

## Synthesis of Allylsilanes from the [2 + 1] Insertion Reaction of Alkenyl Fischer Carbene Complexes with Silanes

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Alkenyl Fischer carbene complexes undergo mild insertion reactions with organosilanes to give allylsilanes in good yields.

Fischer carbene complexes have been shown to act as carbenoids in undergoing [2 + 1] insertion reactions into Sn-H,<sup>1</sup> Si-H,<sup>2</sup> C-H<sup>3</sup> and C-C bonds,<sup>4</sup> the applications of which however, have yet to be fully investigated. Given the mild and neutral conditions of these insertion reactions, they have potential as a route to valuable organic intermediates. Since allylsilanes have been demonstrated to be highly versatile synthetic reagents,<sup>5</sup> a new method of preparation of highly functionalised derivatives is desirable. We now report our preliminary success in applying the [2 + 1] insertion of alkenyl Fischer carbene complexes with triorganosilanes to give allylsilanes† in good yields.

The alkenyl carbene complexes all underwent a smooth insertion reaction with triethylsilane in hexanes at 60 °C to give allylsilanes. The reaction is chemoselective at the metal-carbene bond without any significant hydrosilylation at the alkenyl site. Added pyridine increased neither the rate nor the yield significantly. Both sterically bulky complexes and the more electron-rich β-methoxy carbene complexes were slower in their rate of the insertion presumably because of steric hindrance and a decrease in electrophilicity of the carbene carbon, respectively. The tungsten analogue of complex 1 gave the allylsilane 7 (75%) in a much slower (8 days) reaction possibly as a result of an increase in metal-carbon bond strength in going from chromium to tungsten.<sup>6</sup>

The insertion is stereospecific with retention of the *E* geometry of the double bond for complex 1 as evidenced from the *trans* coupling constant of 7 (16.0 Hz). However, for the strained carbene complexes 5 and 6, we observed some double-bond isomerisation to exocyclic olefins forming alkenylsilanes, probably as a result of release of ring strain in the bicyclic skeleton.

The use of triphenylsilane instead of triethylsilane had a marked effect in increasing the rate by about 10 times and the yields of reaction by 20%, the reaction taking only 30 min at 60 °C. The triphenylsilyl group although longer than the triethylsilyl group may be effectively less hindering as a result of the propeller effect of the phenyl rings.

### Experimental

**Typical Procedure.**—Triethylsilane (0.029 g, 0.25 mmol) and the carbene complex 1 (65 mg, 0.19 mmol) were dissolved in hexane (8 cm<sup>3</sup>) in a vacuum-tight Teflon-stoppered round-bottom flask. The deep red solution was deoxygenated by the freeze-pump-thaw method (3 cycles) and then was stirred and heated to 60 °C under nitrogen. After 1 h, the resulting brownish yellow suspension was concentrated by rotary evaporation and purified by flash chromatography on silica gel

**Table 1** [2 + 1] Insertion of alkenyl Fischer carbene complexes with silanes

		(1)		
R	R'	Reaction time	Product	% Yield
	Et	1 h	7	68
	Et	25 min	8	57
	Et	15 h	9	63
	Et	30 min	10	47
	Et	20 h	11	40 <sup>a</sup>
	Et	7 h	12	69 <sup>b</sup>
	Ph	30 min	13	87
	Ph	30 min	14	64

<sup>a</sup> Mixtures of diastereoisomers. <sup>b</sup> Mixtures of diastereoisomers and *exo*-double bond isomers.

with hexane as the eluent to afford the allylsilane 7 as colourless liquid (34 mg, 68%); *R*<sub>f</sub> 0.22 (hexane); δ<sub>H</sub>(CDCl<sub>3</sub>; 250 MHz) 0.57–0.67 (m, 6 H), 0.98 (t, *J* 7.9, 9 H), 3.35 (s, 3 H), 3.74 (d, *J* 7.3, 1 H), 6.24 (dd, *J* 7.3, 16.0, 1 H), 6.43 (d, *J* 16.0, 1 H) and 7.19–7.38 (m, 5 H); δ<sub>C</sub>(CDCl<sub>3</sub>; 62.9 MHz) 2.02, 7.39, 59.10, 77.60, 126.05, 126.81, 127.43, 128.55, 130.28 and 137.83; *m/z* (% rel intensity) 262 M<sup>+</sup> (1), 247 (88), 233 (33), 161 (7), 147 (6), 131 (13), 115 (58) and 87 (100) (Found: C, 73.5; H, 10.2. C<sub>16</sub>H<sub>26</sub>OSi requires C, 73.28; H, 9.92).

We have shown that alkenyl Fischer carbene complexes undergo mild and chemoselective insertion reactions with organosilanes to give allylsilanes in good yields. Further applications of the insertion reaction are in progress.

† All new compounds have satisfactory spectral and analytical data.

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