Coupling Reactions between Grignard Reagents and Silicon–Hydrogen Bonds, Catalysed by a Nickel(II) Complex

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Summary A new method for Si–C bond formation involves coupling reactions of Grignard reagents with Si–H bonds in the presence of transition metal catalysis: the stereochemistry of the reactions is given.

THE coupling reactions of organomagnesium compounds with Si–F, Si–Cl, and Si–OMe bonds of (I) are highly stereospecific.[1] They proceeded with retention or inversion of configuration, depending both on leaving group and reagent. Although Gilman and Zuech proved that phenylmagnesium bromide can react with diphenylsilane,[2] it is well known that Grignard reagents are unreactive toward silicon hydrides.[3]

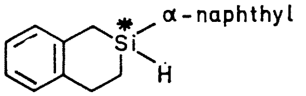
We have now prepared some tetrasubstituted silanes (II) containing the 2-(1,2,3,4-tetrahydro-2-α-naphthyl-2-silanaphthyl) group by coupling organomagnesium compounds with a Si–H bond in the presence of transition metal catalysis.

From the reaction of various RMgX with the cyclosilane (I) in diethyl ether, at ambient temperature, and with 5% of bis(triphenylphosphine)nickel chloride,[4,5] good yields of tetrasubstituted silanes are obtained (Table). Saturated Grignard reagents do not react and crotylmagnesium bromide gives only the linear product. The predominant stereochemistry (Table) is retention of configuration based on relative configurations previously determined.[1,6,7] The stereochemical data agree with those obtained with the corresponding organolithium[7] or organosodium[8] reagents, when coupled with the same Si–H bond. The ability of this catalyst to promote coupling between Grignard reagents and Si–H bonds permits the synthesis of optically active unsaturated silicon compounds with good optical purity; Grignard compounds are much easier to prepare than their lithium or sodium analogues (R = allyl, crotyl, benzyl, vinyl). The use of silanes, which are difficult to racemise, instead of chloro- or fluoro-silanes in organometallic synthesis with Grignard reagents leads to a better stereoselectivity.

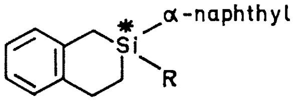
TABLE

	$[\alpha]_D$	Retention of configuration
MeMgBr	+ 78°	95%
PhMgBr	+122°	95
Vinyl·MgBr	+ 96°	96
Allyl·MgBr	+ 97°	98
Benzyl·MgCl	+ 90°	95
Crotyl·MgBr	+ 96°	98*
Pr^nMgBr	No reaction	

* Only linear compound obtained.



(I)



(II)

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