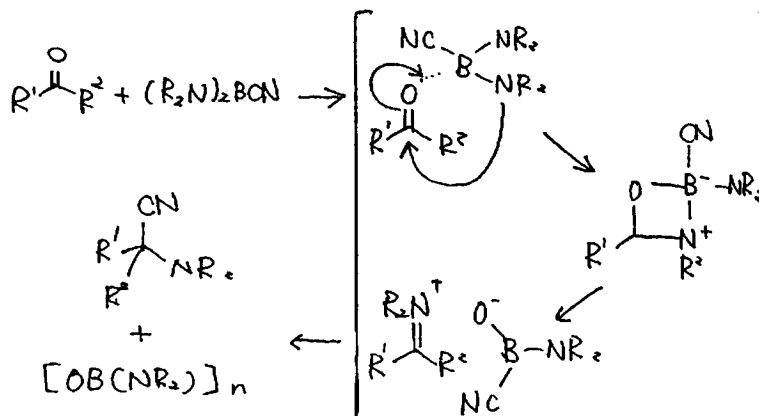
Michinori Suginome,* Akihiko Yamamoto and Yoshihiko Ito

Chem. Commun. 2002, 1392

Strecker-type Reaction Using Aminocyanoboranes



entry	R ¹	R ²	cyanoborane (NR ₂)	yield/%
1	Ph	H	NEt ₂	92
2	<i>p</i> -MeOC ₆ H ₄	H	NEt ₂	93
3	<i>p</i> -NO ₂ C ₆ H ₄	H	NEt ₂	92
4	2-furyl	H	NEt ₂	94
5	2-pyridyl	H	NEt ₂	99
6	(<i>S</i>)-PhCH=CH	H	NEt ₂	95
7	<i>n</i> -Hex	H	NEt ₂	96
8	PhCH ₂ CH ₂	H	NEt ₂	94
9	<i>o</i> -Hex	H	NEt ₂	98
10	<i>t</i> -Bu	H	NEt ₂	97
11	<i>o</i> -Hex	H	NBn ₂	92
12	<i>o</i> -Hex	H		99
13	<i>o</i> -Hex	H		99
14	Me	Me	Mor	99
15	PhCH ₂ CH ₂	Me	Mor	99
16	Ph	Me	Mor	92
17	(CH ₃) ₂	Me	Mor	96
18	(CH ₃) ₂	Me	Mor	92



①

	$R-C\equiv C-H$	$R-C=C$	$R-C\equiv C$	$R-C=C$	$R-C=C$
Ni	$R-Ni-Si$ $R-C=C-B$ \rightarrow dimerization	NO trial or reaction?	NO trial or reaction?	NO trial or reaction?	$R-C=C$ $R-C=C$ $99 : 1$
Pd	$R-Pd-Si$ $R-C=C-B$	NO reaction.	$R-Pd$ $R-C=C-B$	NO reaction.	NO reaction
Pt	$R-Pt-Si$ $R-C=C-B$ $90-95 : 10-5$	$R-C=C-Pt-Si$	$R-C=C-Pt-Si$	$R-C=C-Pt-Si$	$48 : 52$ because of isomerization

$Pt > Pd > B > Ni > Si$
 2.28 2.2 2.04 1.91 1.9

