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Nickel and Palladium Catalysed Coupling of Vinyl Selenides with Trimethylsilylmethylmagnesium Chloride : A New Synthesis of Allyl Silanes

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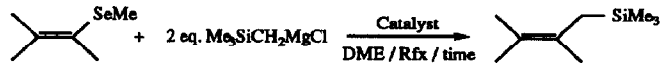
Abstract : A new access to allyl silanes by the Ni and Pd catalysed cross-coupling reactions of vinyl selenides and trimethylsilylmethylmagnesium chloride (DME / Rfx / 65-83 % yield) is reported.

As a result of the progressive recognition of their unique chemical reactivity, organosilicon compounds find increasing applications in organic synthesis [1]. Among others, allyl silanes are of particular importance [2], and a fair variety of methods are now available for their preparation [3]. On the other hand, it has also been recognised that transition metal (especially nickel and palladium) catalysed C-C bond forming reactions could be applied to the coupling of the appropriate vinyl (or aryl) and silicon moieties in order to produce the desired allyl silanes [4]. Herein we report our preliminary findings on a novel combination of reagents in this type of process, the coupling of vinyl selenides [5] with trimethylsilylmethylmagnesium chloride ($TMSCH_2MgCl$).

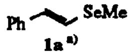
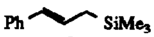
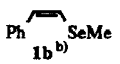
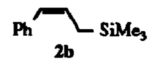
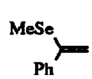
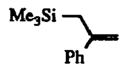
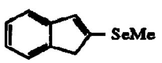
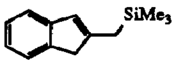
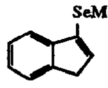
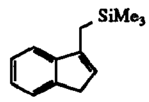
In a typical experiment 209 mg (1 mM) of vinyl selenide **1d**, 33 mg (5 mol.%) of $NiCl_2(PPh_3)_2$ and 4 ml of dimethoxyethane (DME, freshly distilled from sodium, THF and ether gave much lower yields) were placed under argon and 2.2 ml of an ethereal stock solution of $TMSCH_2MgCl$ (1M) was added by a syringe. The mixture was refluxed for 1 h, cooled to room temperature and diluted with 30 ml of ether. After washing twice with a 1N solution of sodium hydroxide and twice with water, the ethereal solution was dried and concentrated. The reddish-brown crude product was purified by column chromatography (basic Al_2O_3, activity grade IV, eluent pentane) to give 156 mg (77 % yield) of **2d** as a white solid, which can be recrystallized from pentane : m.p. 56 °C. The results of the other coupling reactions are displayed in the Scheme [6].

Entries 1-8 show that all these reactions are efficiently catalysed by both of the Ni and Pd complexes, but in general, they are considerably faster using $NiCl_2(PPh_3)_2$, and they take place with a high degree of conservation of the double bond geometry (entries 1-4). The results in entries 9 and 10 are surprising in that the main product appears to be indene in both cases; the indene : **2e** ratio being higher using $PdCl_2(PPh_3)_2$ than with $NiCl_2(PPh_3)_2$. The origin of this reduction of **1e** is not clear at present, but it is remarkable that, among the methylselenostyrenes, vinyl selenide **1c** (structurally related to **1e**) gives the lowest yield in allyl silane.

As for many transition metal catalysed reactions, not only the metal, but also the nature of the phosphine ligand plays a crucial role. This is also true here: when the reaction of entry 3 was tried under the same conditions and using $NiCl_2(dppe)$ as catalyst, after 10 h of reaction only 40 % conversion of **1b** into **2b** was reached.



1 **2**

Entry	Vinyl Selenide	Catalyst	time	Allyl Silane, Yield	
1	 **1a**[a]	5 mol % $NiCl_2(PPh_3)_2$	1.5 h	 **2a**	79 %[a]
2		5 mol % $PdCl_2(PPh_3)_2$	1.5 h		77 %[a]
3	 **1b**[b]	5 mol % $NiCl_2(PPh_3)_2$	3 h	 **2b**	73 %[c]
4		5 mol % $PdCl_2(PPh_3)_2$	6.5 h		70 %[c]
5	 **1c**	5 mol % $NiCl_2(PPh_3)_2$	4.5 h	 **2c**	71 %
6		5 mol % $PdCl_2(PPh_3)_2$	8.5 h		65 %
7	 **1d**	5 mol % $NiCl_2(PPh_3)_2$	1 h	 **2d**	77 %
8		5 mol % $PdCl_2(PPh_3)_2$	4.5 h		83 %
9		5 mol % $NiCl_2(PPh_3)_2$	6.5 h		(-)[d]
10	**1e**	5 mol % $PdCl_2(PPh_3)_2$	6 h	**2e**	(-)[e]

a) Mixture of stereoisomers (**1a**/**1b** = 87/13); b)Obtained from phenylacetylene (MeSeNa/EtOH/Rfx/24 h) as a 93/7 mixture of **1b** and **1c** wich isomerises on standing (-18 °C, 3 weeks) into a 91/ 3/ 6 mixture of **1a**/**1b**/**1c**, the latter mixture was used in the coupling reaction; c) GC analysis showed this to be a 94/2/4 mixture of **2a**/**2b**/**2c**; d) Complex mixture of products containing a large amount of a 2/1 mixture of indene and **2e**; e) Same as d) with indene/**2e** = 4/1

References and notes:

1) I. Fleming, J. Dunogues and R. Smithers in "Organic Reactions", J. Wiley and Son Inc., **1989**, Vol. 37, p. 57

2) I. Fleming in "Frontiers of Organosilicon Chemistry", Eds. A.R. Bassindale and P.P. Gaspar, The Royal Society of Chemistry, Cambridge, **1991**, p.321

3) For a review, see T.K. Sarkar, *Synthesis*, **1990**, 969 and 1101

4) Couplings of Me_3SiCH_2-metals have been described: i) with vinyl/aryl halides: a) K. Tamao, K. Sumitani, Y. Kiso, M. Zembayashi, A. Fujioka, S.-I. Kodama, I. Nakajima, A. Minato, M. Kumada, *Bull. Chem. Soc. Jpn.*, **1976**, *49*, 1958; b) T. Hayashi, M. Konishi, H. Ito, M. Kumada, *J. Am. Chem. Soc.*, **1982**, *104*, 4962; c) T. Hayashi, K. Kabeta, I. Hamachi, M. Kumada, *Tetrahedron Lett.*, **1983**, *24*, 2865; d) T. Hayashi, M. Konishi, Y. Okamoto, K. Kabeta, M. Kumada, *J. Org. Chem.*, **1986**, *51*, 3772; e) E.-I. Negishi, F.-T. Luo, C.L. Rand, *Tetrahedron Lett.*, **1982**, *23*, 27; f) P. Albaugh-Robertson, J.A. Katzenellenbogen, *Tetrahedron Lett.*, **1982**, *23*, 723; g) G.D. Prestwich, C. Wawrzenczyk, *Tetrahedron Lett.*, **1989**, *30*, 403; ii) with vinyl phosphonates : h) T. Hayashi, T. Fujiwa, Y. Okamoto, Y. Katsuro, M. Kumada, *Synthesis*, **1981**, 1001; i) S.J. Danishefsky, N.J. Mantlo, *J. Am. Chem. Soc.*, **1988**, *110*, 8129; iii) with silyl enol ethers: j) T. Hayashi, Y. Katsuro, M. Kumada, *Tetrahedron Lett.*, **1980**, *21*, 3915; iv) with vinyl triflates : k) M.G. Saulnier, J.F. Kadow, M.M. Tun, D.R. Langley, D.M. Vyas, *J. Am. Chem. Soc.*, **1989**, *111*, 8320.

5) Vinyl selenides are reaily accessible compounds i) from alkynes $^{a-f}$ by nucleophilic addition of selenolates or by radical addition of selenols; ii) from ketones and aldehydes by simple functional group manipulations $^{g-j}$. a) E.G. Kataev, V.N. Petrov, *Zh. Obshch. Khim.*, **1962**, *32*, 3699; b) L.M. Kataeva, L.N. Anonimova, L.K. Yuldasheva, E.G. Kataev, *Zh. Obshch. Khim.*, **1962**, *32*, 3965; c) J. Gosselk, *Angew. Chem. Int. Ed. Engl.*, **1963**, *2*, 660; d) J.V. Comasseto, J.T.B. Ferreira, N. Petragnani, *J. Organomet. Chem.*, **1981**, *216*, 287; e) H. Okamura, M. Miura, K. Kosugi, H. Takei, *Tetrahedron Lett.*, **1980**, *21*, 87; f) M. Renard, L. Hevesi, *Tetrahedron*, **1985**, *41*, 5939; g) M. Sevrin, W. Dumont, A. Krief, *Tetrahedron Lett.*, **1977**, 3835; h) K.M. Nsunda, L. Hevesi, *J. Chem. Soc. Chem. Commun.*, **1987**, 1518; i) W. Dumont, D. Van Ende, A. Krief, *Tetrahedron Lett.*, **1979**, 485; j) J. N. Denis, S. Desauvage, L. Hevesi, A. Krief, *Tetrahedron Lett.*, **1981**, *22*, 4009

6) All new compounds gave satisfactory elemental analyses, and their spectral (IR, MS, ^1H and ^{13}C NMR) data agree with the proposed structures.

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