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SELECTIVE SYNTHESIS OF (*E*)-CROTYLSILANES BY REACTION OF CROTYLMAGNESIUM BROMIDE WITH HYDROSILANES IN THE PRESENCE OF DICHLORO[1,1'-BIS(DIPHENYLPHOSPHINO)FERROCENE]NICKEL(II)

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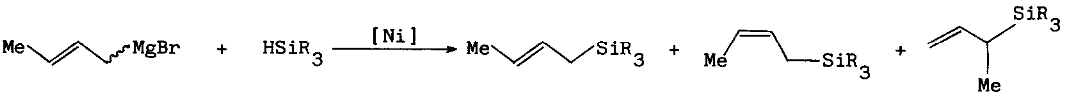
Summary: Dichloro[1,1'-bis(diphenylphosphino)ferrocene]nickel(II) was found to be an effective catalyst for the reaction of crotylmagnesium bromide with hydrosilanes to give (*E*)-crotylsilanes selectively.

We have previously reported that (*E*)-crotylsilane is a useful reagent for the reaction with aldehydes giving erythro homoallyl alcohols stereoselectively.[1,2] However, the selective synthesis of (*E*)-crotylsilanes has not been fully developed except for a few examples.[3] Here we report that (*E*)-crotylsilanes can be prepared selectively by use of dichloro[1,1'-bis(diphenylphosphino)ferrocene]nickel(II) [$NiCl_2$(dppf)][4] as a catalyst for the reaction of crotylmagnesium bromide with hydrosilanes.[5]

Hydrosilanes (1) were allowed to react with crotylmagnesium bromide (5 equiv) in the presence of several nickel complexes (5 mol%) in ether at ambient temperature (eq. 1). The results obtained are summarized in Table 1.



(1)

1a: $HSiMePh_2$ (*E*)-**2** (*Z*)-**2** **3**
1b: $HSiMe_2Ph$

Table 1 shows that $NiCl_2$(dppf) is the most selective catalyst. Thus, the reaction of diphenylmethylsilane (**1a**) catalyzed by $NiCl_2$(dppf) gave (*E*)-crotyldiphenylmethylsilane (**2a**)[6] in 98% selectivity, though the conversion was rather low under the standard reaction conditions (entry 1). High yield of (*E*)-**2a** could be obtained by using a large amount of the Grignard reagent (20 equiv) (entry 2). The triphenylphosphine complex $NiCl_2(PPh_3)_2$ was more catalytically active than $NiCl_2$(dppf) but much less selective producing (*E*)-**2a**, (*Z*)-**2a**, and α-methallyldiphenylmethylsilane (**3a**) in a ratio of 70 : 23 : 7 (entry 3).[7] Other nickel complexes, $NiCl_2$(dppp), $NiCl_2$(dppe), $Ni(acac)_2$, and $NiBr_2$ also catalyzed the reaction giving crotylsilanes **2a** selectively, but more than 10% of (*Z*)-**2a** was formed in addition to (*E*)-**2a** (entries 4-7). The high selectivity of $NiCl_2$(dppf) catalyst was also observed in the reaction of phenyldimethylsilane (**1b**). (*E*)-Crotylphenyldimethylsilane (**2b**)[8] could be obtained in 98% selectivity (entry 8). Here again other nickel catalysts were found to be less selective giving considerable amounts of isomeric byproducts (*Z*)-**2b** and **3b** (entries 9 and 10). For the reaction of trialkylsilanes such as diethylmethylsilane, the nickel complexes were not catalytically active, starting hydrosilanes being recovered.

Table 1. Reaction of Hydrosilanes (**1**) with Crotylmagnesium Bromide in the Presence of Nickel Catalysts.[a]

Entry	Hydrosilane	Catalyst[b]	Time (h)	Yield[c] (%)	Ratio[d] (*E*)-**2** : (*Z*)-**2** : **3**
1	$HSiMePh_2$ (**1a**)	$NiCl_2$(dppf)	16	39	98 : 2 : 0
2[e]		$NiCl_2$(dppf)	41	90 (88)[f]	98 : 2 : 0
3		$NiCl_2(PPh_3)_2$	16	53	70 : 23 : 7
4		$NiCl_2$(dppp)	16	30	86 : 14 : 0
5		$NiCl_2$(dppe)	16	33	90 : 10 : 0
6		$Ni(acac)_2$	16	31	88 : 12 : 0
7		$NiBr_2$	16	43	90 : 10 : 0
8[e]	$HSiMe_2Ph$ (**1b**)	$NiCl_2$(dppf)	69	72	98 : 2 : 0
9		$NiCl_2(PPh_3)_2$	45	73	52 : 23 : 25
10		$NiCl_2$(dppp)	45	42	86 : 14 : 0

[a] CrotylMgBr/**1**/Catalyst = 5/1/0.05, unless otherwise noted. [b] dppp = 1,3-bis(diphenylphosphino)propane. dppe = 1,2-bis(diphenylphosphino)ethane. [c] Determined by GLC using an internal standard. [d] Determined by ^1H NMR and GLC. [e] CrotylMgBr/**1**/Catalyst = 20/1/0.05. [f] Isolated yield.

In view of the mechanism proposed by Corriu and coworkers,[9] the allylation is considered to proceed via a nickel(II) intermediate bearing both silyl and π-crotyl groups from which the allylsilanes are released by reductive coupling. Though the precise effect of the dppf ligand remains to be clarified, it may be said that sterically bulkier dppf ligand[10] can make the methyl substituent in the π-crotyl group located in the syn position with respect to the central hydrogen to form (*E*)-crotylsilanes.[11]

REFERENCES AND NOTES

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2. Concerning the reaction of allylsilanes with aldehydes in the presence of a Lewis acid, see A. Hosomi and H. Sakurai, *Tetrahedron Lett.*, 1295 (1976); H. Sakurai, *Pure Appl. Chem.*, **54**, 1 (1982).
3. Nickel-catalyzed cross-coupling of (*E*)-propenyl bromide with trimethylsilylmethylmagnesium chloride gave (*E*)-crotyltrimethylsilane (ref 1).
4. T. Hayashi, M. Konishi, K. Yokota, and M. Kumada, *Chem. Lett.*, 767 (1980).
5. R. J. P. Corriu and J. P. Masse, *J. Chem. Soc., Chem. Commun.*, 213 (1970); R. J. P. Corriu, J. P. Masse, and B. Meunier, *J. Organomet. Chem.*, **55**, 73 (1973).
6. (*E*)-**2a**: ^1H NMR (CCl_4) δ 0.47 (s, 3H), 1.58 (d, *J* = 5 Hz, 3H), 1.89 (d, *J* = 6 Hz, 2H), 5.20-5.45 (m, 2H), 7.20-7.65 (m, 10H). For (*Z*)-**2a** and **3a**, their methyl doublets appeared at 1.41 (*J* = 5 Hz) and 1.08 (*J* = 7 Hz), respectively.
7. Corriu and coworkers have reported that the reaction of their cyclic hydrosilane with crotylmagnesium bromide catalyzed by $NiCl_2(PPh_3)_2$ gave only linear compound (ref 5).
8. J. Slutsky and H. Kwart, *J. Am. Chem. Soc.*, 95, 8678 (1973).
9. E. Colomer, R. J. P. Corriu, and B. Meunier, *J. Organomet. Chem.*, **71**, 197 (1974).
10. It has been shown that $PdCl_2$(dppf) has larger P-Pd-P angle than other bidentate phosphine-palladium complexes (T. Hayashi, M. Konishi, Y. Kobori, M. Kumada, T. Higuchi, and K. Hirotsu, *J. Am. Chem. Soc.*, in press).
11. We thank the Kawakami Foundation for partial financial support of this work.

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