

Complete Reversal of Stereoselectivity in Rhodium Complex-catalysed Hydrosilylation of Alk-1-yne

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[Rh(cod)Cl]₂-catalysed hydrosilylation of hex-1-yne with Et₃SiH in EtOH or DMF is highly selective for the formation of (*Z*)-vinylsilane, whereas [Rh(cod)Cl]₂-PPh₃ in MeCN or PrⁿCN is highly selective for the formation of (*E*)-vinylsilane; the active species for *cis* addition has been revealed to be Rh^I cationic complex generated *in situ*.†

Hydrosilylation of alkynes has synthetic value, because the vinylsilane products are versatile intermediates in organic synthesis.¹ The most straightforward and simple method for the preparation of vinylsilanes is hydrosilylation of alkynes. With alk-1-yne, the formation of three isomers is possible, and much effort has been expended in developing highly selective hydrosilylation.²

In the course of our studies,³ we investigated Rh-catalysed hydrosilylation of hex-1-yne with Et₃SiH in various solvents; both stereoisomers were obtained in high yields with high selectivities by choosing the reaction conditions.

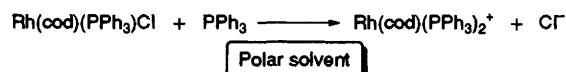
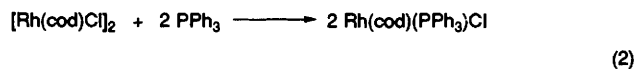
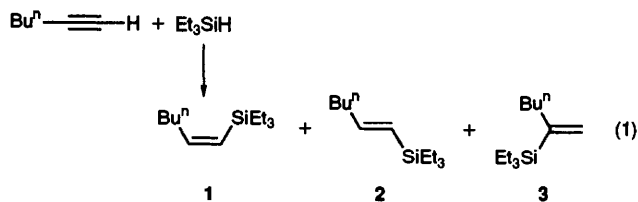
The hydrosilylation of hex-1-yne with Et₃SiH was carried out in various solvents, using [Rh(cod)Cl]₂ as a catalyst [eqn. (1)]. Results are summarized in Table 1. A high degree of selectivity forming (*Z*)-vinylsilane **1** was attained using EtOH or DMF (entries 5 and 6). The reactions in benzene, acetone

Table 1 [Rh(cod)Cl]₂-catalysed hydrosilylation of hex-1-yne with Et₃SiH^a

Entry	Solvent	Yield (%) ^b	Product ratio ^c		
			1	2	3
1	Benzene	85	82	15	3
2	Acetone	89	68	29	3
3	THF	68	90	5	5
4	CH ₂ Cl ₂	91	77	13	10
5	EtOH	85	94	4	2
6	DMF	80	97	1	2
7 ^{d,e}	MeCM	93	2	97	1
8 ^d	MeCN	18	36	33	31
9 ^{d,e}	Pr ⁿ CN	85	2	96	2

^a A mixture of hex-1-yne (8 mmol), Et₃SiH (12 mmol), [Rh(cod)Cl]₂ (0.004 mmol) and solvent (12 ml) was stirred at room temp. for 41 h. ^b Isolated yield based on the amount of hex-1-yne charged. ^c Determined by ¹H NMR. ^d [Rh(cod)Cl]₂ (0.012 mmol). ^e PPh₃ (0.048 mmol).

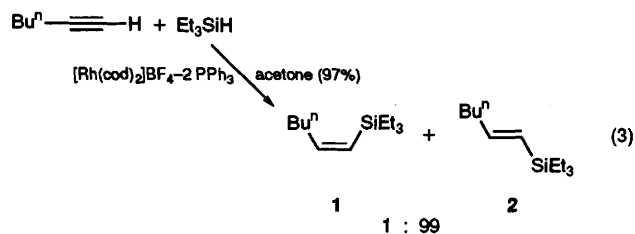
† Abbreviations used: cod = cycloocta-1,5-diene, DMF = dimethylformamide, THF = tetrahydrofuran.



and CH_2Cl_2 were less selective (entries 1, 2 and 4). Rhodium complexes are known to show selectivity forming (*Z*)-vinylsilane via the *trans* addition of Si-H across the carbon-carbon triple bond, a very rare event in transition metal complex-catalysed hydrometallation of alkynes, in the hydrosilylation of alk-1-yne.⁴ The mechanism of *trans* addition proposed involves the isomerization of a β -silylalkenylrhodium complex via a zwitterionic carbene complex.⁵ Polar solvents such as EtOH or DMF stabilize the intermediate and hence increased the selectivity forming (*Z*)-vinylsilane 1.

Using PPh_3 in nitrile solvent allowed a complete reversal of the stereochemistry. (*E*)-Vinylsilane 2 was obtained in 97% selectivity when $[\text{Rh}(\text{cod})\text{Cl}]_2$ and 2 equiv. of PPh_3 per Rh atom was used as a catalyst (entry 7). The same reaction catalysed by $[\text{Rh}(\text{cod})\text{Cl}]_2$ alone resulted in a non-selective formation of products with poor yields (entry 8). The reaction using PPh_3 in Pr^nCN gave a similar result (entry 9). The addition PPh_3 in other solvents was less effective. This is the first example of a highly selective synthesis of either (*E*)- or (*Z*)-vinylsilane by the same metal complex catalysed-hydrosilylation of the same alkyne with the same hydrosilane.

Rhodium phosphine species appeared to be necessary for the selective formation of (*E*)-vinylsilane 2. The reaction of $[\text{Rh}(\text{cod})\text{Cl}]_2$ with PPh_3 is reported to give a monomeric phosphine species [eqn. (2)].⁶ When the reaction was carried out in polar solvent, the coordination of another molecule of PPh_3 to a monomeric phosphine species caused the dissociation of a chloro ligand to give a cationic species, which could be isolated as a tetraphenylborate or a perchlorate salt.⁷ Since it can be assumed that the Rh^{I} cationic complex generated by the dissociation of a chloro ligand in MeCN would catalyse the



reaction via the *cis* addition, we examined the Rh^{I} cationic complex catalysed hydrosilylation of hex-1-yne with Et_3SiH .

We carried out the reaction catalysed by $[\text{Rh}(\text{cod})_2\text{BF}_4 + \text{PPh}_3$ in acetone [eqn. (3)]. As expected, the (*E*)-vinylsilane 2 was obtained (99% selectivity). The present result clearly indicates that Rh^{I} cationic complex is the active species in *cis* addition.

Further mechanistic studies and Rh^{I} cationic complex-catalysed hydrosilylations are in progress.

Received, 4th May 1993; Com. 3/02539J

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