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

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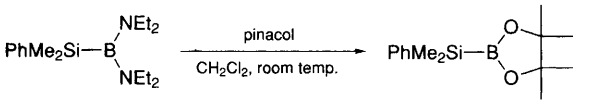
Addition of the silicon–boron bond across carbon–carbon triple bonds, *i.e.* silaboration is most effectively catalysed by a palladium(0)–*tert*-alkyl isocyanide complex to give (*Z*)-1-boryl-2-silyl alkenes with high regio- and stereo-selectivity, which are useful for synthesis of stereodefined alkenylsilanes.

With the exploitation of organosilicon compounds in synthetic organic chemistry, development of selective synthetic methods for the preparation of organosilicon compounds is highly desireable.[1] The transition metal catalysed addition of silicon-containing intermetallic compounds to unsaturated organic compounds *via* bis-silylation,[2] silastannation[3] or carbosilylation[4] has been extensively studied, with the aim of finding effective syntheses for stereodefined organosilicon compounds.

We have developed palladium-catalysed bis-silylation of unsaturated organic compounds, which is useful in stereoselective organic synthesis.[5] The use of palladium(0)–*tert*-alkyl isocyanide complexes is crucial for promoting the bis-silylation reaction effectively;[2c] it has been suggested that this is due to the palladium–isonitrile complex's ability to undergo oxidative addition to the silicon–silicon bond to form a bis(organosilyl)bis(*tert*-alkyl isocyanide)palladium(II) complexes.[6] It is also worth noting that the palladium–isonitrile complex presented a specific catalytic activity for the silastannation, unlike palladium–phosphine complex.[3e]

Herein we disclose that the addition of a silicon–boron bond across a carbon–carbon triple bond takes place effectively in a regio- and stereo-selective manner in the presence of a palladium(0)–*tert*-alkyl isocyanide complex catalyst.[7] It has also been found that the silaboration reaction is catalysed by tetrakis(triphenylphosphine)platinum(0) complex. Finally, the transformation of (*Z*)-1-boryl-2-silyl alkenes thus obtained into stereodefined alkenylsilanes demonstrates the usefulness of this silaboration reaction in selective organic synthesis.

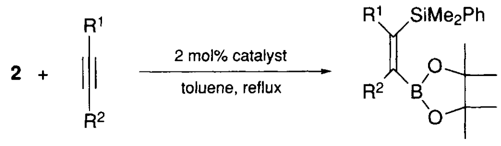
Silylborane **2**, prepared from diamino derivative **1** [eqn. (1)],[8] was reacted with oct-1-yne in refluxing toluene in the presence of $Pd(OAc)_2$ (0.02 equiv.) and 1,1,3,3-tetramethylbutyl isocyanide (0.30 equiv.) [eqn. (2), Table 1].† The reaction was completed within 1 h and furnished silaboration product **3a**, which was isolated in good yield by bulb-to-bulb distillation (Table 1, entry 1). It is noteworthy that the silaboration reaction proceeded even at 50 °C (entry 2) and afforded (*Z*)-1-boryl-2-silyloct-1-ene **3a** as a single product with high stereo- and regio-selectivity. An NOE experiment for **3a** revealed that the silyl and boryl groups had added to the carbon–carbon triple bond in a *cis* fashion, with the latter group at the terminal position. In contrast, tetrakis(triphenylphosphine)palladium(0) catalysed silaboration of oct-1-yne sluggishly and resulted in the formation of several by-products on prolonged reaction (entry 3), while Wilkinson's complex [$RhCl(PPh_3)_3$], effective for catalytic hydroboration,[9] completely failed to promote the reaction (entry 4). Tetrakis(triphenylphosphine)platinum(0), which is the catalyst of choice for the diboration of alkynes,[10] also catalysed the silaboration in refluxing toluene, forming a 9 : 1 mixture of the two regioisomers (entry 5). However, it is noted that, unlike the palladium–isonitrile complex, the platinum–phosphine complex exhibited low catalytic activity at 50 °C, giving **3a** in low yield (entry 6).



1

2 (68%)

(1)



2 +

3a–h

(2)

On the basis of this survey of the transition-metal complex catalysts, silaboration of various alkynes was examined in the presence of the palladium–isonitrile complex catalyst in refluxing toluene (Table 2). Phenylacetylene and terminal alkynes with protected hydroxy groups, *i.e.* tetrahydropyranyloxy (THPO) and methoxyethoxymethoxy (MEMO) groups, also afforded **3b–d** as single isomers in good yields (entries 1–3). A conjugated enyne, 1-ethynylcyclohexene, gave the 1,2-silaboration product **3e** in good yield without the formation of the 1,4-addition product (entry 4). A sterically bulky trimethylsilylacetylene also underwent the silaboration in

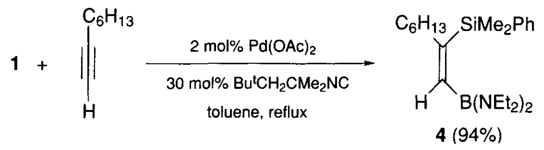
Table 1 Transition metal catalysed reactions of silylborane **2** with oct-1-yne ($R^1 = C_6H_{11}$, $R^2 = H$)[a]

Entry	Catalyst (equiv.)	*T*/°C	*t*/h	Yield of **3a** (%)	Regioselectivity[b]
1	$Pd(OAc)_2$ (0.02) + $Bu^tCH_2CMe_2NC$ (0.3)	110	1	92	>99 : 1
2	$Pd(OAc)_2$ (0.02) + $Bu^tCH_2CMe_2NC$ (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%).

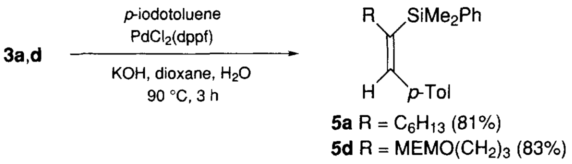
moderate yield, affording a mixture of the two regio-adducts with the terminal alkenylborane predominating (94 : 6) (entry 5). The silaboration reaction was also applicable for internal alkynes. Thus, diphenylacetylene furnished (*Z*)-1-boryl-2-silylstilbene **3g** in 74% yield (entry 6) under the same reaction conditions, but dec-5-yne gave (*Z*)-5-boryl-6-silyloct-5-ene **3h** in only 24% yield (entry 7).

In addition to the pinacol derivative **2**, diamino derivative **1** also provided the corresponding silaboration product **4** in good yield with high regio- and stereo-selectivity in the presence of the palladium–isonitrile catalyst [eqn. (3)].



(3)

The present silaboration reaction allows regio- and stereo-selective formation of alkenyl-silicon and -boron moieties, which have wide synthetic potential in many functionalizations and carbon–carbon bond forming reactions. For example, cross-coupling reactions of **3a** and **3d** with *p*-iodotoluene occurred at the boryl moiety under the Suzuki–Miyaura conditions [$PdCl_2$(dppf)‡ and KOH] to give alkenylsilanes **5a** and **5d**, respectively, in good yields [eqn. (4)].[11] During the reaction, the stereochemistry of the carbon–carbon double bonds was retained to afford exclusively (*Z*)-alkenylsilanes.



(4)

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Table 2 Silaboration of alkynes ($R^1C{\equiv}CR^2$) 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_3Si	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.

Footnotes

† Typical experimental procedure: To palladium(II) acetate (9.0 mg, 0.040 mmol) was added 1,1,3,3-tetramethylbutyl isocyanide (84 mg, 0.60 mmol) with stirring at room temperature under nitrogen. The colour of the mixture immediately changed to a vivid red, indicating the formation of the palladium(0)–isonitrile complex. Toluene (0.5 ml), **2** (524 mg, 2.0 mmol) and oct-1-yne (331 mg, 3.0 mmol) were added, and the reaction mixture was heated under reflux for 1 h. The cooled reaction mixture was subjected to a short column of silica gel (hexane–diethyl ether, 4 : 1) followed by bulb-to-bulb distillation (0.1 mmHg) to afford **3a** (684 mg, 92%); ^1H NMR ($CDCl_3$) δ 0.44 (s, 6 H), 0.85 (t, *J* 6.6 Hz, 3 H), 1.07 (s, 12 H), 1.14–1.38 (m, 10 H), 2.18–.2.25 (m, 2 H), 6.18 (t, *J* 1.3 Hz, 1 H), 7.26–7.31 (m, 3 H), 7.51–7.55 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ −0.9, 14.1, 22.5, 24.6, 29.1, 29.6, 31.7, 42.6, 83.0, 127.4, 128.3, 134.0, 140.5, 166.7; ν_{max}/cm^{-1} 2940, 1584, 1356, 1256 (Calc. for $C_{22}H_{37}O_2BSi$: C, 70.95; H, 10.01. Found: C, 70.70; H, 10.25%).

‡ dppf = 1,1′-bis(diphenylphosphino)ferrocene.

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