Geminal Difunctionalization of Alkenylidene-Type Carbenoids by Using Interelement Compounds

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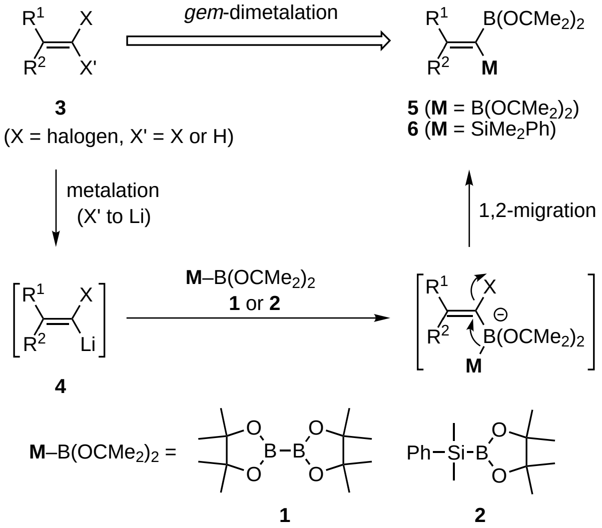
Interelement compounds contain either an interelement linkage or a homo-/heteroelement–element bond, and have recently been employed in the presence of a transition metal catalyst extensively for the functionalization of unsaturated carbon–carbon bonds.[1] Thus, the same or different elements can be introduced into unsaturated substrates simultaneously and directly to give products having two metal– or heteroatom–carbon bonds that allow further elaborative synthetic transformations. The addition of a reagent with a B–B, Si–B, or Si–Si bond to unsaturated carbon–carbon bonds provides an especially attractive and straightforward method to directly introduce boryl and/or silyl groups into organic molecules by *vic*- or 1,4-diboration,[2] silylboration,[3] or disilylation.[4]

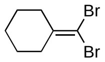
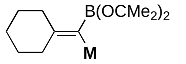
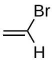
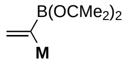
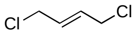
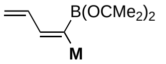
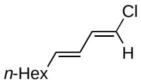
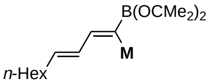
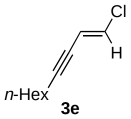
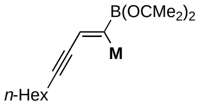
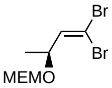
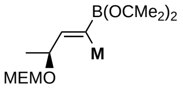
Herein we report that bis(pinacolato)diboron (**1**)[5] and (dimethylphenylsilyl)(pinacolato)borane (**2**)[6] react with 1-halo-1-lithioalkenes **4**,[7] alkylidene-type carbenoids available from 1,1-dihaloalkenes or 1-haloalkenes **3**, to afford 1,1-diborylalkenes **5**[8] or 1-boryl-1-silylalkenes **6**,[9] respectively. These products are readily converted into tri- or tetrasubstituted alkenes through various transition metal catalyzed carbon–carbon bond formations (Scheme 1).



Scheme 1. Geminal difunctionalization of alkenylidene-type carbenoids using interelement compounds.

Reagent **4a** was prepared by lithiation of (1,1-dibromomethylene)cyclohexane (**3a**) with butyllithium (1.05 mol) in THF/diethyl ether (2:1) at −110 °C. Compound **1** (1.1 mol) was added to this solution at −110 °C and the resulting mixture was stirred at −110 °C for 10 min, gradually allowed to warm to room temperature, and stirred for 12 h (overnight). Work-up and chromatography (silica gel, hexane/ethyl acetate) gave 1,1-(diborylmethylene)cyclohexane **5a** in 93 % yield (Table 1, entry 1).[10] Using **2** in place of **1**, we obtained 1,1-(boryl(silyl)methylene)cyclohexane **6a** in 75 % yield (Table 1, entry 2). We next applied the reaction to an unsubstituted carbenoid, 1-bromo-1-lithioethene (**4b**), available by treatment of vinyl bromide (**3b**) with lithium 2,2,6,6-tetramethylpiperidide (LiTMP), and isolated 1,1-diborylethene **5b** (or **6b**) in high yields (Table 1, entries 3 and 4, respectively). As (*E*)-1,4-dihalo-2-butene is known to give predominately (*Z*)-1-halobutadiene,[11] (*E*)-1,4-dichloro-2-butene (**3c**) was treated with two equivalents of LiTMP at −90 °C to stereoselectively give (*Z*)-1-chloro-1-lithio-1,3-butadiene (**4c**),[12b] which was allowed to react with **1** (or **2**) and afforded dienyldiborane **5c** (or dienyl(silyl)borane **6c**) in high yields (Table 1, entries 5 and 6, respectively). Noteworthy is that the stereochemistry of **6c** was exclusively *E*[13] in accord with the

Table 1. Reaction of alkylidene-type carbenoids with the diboron or silylborane reagent.

Entry	Substrate	Method[a]/ Reagent[b]	Product[c]		Yield [%]
1		A/**1**		**5a**	93
2	**3a**	A/**2**		**6a**	75
3		B/**1**		**5b**	91
4	**3b**	B/**2**		**6b**	81
5		C/**1**		**5c**	89
6	**3c**	C/**2**		**6c**[d]	75
7		D/**1**		**5d**	82
8	**3d**	D/**2**		**6d**[d]	89
9		C/**1**		**5e**	48
10	**3e**	C/**2**		**6e**[e]	49
11		E/**1**		**5f**	65
12[f]	**3f**	F/**2**		**6f**[d]	44

[a] A) BuLi (1.05 mol), THF/Et$_2$O (2:1), −110 °C, 10 min. B) LiTMP (1.10 mol), THF/Et$_2$O (2:1), −110 °C, 15 min. C) LiTMP (2.10 mol), THF, −90 °C, 15 min. D) BuLi (1.05 mol),THF, −90 °C, 15 min. E) BuLi (1.05 mol), THF/Et$_2$O (2:1), −110 °C, 10 min. F) BuLi (0.95 mol), Et$_2$O, −110 °C, 30 min. [b] **1** = [(Me$_2$CO)$_2$B]$_2$, **2** = PhMe$_2$Si–B(OCMe$_2$)$_2$. [c] M = B(OCMe$_2$)$_2$ for **5**; M = SiMe$_2$Ph for **6**. Yields of isolated product are given. [d] Single isomer. [e] *E*/*Z* = 1:1. [f] MEMO = CH$_3$OCH$_2$CH$_2$OCH$_2$O.

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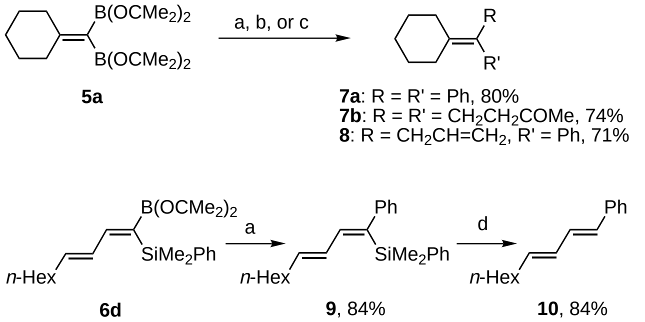
configuration of **4c** and with a mechanism involving stereoselective formation of an intermediate borate complex followed by stereospecific 1,2-migration.[14],[15] To extend the scope of the reaction, we treated **3d** with LiTMP, and **3e** with BuLi, to produce the conjugated alkylidene-type carbenoids **4d** and **4e**, respectively, which were subsequently treated with **1** (or **2**) to give rise to diene **5d** (or **6d**) and enyne **5e** (or **6e**), respectively (Table 1, entries 7–10). The stereochemistry (*Z*) of **6d** was completely controlled,[13] whereas **6e** was isolated as a stereoisomeric mixture due probably to facile isomerization of carbenoid **4e**.[12b] Stereoselective preparation of an alkylidene-type carbenoid is possible when a substrate contains a control element like an alkoxy group. For example, a stereoselective bromine–lithium exchange reaction takes place when 0.95–0.98 mol of BuLi is added to **3f** in diethyl ether at −110 °C.[16] The resulting (*E*)-1-bromo-1-lithioalkene reagent **4f** was treated with **2** to afford **6f** as a single isomer (Table 1, entry 12).[11] Similarly, the same substrate gave **5f** upon treatment with **1** (Table 1, entry 11).

These results clearly demonstrate that the *gem*-diboration and *gem*-silylboration reaction involve 1,2-migration of a boryl[17] or silyl[18] group with inversion of configuration.[19] In particular, the configurations of **4f** and **6f** clearly demonstrate that lithium in (*E*)-**4f** was initially replaced by boron in **2** and then silyl migration took place with inversion of configuration.

The products **5** and **6** serve as potential substrates for the Miyaura–Suzuki coupling reaction.[20] Coupling of **5a** with iodobenzene afforded 1,1-diphenylmethylenecyclohexane (**7a**; Scheme 2). Double conjugate addition of **5a** to methyl vinyl ketone (MVK) was catalyzed by a Rh complex to give 1,7-diketone **7b**.[21] Stepwise coupling is also possible: allylation followed by phenylation of **5a** afforded **8** in a high overall yield. Similarly, **6d** coupled with iodobenzene to afford trisubstituted 1-silylalkene **9**, which after protodesilylation, gave (*E*,*E*)-diene **10** clearly demonstrating the stereochemical course of the sequence of reactions (Scheme 2).[22]



Scheme 2. Miyaura–Suzuki coupling reaction of the resulting *gem*-bismetalated olefins. a) for **7a**: PhI (3 mol), $[Pd(PPh_3)_4]$ (3 mol%), aq. KOH (6 mol), dioxane, 90 °C, 24 h. b) for **7b**: MVK (4 mol), $[Rh(acac)(CO)_2]$/dppb (6 mol%), MeOH/H_2O, 50 °C, 24 h. c) for **8**: 1) $CH_2{=}CHCH_2Br$ (1 mol), $[Pd(PPh_3)_4]$ (3 mol%), aq. KOH (3 mol), dioxane, 70 °C, 24 h; 2) PhI (1 mol), $[Pd(PPh_3)_4]$ (3 mol%), aq. KOH (3 mol), dioxane, 70 °C, 24 h. d) TBAF (2 mol), THF, 60 °C, 2 h. acac = acetylacetonate, dppb = 1,4-bis(diphenylphosphanyl)butane, TBAF = tetrabutylammonium fluoride.

In summary, lithium carbenoids **4** are shown to react with **1** or **2** successfully to afford 1,1-diborylalkenes **5** or 1-boryl-1-silylalkenes **6** stereoselectively. Synthetic elaborations of these alkenylborates are readily achieved for extension of the olefinic carbon framework.

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(50 MHz, $CDCl_3$): $\delta = 24.7, 26.4, 28.7, 37.4, 82.7, 171.5$. IR: (nujol) 1615, 1320, 1285, 1265, 1245, 1220, 1140, 1105, 1010, 985, 965, 890, 855, 670 cm^{-1}; MS: m/z (%): 350 ([M^++2], 0.2), 349 ([M^++1], 2), 348 ([M^+], 8), 347 ([$M^+ - 1$], 4), 333 ([$M^+ -$ Me], 8), 291 (100); elemental analysis calcd for $C_{19}H_{34}B_2O_4$ (%): C 65.56, H 9.84; found: C 65.31, H 10.03.

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Nitroxide Radicals as Templating Agents in the Synthesis of Magnets Based on Three-Dimensional Oxalato-Bridged Heterodimetallic Networks**

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Building an extended compound with a particular crystal structure from molecular precursors in solution is still a challenge in many areas of chemistry.[1] Coordination chemistry provides a useful algorithm for this purpose (lattice engineering) because coordination geometries are well defined by strong and highly directional bonds. This concept is especially relevant in the synthesis of molecular magnetic materials since metal complexes provide the spin carriers (metal ions) and ligands through which magnetic interactions can occur.[2]

The ability of the oxalate (ox) ion, $C_2O_4^{2-}$, to transmit efficiently magnetic interactions through its bridging mode has been well documented since the pioneering work on dinuclear copper(II) complexes.[3] Later, the use of the homoleptic species $[M(ox)_3]^{3-}$ ($M = Cr^{III}, Fe^{III}$) provided an easy access to systems of higher dimensionality.[4] Only two families of high-dimensional oxalato complexes displaying magnetic order have been described: a) two-dimensional (2D) heterodimetallic compounds of formula $A[M^{II}M^{III}(ox)_3]$ (A = quaternary onium cation, M = metal) with a honeycomb-layered structure[5] and b) three-dimensional (3D) homometallic compounds of formula $A[M_2^{II}(ox)_3]$ or $A[M^{II}M^{III}(ox)_3](ClO_4)$ ($A = [M(bpy)_3]^{2+}$) with a cubic chiral packing.[6] The resulting dimensionality depends on the type of A^{m+} ion used, so that these cations can be considered as *templating agents* for the overall structure.[7] There is a fine interplay between molecular recognition and chirality in this kind of system: 2D structures are achiral but, within each layer, all the M^{III} sites have the same chirality while all the M^{II} sites have the opposite one; in the 3D systems, both sites adopt the same configuration. In all cases, the enantioselective synthesis of the optically active stereoisomers using chiral building blocks is possible.[8] Besides their role as structure-directing agents, the A^{m+} ions can also introduce physical properties of interest to the magnetic system, leading to multiproperty materials. Along this line, we have synthesized a family of 2D compounds where the "innocent" quaternary onium cation has been replaced by redox-active species of the decamethylmetallocenium type[9] or organic donors such as BEDT-TTF (2,2′-bis(5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]di-

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