

**SILYL-SUBSTITUTED π -ALLYLNICKEL HALIDES.
A CONVENIENT SYNTHESIS OF ALLYLSILANES.**

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Abstract: 2-Trimethylsilylmethyl- π -allylnickel bromide can be prepared cleanly in high yields from 3-bromo-2-(trimethylsilylmethyl)propene and Ni(COD)₂. The reagent so generated reacts with a variety of organic halides, generating functionalized allylsilanes.

As part of a program aimed toward development of stereocontrolled cyclization reactions, we required efficient entry into allylsilanes in which suitable electrophiles had been incorporated. Due to the recent explosion of synthetic methods utilizing organosilicons, many techniques have been developed which allow facile synthesis of allylsilanes from readily available precursors.² Among the more general techniques utilized are silylation of allylmetallics with trimethylsilyl chloride² and silylation of allylic halides with silyllithium or silylcopper reagents.³ While both of these approaches to allylsilanes are useful in instances where unreactive functional groups are involved, it was less clear that highly reactive electrophiles (such as aldehydes and ketones) could be tolerated under these conditions without invocation of tedious protection-deprotection steps.

As a consequence, we sought to develop methods allowing incorporation of allylsilanes in which a variety of potential electrophiles could be tolerated. Silyl-substituted π -allylnickel halides appeared ideal for the task since both potential nucleophiles (π -allylnickel halide⁴ and allylsilane,^{2,5} respectively) have remarkably different reactivity profiles (Table I). These nucleophiles could thus be expected to be independently triggered in reactions with various electrophiles.

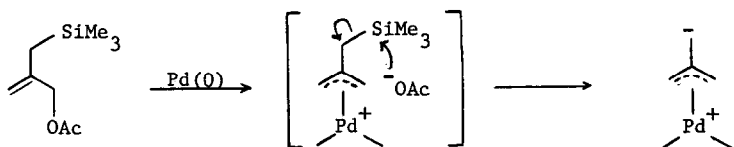
Table I. Comparative Reactivity of Allylsilanes/Lewis Acids and π -Allylnickel Halides with Various Electrophiles

Allylsilane Reactivity	Electrophile	π -Allylnickel Halide Reactivity
+	Acid halide	-
+	Acetal, Ketal	-
+	Aldehyde	±
+	Ketone	±
+	Epoxide	±
±	Alkyl halide	+
-	Aryl halide	+
-	Vinyl halide	+

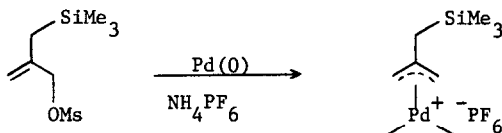
Key: + = Reacts readily; ± = Reacts only under forcing conditions or with certain members of this class; - = No reaction.

Based upon previously reported reactivity patterns of π -allylnickel halides as summarized in Table I,⁴ it appeared quite feasible to generate allylsilanes in the presence of such electrophiles as acid halides, aldehydes and ketones, and perhaps even epoxides. Each of these electrophiles is known to undergo Lewis acid-catalyzed reactions with allylsilanes.^{2,5}

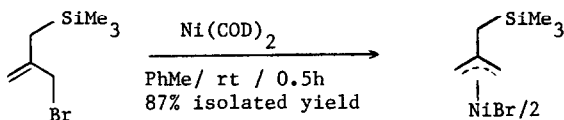
One potential problem of some concern was the possibility that desilylation of the initially-formed complex might occur as is the case with the corresponding π -allylpalladium complexes.⁶



The resulting trimethylenemethane-palladium complexes form the basis for Trost's very elegant approaches to cyclopentanoids by [3+2] cycloaddition processes.⁷ We were interested in maintaining the flexibility afforded by retaining the trimethylsilyl group in the final product. Recently, methods have been developed allowing this to be accomplished in π -allylpalladium complexes. Simple ion exchange reactions with NH_4PF_6 effectively removes the silylophilic acetate ion, allowing isolation of the 2-(trimethylsilylmethyl)- π -allylpalladium complex.⁸



We have found that such procedures are not required in the case of π -allylnickel halides. Treatment of 3-bromo-2-(trimethylsilylmethyl)propene⁹ with bis(1,5-cyclooctadiene)nickel(0)¹⁰ in toluene at room temperature for 0.5h led to quantitative conversion into the corresponding trimethylsilyl-substituted π -allylnickel halide complex. Recrystallization from diethyl ether afforded an 87% yield of pure complex.



Initial experiments have indicated that 3-iodo-2-(trimethylsilylmethyl)propene as well as the corresponding chloride, mesylate and trifluoroacetate do not work as well as the bromide. In most of these cases, extensive homocoupling of the substrates is observed, generating hexadiene derivatives. As a consequence, for all subsequent work the isolated 2-trimethylsilylmethyl- π -allylnickel bromide was utilized for synthetic studies.

It remained to determine whether the π -allylnickel halide complex so formed retained the same reactivity as the previously reported π -allylnickel bromides.⁴ In fact, this complex was found to react with extreme ease under very mild conditions to provide nearly quantitative yields of allylsilanes (Table II).



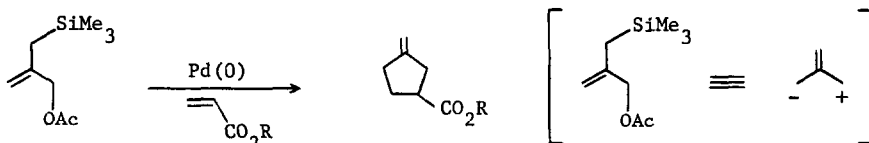
Table II. Reaction of 2-Trimethylsilylmethyl π -Allylnickel Bromide with Organic Halides.

Organic Halide	Solvent/Time(h) ^a	% Isolated Yield (GC)
1-Iododecane	HMPA / 1	100
<u>E</u> -1-Iodo-1-Hexene	DMF / 66	76
<u>Z</u> -1-Iodo-1-Decene	DMF / 16	83
Iodocyclohexane	HMPA / 2	88
Iodobenzene	DMF / 16	(94)
<u>p</u> -Bromoanisole	DMF / 16	78(95)
2-Iodoacetaldehyde, dimethyl acetal	HMPA / 5	76
3-Iodopropionaldehyde, ethylene glycol acetal	HMPA / 1	93
2-Chlorocyclohexanone	HMPA / 2	98

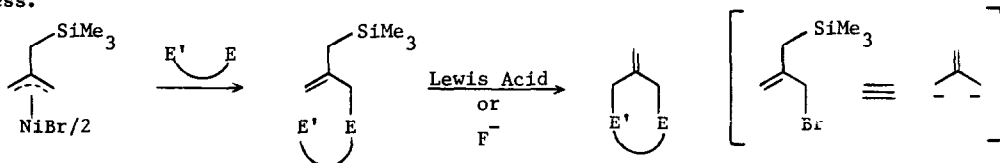
^aAll reactions were run at ambient temperature.

Of special note is the fact that ketones can readily be accommodated without protection under the mild reaction conditions. Furthermore, coupling with vinyl halides appears to be completely stereospecific.^{4b} Both E- and Z-alkenyl iodides react with complete retention of configuration.

As synthons for cyclization reactions, 2-trimethylsilylmethyl- π -allylnickel halides nicely complement trimethylenemethane palladium complexes⁷ as well as other similar "conjunctive" reagents.¹¹ The latter serve as dipolar [3+2] cycloaddition adducts, reacting with unsaturated esters and related substrates to generate cyclopentanoids.



On the other hand, silyl-substituted π -allylnickel bromides are potential dianionic synthons. Furthermore, due to this unique reactivity pattern, these reagents have an added advantage in being able to serve as net [3+n] cyclization synthons (where $n=2,3$, or 4). Thus, we anticipate that five-, six- and seven-membered rings may all be accessed² by a simple two-step process.



Work continues in this area in exploring other silyl-substituted synthons for cyclization, as well as in use of these reagents for stereocontrolled construction of carbocyclic ring systems.

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REFERENCES AND NOTES

1. National Science Foundation Predoctoral Fellow, 1984-1987.
2. (a) E. Colvin, "Silicon in Organic Synthesis," Butterworths, London, 1981. (b) W. P. Weber, "Silicon Reagents for Organic Synthesis," Springer-Verlag, New York, 1983.
3. J.G. Smith, S.E. Drozda, S.P. Petraglia, N.R. Quinn, E.M. Rice, B.S. Taylor, M. Viswanathan, J. Org. Chem., **49**, 4112 (1984).
4. (a) E.J. Corey, M.F. Semmelhack, J. Am. Chem. Soc., **89**, 2755 (1967). (b) L.S. Hegedus, R.K. Stiverson, J. Am. Chem. Soc., **96**, 3250 (1974). (c) L.S. Hegedus, S.D. Wagner, E.L. Waterman, K. Siirala-Hansen, J. Org. Chem., **40**, 593 (1975). (d) L.S. Hegedus, S. Varaprath, Organometallics, **1**, 259 (1982). (e) D.C. Billington, Chem. Soc. Rev., **14**, 93 (1985). (f) L.S. Hegedus, D.H.P. Thompson, J. Am. Chem. Soc., **107**, 5663 (1985).
5. I. Fleming, I. Paterson, Synthesis, 446 (1979).
6. B.M. Trost, D.M.T. Chan, J. Am. Chem. Soc., **101**, 6432 (1979).
7. (a) B.M. Trost, D.M.T. Chan, J. Am. Chem. Soc., **101**, 6429 (1979). (b) B.M. Trost, P. Renaut, J. Am. Chem. Soc., **104**, 6668 (1982). (c) B.M. Trost, T.N. Nanninga, T. Satoh, J. Am. Chem. Soc., **107**, 721, 721 (1985). (d) B.M. Trost, T.N. Nanninga, J. Am. Chem. Soc., **107**, 1075 (1985).
8. M.D. Jones, R.D.W. Kemmitt, J. Chem. Soc., Chem. Comm., 811 (1985).
9. Prepared from the corresponding mesylate by treatment with NaBr in DMF. (a) B.M. Trost, J.E. Vincent, J. Am. Chem. Soc., **102**, 5680 (1980). (b) B.M. Trost, D.M.T. Chan, T.N. Nanninga, Org. Syntheses, **62**, 58 (1984).
10. R. A. Schunn, Inorganic Syntheses, **15**, 5 (1974).
11. (a) Y. Ito, K. Nakayama, K. Yonezawa, T. Saegusa, J. Org. Chem., **39**, 3273 (1974). (b) S. Knapp, U. O'Connor, D. Mobilio, Tet. Lett., 4557 (1980). (c) I. Shimizu, Y. Ohashi, J. Tsuji, Tet. Lett., **25**, 5183 (1984). (d) D.L. Boger, C.E. Brotherton, J. Am. Chem. Soc., **106**, 805 (1984). (e) M. Miyashita, T. Yanami, T. Kumazawa, A. Yoshikoshi, J. Am. Chem. Soc., **106**, 2149 (1984). (f) I. Shimizu, Y. Ohashi, J. Tsuji, Tet. Lett., **26**, 3825 (1985). (g) J.P. Marino, E. Laborde, J. Am. Chem. Soc., **107**, 734 (1985).

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