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Ni-Catalyzed Si–B Addition to 1,3-Dienes: Disproportionation in Lieu of Silaboration

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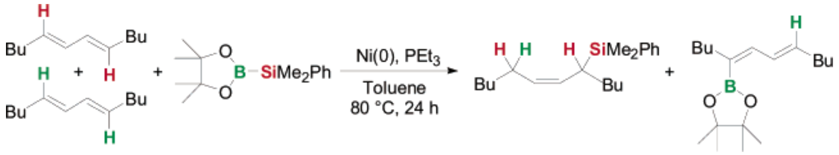
ABSTRACT



Upon attempted silaboration of acyclic 1- and 1,4-substituted 1,3-dienes, a new disproportionation reaction was discovered, yielding 1:1 mixtures of allylsilanes and dienylboranes. It was demonstrated that, as a key step in this new catalytic process, hydrogen is being transferred from one diene moiety to another.

Interelement[1] compounds undergo additions to a wide range of unsaturated substrates catalyzed by transition metals.[2] In one step, two functionalities are added to the same molecule, giving a densely functionalized building block for further transformations. The addition of interelement linkages to 1,3-dienes has been accomplished using silicon-, germanium-, tin-, and boron-containing homo- and heteroelement compounds (Figure 1). Most commonly the addition proceeds in a 1,4 fashion,[2a] but 1,2[3] and 1,1[3b,4] additions have also been observed. 2-Substituted and 2,3-disubstituted dienes have most often been used as substrates, and few additions to 1-substituted dienes[3a,5] have been reported. Although disilylations,[6] silaborations,[5] and diborations[7] have been achieved with cyclic 1,4-disubstituted 1,3-dienes, there are, to the best of our knowledge, no reports of element-element additions to acyclic 1,4-disubstituted dienes.

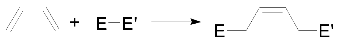


Figure 1. 1,4-Addition of an interelement compound to a 1,3-diene. E,E′ = Si, Ge, B or Sn.

We have recently developed an asymmetric version of the *cis*-1,4-silaboration of 1,3-cyclohexadiene using Pt(0) and phosphoramidite ligands.[8] In our efforts to widen the scope of the reaction we decided to investigate the silaboration of acyclic conjugated dienes. Previously butadiene, 2,3-dimethyl-1,3-butadiene, isoprene, and 2-methyl-1,3-pentadiene have been successfully silaborated, whereas attempted additions of a silylborane to 2,4-hexadiene and 4-methyl-1,3-pentadiene met with little success.[9] We decided to start our

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[1] Tamao, K.; Yamaguchi, S. *J. Organomet. Chem.* **2000**, *611*, 3−4.

[2] (a) Beletskaya, I.; Moberg, C. *Chem. Rev.* **2006**, ASAP. (b) Suginome, M.; Ito, Y. *Chem. Rev.* **2000**, *100*, 3221−3256. (c) Beletskaya, I.; Moberg, C. *Chem. Rev.* **1999**, *99*, 3435−3461.

[3] (a) Ishiyama, T.; Yamamoto, M.; Miyaura, N. *Chem. Commun.* **1997**, 689−690. (b) Tanaka, M.; Uchimaru, Y.; Lautenschlager, H.-J. *Organometallics* **1991**, *11*, 16−18.

[4] (a) Ishikawa, M.; Okazaki, S.; Naka, A.; Tachibana, A.; Kawauchi, S.; Yamabe, T. *Organometallics* **1995**, *14*, 114−120. (b) Lee, J.; Lee, T.; Lee, S. S.; Park, K.-M.; Kang, S. O.; Ko, J. *Organometallics* **2002**, *21*, 3922−3929.

[5] Suginome, M.; Matsuda, T.; Yoshimoto, T.; Ito, Y. *Org. Lett.* **1999**, *1*, 1567−1569.

[6] Ishikawa, M.; Nisimura, Y.; Sakamoto, H.; Ono, T.; Ohshita, J. *Organometallics* **1992**, *11*, 483−484.

[7] Clegg, W.; Johann, T. R. F.; Marder, T. B.; Norman, N. C.; Orpen, A. G.; Peakman, T. M.; Quayle, M. J.; Rice, C. R.; Scott, A. S. *J. Chem. Soc., Dalton Trans.* **1998**, 1431−1438.

[8] Gerdin, M.; Moberg, C. *Adv. Synth. Catal.* **2005**, *347*, 749−753.

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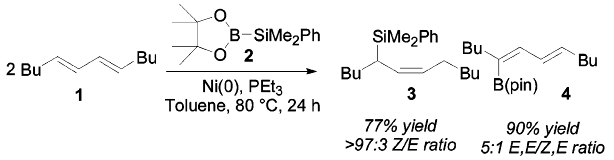
investigation by the silaboration of (*E*,*E*)-5,7-dodecadiene using **2** and different metal−ligand combinations.[10] With Pt(0) and PPh_3, PEt_3, or $P(OPh_3)$ we observed little or no conversion of the starting materials. Switching to Ni(0), prepared by treatment of $Ni(acac)_2$ with DIBALH, gave immediate results. Although no reaction was observed using PPh_3 as the ligand, both PPh_2Cy and PCy_3 resulted in around 30% consumption of the starting silylborane whithin 24 h at 80 °C. PEt_3 turned out to give an almost complete consumption of both starting materials, even though 2 equiv of the diene were used. Instead of the expected 1:1 adduct, two products, identified as 5-(dimethylphenylsilyl)-6-dodecene (**3**) and 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)-5,7-dodecadiene (**4**), were formed in a 1:1 ratio (crude ^{1}H NMR). Allylsilane **3**, the product of a formal hydrosilylation of the diene,[11] was isolated as the essentially pure *Z* isomer, whereas dienylborane **4** was obtained as a 5:1 mixture of the *E*,*E* and *Z*,*E* isomers (Scheme 1). The same products were obtained when $Ni(COD)_2$ was employed in place of in situ formed Ni(0).

Scheme 1. Addition of Silylborane **2** to (*E*,*E*)-5,7-Dodecadiene[a]

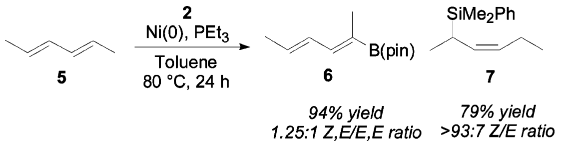


[a] Isolated yields, based on starting silylborane **2**.

This type of disproportionation does not seem to have been previously observed in element-element additions to 1,3-dienes. However, hydrogen transfer was shown to accompany the Rh-catalyzed addition of dialkyl disulfides to 1,2-dienes, resulting in 1:1 mixtures of (*E*)-alkylthio-1,3-dienes and (*E*)-2-alkylthio-2-alkenes.[12] In addition, during dimerization-double stannation of 1,3-dienes, hydrostannation was observed when bulky distannanes were employed, but no observation of stannyldienes was reported.[13]

These intriguing results prompted us to investigate the generality of this disproportionation reaction. 2,4-Hexadiene (**5**), which previously resisted silaboration,[5] was selected as a suitable substrate as it is 1,4-disubstituted, symmetrical, and readily available.[14] When subjecting **5** to the same reaction conditions as **1**, the outcome was very similar (Scheme 2). The silylborane was almost completely consumed, forming **6** and **7** in good yields and in almost equal amounts (crude ^{1}H NMR). The allylsilane **7** was formed with high *Z* selectivity,[15] whereas **6** was obtained as a 1.25:1 mixture of *Z*,*E* and *E*,*E* isomers. It is notable that the unsubstituted double bond has pure *E* configuration, although the starting 2,4-hexadiene consisted of a mixture of isomers. We did not observe any products from normal silaboration. At 60 °C the reaction was severely retarded and no conversion of the starting silylborane was observed (^{1}H NMR).

Scheme 2. Addition of Silylborane **2** to 2,4-Hexadiene[a]



[a] Isolated yields, based on starting silylborane **2**.

When the sterically demanding (*E*,*E*)-2,2,7,7-tetramethyl-3,5-octadiene was subjected to the standard conditions, no product formation or disapperance of starting materials was observed, and the starting diene could be recovered by chromatography. We next turned to the 1,3- and 1-substituted dienes **9** and **14**. Compound **9** has previously been silaborated using ligand-free conditions, giving two 1,4-addition products (**11** and its regioisomer) in a 2:1 ratio.[5,16] Using Ni(0)/PEt_3 we obtained a mixture of at least four different products: allylsilane **10** (>97:3 *Z*/*E* ratio), 1,4-silaboration product **11** (*Z* stereochemistry), 1,2-silaboration product **12** (*E* stereochemistry), and dienylborane **13**.

The effect of ligand structure on the distribution of procucts obtained from **9** was studied. As can be seen from Table 1 the ratio between the two silaboration products **11** and **12** is heavily influenced by the ligand. Using the small and electron-rich $PPhMe_2$, we obtained the two products in a 1:1.3 ratio, whereas the bulkier and more electron-deficient PPh_3 and PPh_2Cy only gave **11**. The ratio between allylsilane **10** and silaboration products **11** and **12** was less affected by the choice of ligand. It varied between 1.16 (entry 2) and 0.71 (entry 1). Compounds **11**−**13** constituted the major products from the reaction; although they account for most of the silicon added, the fate of a large part of the boron is unknown.[17] A 1:1 correspondence between allylsilane and dienylborane could thus not be verified.

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[9] Silylborane and diene (2 equiv) were reacted in the presence of $Ni(acac)_2$ (5 mol %) and DIBALH (10 mol %) in toluene at 80 °C. See ref 5.

[10] **General Procedure.** Silylborane **2**, diene (2 equiv), ligand (10 mol %), and $M(acac)_2$ (5 mol %) were dissolved in toluene. DIBALH (10 mol %) was then added at −35 °C to reduce the metal. The reaction mixture was heated at 80 °C (Ni) or 110 °C (Pt) for 24 h.

[11] For reviews on hydrosilylation of 1,3-dienes, see: (a) Pietruzka, J. In *Science of Synthesis*; Fleming, I., Ed.; Georg Thieme Verlag: Stuttgart, 2002; Vol. 4, pp 172−176. (b) *Comprehensive Handbook on Hydrosilylation*; Marciniec, B., Ed.; Pergamon: Oxford, 1992; pp 110−114. (c) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai S., Rappaport, Z., Eds.; Wiley Interscience: New York 1989; Vol. 2, pp 1493−1499.

[12] Arisawa, M.; Suwa, A.; Fujimoto, K.; Yamaguchi, M. *Adv. Synth. Catal.* **2003**, *345*, 560−563.

[13] Tsuji, Y.; Kakekhi, T. *J. Chem. Soc., Chem. Commun.* **1992**, 1000−1001.

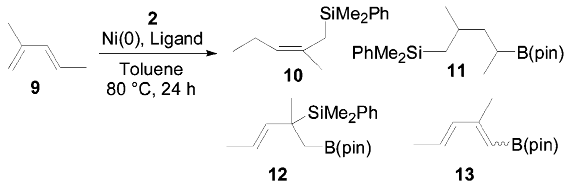
[14] 2,4-Hexadiene, tech., 90%, mixture of isomers. Remaining 10% is positional double bond isomers.

[15] As the starting 2,4-hexadiene was only 90% pure the selectivity of the reaction is most probably higher than 93:7. We were not able to separate **7** from the isomeric impurities.

[16] Suginome, M.; Ito, Y. *J. Organomet. Chem.* **2003**, *680*, 43−50.

[17] Entry 2: compounds **10** + **11** + **12** = 89%, while **11** + **12** + **13** = 53%.

Table 1. Addition of Silylborane **2** to (*E*)-2-Methyl-1,3-pentadiene

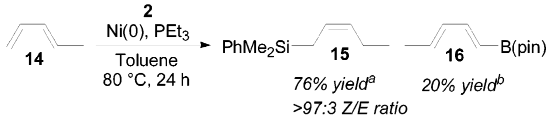


		yield (%)[a]			
entry	ligand	**10**	**11**	**12**	**13**
1	PMe_2Ph	38	23	31	11
2	PEt_3	48	32	9	12
3	PPh_3	41	46	0	32
4	PPh_2Cy	37	49	0	19
5	$P(OPh)_3$	0	0	0	0

[a] Based on starting silylborane **2** and determined by ^1H NMR using 1-methoxynaphthalene as internal standard.

Subjecting **14** to the standard reaction conditions[10] afforded allylsilane **15** and dienylborane **16** as major products, accompanied by products from silaboration. The allylsilane **15** was isolated in 76% yield with excellent *Z* stereoselectivity, but we were not able to separate dienylborane **16** from the silaboration products (Scheme 3). It was, however, possible to determine the stereochemistry of **16** as *E*,*E* from its coupling constants.

Scheme 3. Addition of Silylborane **2** to 1,3-Pentadiene[a]

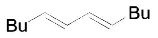
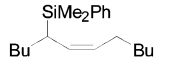
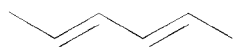
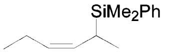
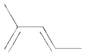
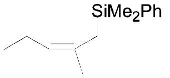
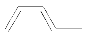
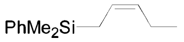


[a] Isolated yield, based on starting silylborane **2**. [b]Based on starting silylborane **2** and determined by ^1H NMR using 1-methoxynaphthalene as internal standard.

As the allylsilanes are produced in a formal hydrosilylation reaction with the expected *Z* stereochemistry,[11a,18] we decided to study whether the same products were obtained by hydrosilylation using dimethylphenylsilane instead of silylborane **2**, under otherwise identical reaction conditions. As can be seen in Table 2 all dienes did indeed react smoothly to furnish the expected products in good to excellent yields with the same high stereoselectivity as in the disproportionation reactions.

According to the commonly accepted mechanism, element-element additions to 1,3-dienes, as well as to other unsaturated compounds, proceed by oxidative addition of the interelement compound to a metal(0) complex, followed by insertion of the unsaturated bond into one of the metal-element linkages, and final reductive elimination.[19] In silaborations, insertion into the metal-boron bond is preferred.[19a] The presently observed disproportionation can be explained by β-elimination competing with reductive elimination. The resulting Si-M-H species then reacts with another diene molecule to yield the allylsilanes. Alternatively, initial sp^2-hydrogen activation, as suggested for additions of strained Si−Si and Ge−Ge bonds to unsaturated substrates,[20] followed by reductive elimination to form the dienylborane and hydrosilylation of a second diene would rationalize the formation of the products observed. We favor the first alternative, which avoids the formation of Ni(IV) intermediates.

Table 2. Ni(0)/PEt_3 Catalyzed Hydrosilylation of Dienes

entry	diene	product	yield (%)[a]
1			86
2			85
3			97
4			89

[a] Isolated yield based on starting $PhMe_2SiH$. Conditions: $Ni(acac)_2$ (5 mol %), DIBALH (10 mol %), PEt_3 (10 mol %), $PhMe_2SiH$, diene (2 equiv), toluene, 80 °C, 24 h.

To shed light on the mechanism we decided to investigate the disproportionation of **1** and **2**, trying to identify the hydrogen source. When toluene-d_8 was used as solvent no incorporation of deuterium in the products was observed. To study whether hydrogen transfer from one diene moiety to another occurred 5,8-dideuterido-**1** was synthesized from 1-hexyne and DIBALD. When subjecting this substrate to the standard reaction conditions, 5,8,8-trideuterio-**3** and 8-deuterio-**4** were formed, accompanied only by trace amounts of **4** and dideuterio-**3**, attributable to isotopic impurities present in the starting diene (Scheme 4). Thereby it was verified that the diene acts as the hydrogen source in the disproportionation reaction between **1** and **2**.

The hydrogen transfer observed can thus be explained by a mechanism where β-elimination from the Ni(II) complex obtained by insertion of the diene competes with reductive elimination. Addition of the simultaneously formed $HNiSiMe_2Ph$ (or $DNiSiMe_2Ph$) to a second equivalent of diene then affords the allylsilane with the expected *Z* configuration of

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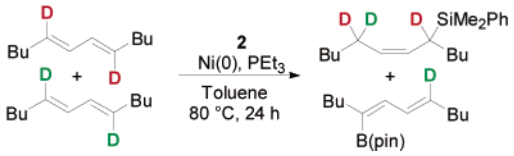
(18) (a) Onozawa, S.; Sakakura, T.; Tanaka, M. *Tetrahedron Lett.* **1994**, *35*, 8177−8180. (b) Bareille, L.; Becht, S.; Cui, J. L.; Le Gendre, P.; Moïse, C. *Organometallics* **2005**, *24*, 5802−5806.

(19) For examples of mechanistic investigations, see: (a) Sagawa, T.; Asano, Y.; Ozawa, F. *Organometallics*, **2002**, *21*, 5879−5886. (b) Ozawa, F. *J. Organomet. Chem.* **2000**, *611*, 332−342. (c) Lesley, G.; Nguyen, P.; Taylor, N. J.; Marder, T. B. *Organometallics* **1996**, *15*, 5137−5154. (d) Iverson, C. N.; Smith, M. R., III. *Organometallics* **1996**, *15*, 5155−5165. (e) Sagawa, T.; Sakamoto, Y.; Tanaka, R.; Katayama, H.; Ozawa, F. *Organometallics* **2003**, *22*, 4433−4445.

(20) (a) Ishikawa, M.; Okazaki, S.; Naka, A.; Tachibana, A.; Kawauchi, S.; Yamabe, T. *Organometallics* **1995**, *14*, 114−120. (b) Kang, Y.; Lee, J.; Kong, Y. K.; Kang, S. O.; Ko, J. *Organometallics* **2000**, *19*, 1722−1728. (c) Lee, J.; Lee, C.; Lee, S. S.; Kang, S. O.; Ko, J. *Chem. Commun.* **2001**, 1730−1731.

Scheme 4. Deuterium Transfer

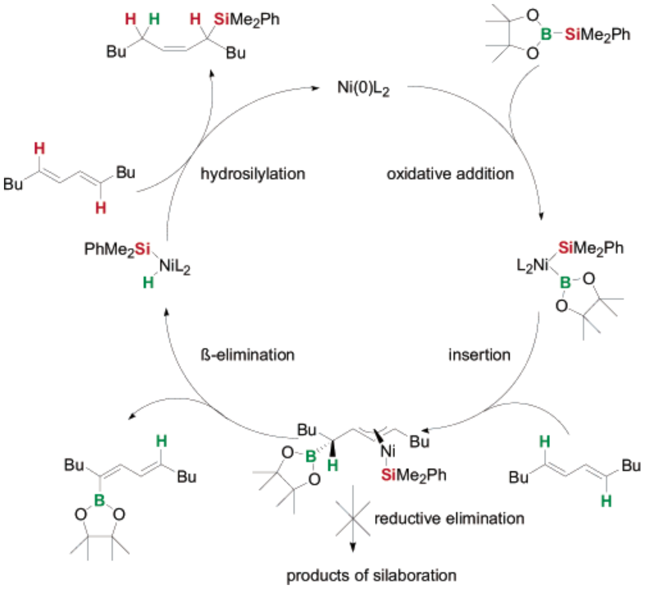


the olefinic bond.[11a,18] The stereochemistry of the dienylborane, with pure *E* configuration of the nonfunctionalized olefinic bond irrespective of the configuration of the starting diene, provides strong support for the intermediacy of a π-allyl nickel complex that can undergo *syn-anti* isomerization.

In summary, a new disproportionation process was discovered upon reaction of silylborane **2** with terminally substituted dienes under Ni(0)/PEt$_3$ catalysis. It seems that the terminal substituents on the diene play an instrumental role in the reaction; when 1,4-disubstituted dienes were used only disproportionation and no silaboration was observed. Dienes with only one terminal substituent gave a mixture of the two types of products. In the reaction with (*E*,*E*)-5,7-dodecadiene it was demonstrated that hydrogen is being transferred from one diene moiety to another.

Acknowledgment. This work was supported by the Swedish Research Council.

Scheme 5. Proposed Mechanism for the Ni-Catalyzed Disproportionation of (*E*,*E*)-5,7-Dodecadiene with Silylborane **2**



Supporting Information Available: Experimental procedures and characterizations including stereochemical assignments of all new compunds. This material is available free of charge via the Internet at http://pubs.acs.org.

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