Methylene Insertion Reactions of Samarium Carbenoids into Boron–Hydrogen and Phosphorus–Hydrogen Bonds

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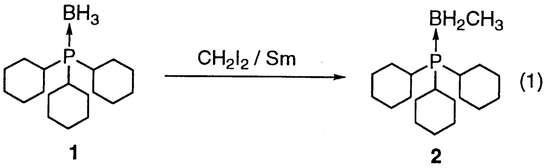
A samarium carbenoid, generated from diiodomethane and samarium metal, reacts with phosphine–boranes to afford phosphine–monomethylborane in good yields. The P–H bonds of secondary phosphine–boranes or secondary phosphine oxides are subjected to methylene insertion with the same carbenoid to give the corresponding P-methylated derivatives.

Among various carbenes and metal carbenoids,[1] samarium carbenoid[2] is known to exhibit unique reactivities. For instance, it reacts regio- and stereoselectively with allylic alcohols[2a–f] or metal enolates[2g] to give the corresponding cyclopropane derivatives, and it reacts also with carbonyl compounds to afford iodohydrins.[3] Taking these characteristic reactivities into account, we have tried to develop a new methylene transfer reaction which is not achieved by the use of other carbenoid reagents. Here we wish to report new methylene insertion reactions of samarium carbenoid into B–H and P–H bonds.

Our continuing study on phosphine–boranes has required development of carbon–boron bond forming reactions occurring at the boranato group.[4] This requirement as well as our interest in the utilization of lanthanide reagents in organic syntheses led us to examine the reactions of phosphine–boranes with samarium carbenoids.[5] Several preliminary experiments using tricyclohexylphosphine–borane (**1**) as a model substrate indicated that it was subjected to methylene insertion into the B–H bond by treatment with diiodomethane in the presence of samarium metal to afford tricyclohexylphosphine–methylborane (**2**) (Eq. 1). Further examination of the reaction conditions showed that the reaction best occurred in tetrahydropyran (THP) at –40 °C through to room temperature (Entry 7 in Table 1).[6] Under these reaction conditions, various phosphine–boranes, including an optically active one, were allowed to react with diiodomethane or 1,1-diiodoethane in the presence of samarium. The results are summarized in Table 2.



(1)

1 **2**

All trialkylphosphine–boranes except tri-*t*-butylphosphine–borane reacted smoothly to give the corresponding phosphine–monomethylboranes or phosphine–monoethylboranes in good yields (Entries 1–7). Dimethylphenylphosphine–borane and dibutylphenylphosphine–borane were also subjected to the methylene insertion reaction, though the yields of the products were moderate (Entries 8–10). It is noted that a diastereomerically pure (*R*p)-*l*-menthyloxy(methyl)phenylphoshine–borane was converted into the methylene insertion product without epimerization at the chiral phosphorus (Entry 11). On the other hand, tri-*t*-butylphosphine–borane, diphenylmethylphosphine–borane and triphenylphosphine–borane hardly reacted under these conditions (Entries 12–14). The very low reactivities of these substrates may be caused by steric hindrance or by reduced electron density at the boranato group.

Table 1. Reactions of tricyclohexylphosphine–borane (**1**) with diiodomethane in the presence of samarium

Entry	Molar ratio of **1** : CH_2I_2 : Sm	Solvent	Temp	Yield of compound **2** / % [a,b]
1	1 : 4 : 4	THF	– 78 °C → rt	29 (32)
2	1 : 4 : 4	THF	0 °C → rt	30 (38)
3	1 : 7 : 7	THF	0 °C → rt	53 (9)
4	1 : 10 : 10	THF	0 °C → rt	30 (trace)
5	1 : 7 : 7	CH_3CN	0 °C → rt	25 (48)
6	1 : 7 : 7	THP	0 °C → rt	60 (31)
7	1 : 7 : 7	THP	– 40 °C → rt	72 (20)

[a]Isolated yield. [b]Numbers in parentheses are recovery yields of compound **1**.

The methylene insertion reaction mentioned above was applied to the compounds possessing a P–H bond. A few preliminary results are shown in Table 3. In each case the P-methylated derivative was obtained in good to high yield. It is noteworthy that the reactions proceeded with net retention of configuration at the phosphorus atom.

In order to elucidate the mechanistic aspects of these reactions, tricyclohexylphosphine–borane(d_3) (**3**) and 2-methoxyphenyl(phenyl)phosphine(d_1)–borane (**4**) were allowed to react with diiodomethane in the presence of samarium, followed by quenching with H_2O. The products were identified as compounds **5** and **6**, respectively, by ^1H NMR, FAB MS, and IR.

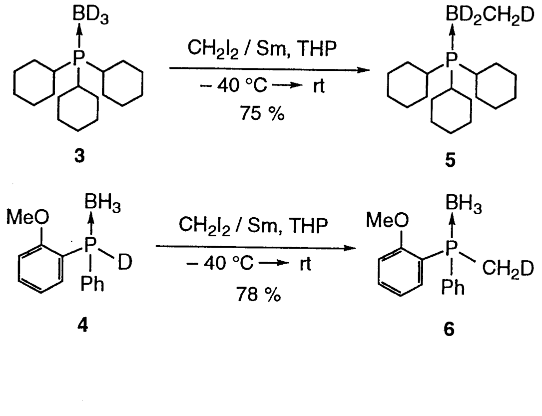
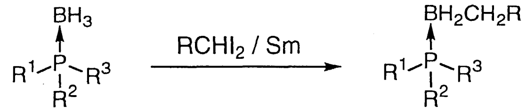
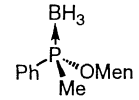
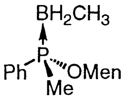


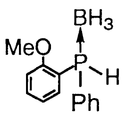
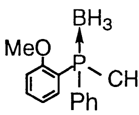
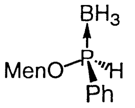
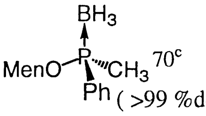
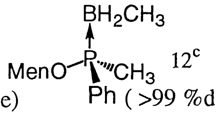
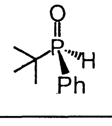
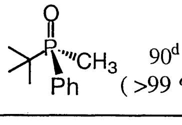
Table 2. Alkylidene insertions into the B–H bond of phosphine–boranes[a]



Entry	Substrate	$RCHI_2$	Product[b]	Yield / %[c]
1	Cy_3PBH_3	CH_2I_2	$Cy_3PBH_2CH_3$	72
2	Cy_3PBH_3	CH_3CHI_2	$Cy_3PBH_2CH_2CH_3$	70
3	(n-Pr)$_3$PBH$_3$	CH_2I_2	(n-Pr)$_3$PBH$_2$CH$_3$	82
4	(n-Pr)$_3$PBH$_3$	CH_3CHI_2	(n-Pr)$_3$PBH$_2$CH$_2$CH$_3$	78
5	(n-Bu)$_3$PBH$_3$	CH_2I_2	(n-Bu)$_3$PBH$_2$CH$_3$	76
6	(n-Bu)$_3$PBH$_3$	CH_3CHI_2	(n-Bu)$_3$PBH$_2$CH$_2$CH$_3$	70
7	(i-Pr)$_3$PBH$_3$	CH_2I_2	(i-Pr)$_3$PBH$_2$CH$_3$	68
8	$PhMe_2PBH_3$	CH_2I_2	$PhMe_2PBH_2CH_3$	62
9	$PhMe_2PBH_3$	CH_3CHI_2	$PhMe_2PBH_2CH_2CH_3$	60
10	Ph(n-Bu)$_2$PBH$_3$	CH_2I_2	Ph(n-Bu)$_2$PBH$_2$CH$_3$	59
11		CH_2I_2		56[c]
12	(t-Bu)$_3$PBH$_3$	CH_2I_2	(t-Bu)$_3$PBH$_2$CH$_3$	trace
13	Ph_2MePBH_3	CH_2I_2	$Ph_2MePBH_2CH_3$	trace
14	Ph_3PBH_3	CH_2I_2	$Ph_3PBH_2CH_3$	—[d]

[a]Reaction conditions: Substrate 1.0 mmol, CH_2I_2 or CH_3CHI_2 7.0 mmol, Sm 7.0 mmol, THP 35 cm^3, –40 °C through to rt. [b]All new compounds afforded satisfactory spectral data (IR, ^{1}H NMR, and FAB MS). [c]Isolated yield. [d]No reaction occurred.

Table 3. Methylene insertion reactions into the P–H bonds of *sec*-phosphine–boranes and phosphine oxide[a]

Substrate	Product, Yield / %[b]
	 86
	 (>99 %de)  (>99 %de)
	 (>99 %ee)

[a]Reaction conditions: Substrate 1.0 mmol, CH_2I_2 4.0 mmol, Sm 4.0 mmol, THP 20 cm^3, –40 °C through to rt. [b]Isolated yield. [c] The diastereomeric excess was determined by ^{1}H NMR (400MHz). [d]The enantiomeric excess was determined by optical rotation.

These results suggest that the methylene unit is inserted directly into the B–H bond or the P–H bond via the transition states depicted in Figure 1.

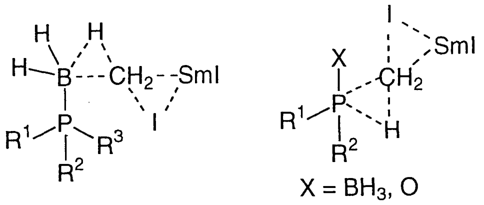


Figure 1. Proposed transition states of the methylene insersions into the B–H or P–H bond.

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References and Notes

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