1,1,1-Trichloro-2,2,2-trimethyldisilane: Reagent for Stereospecific Silylation of π-Allylpalladium Complexes

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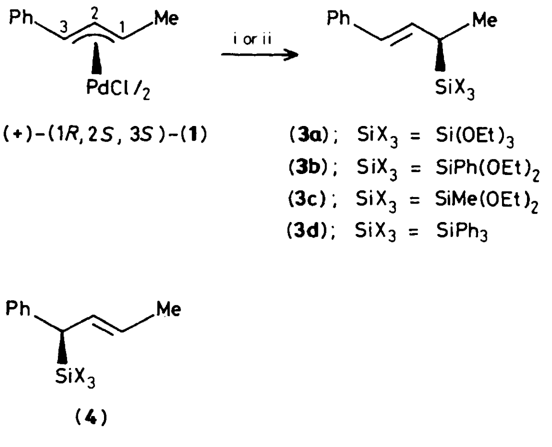
Reaction of optically active π-allylpalladium complexes with $Cl_3SiSiMe_3$ or $Cl_2PhSiSiMe_3$ in the presence of triphenylphosphine was found to proceed with retention of configuration to give optically active allylsilanes in high yields.

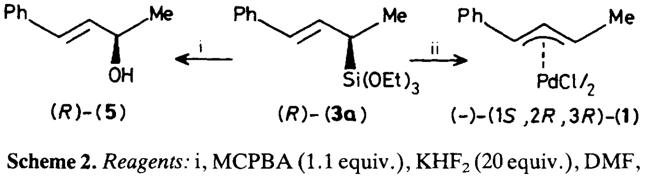
We have previously reported that optically active π-allylpalladium(II) complexes can be prepared by the reaction of optically active allylsilanes with palladium(II) and the chirality transfer proceeds stereospecifically with inversion of configuration.[1] Here we describe that its reverse reactions, *i.e.*, stereospecific silylation of π-allylpalladium(II) complexes, is achieved by making use of the disilanes $Cl_3SiSiMe_3$ or $Cl_2PhSiSiMe_3$ as silylating reagents.[2]

Several disilanes and silyl–metal reagents were examined for their reactivity and stereoselectivity in the silylation of the optically active π-allylpalladium(II) complex, (+)-(1*R*,2*S*,3*S*)-di-μ-chloro-bis(1-methyl-3-phenyl-π-allyl)dipalladium (**1**) {$[\alpha]_D^{20}$ +596° (chloroform), 84% enantiomeric excess (e.e.)}[1] (Scheme 1); 1,1,1-trichloro-2,2,2-trimethyldisilane[3] (**2a**) was found to be the best silylating reagent. Thus, (**2a**) (1.8 mmol) was added to a solution of the π-allylpalladium (**1**) (1.2 mmol) and triphenylphosphine (6.0 mmol) in tetrahydrofuran (THF) (12 ml). The mixture was stirred at 0 °C for 0.5 h and treated with ethanol and triethylamine to give in 80% yield the optically active allylsilane, (*E*)-1-phenyl-3-triethoxysilylbut-1-ene (**3a**) {$[\alpha]_D^{20}$ +11.7° (*c* 2.0, benzene)} as a single product. Formation of its regioisomer (**4a**) or trimethylsilyl analogues was not observed. The allylsilane (**3a**) was determined to be the (*R*) isomer of 79% e.e. by conversion into the known (*R*)-allyl alcohol (**5**)[4] by oxidation with *m*-chloroperbenzoic acid (MCPBA) and KHF_2 in dimethylformamide (DMF), a reaction which has been established to proceed with retention of configuration[5] (Scheme 2). It follows that the trichlorosilyl group attacked the π-allyl carbon atom from the same side as the palladium,† most probably *via* a π-allyl(trichlorosilyl)palladium intermediate. The configuration (*R*) of (**3a**) was confirmed by palladation (inversion of configuration)[1] with dichlorobis(acetonitrile)palladium(II) in methanol which gave (−)-(1*S*,2*R*,3*R*)-(**1**) {$[\alpha]_D^{20}$ −546° (chloroform), 77% e.e.} in quantitative yield. The inversion of the π-allyl group in π-allylpalladium complexes can take place in two steps (silylation and palladation).

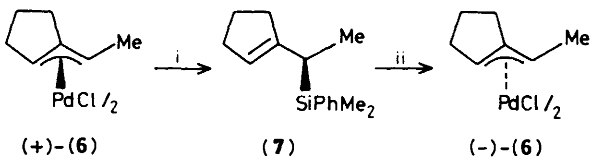


Scheme 1. *Reagents:* i, $Cl_3SiSiMe_3$ (**2a**), $Cl_2PhSiSiMe_3$ (**2b**), or $Cl_2MeSiSiMe_3$ (**2c**) (1.5 equiv.), PPh_3 (5 equiv.), THF, then EtOH and Et_3N; ii, Ph_3SiLi or $Ph_3SiAlEt_2$, PPh_3 (5 equiv.), THF, 25 °C.

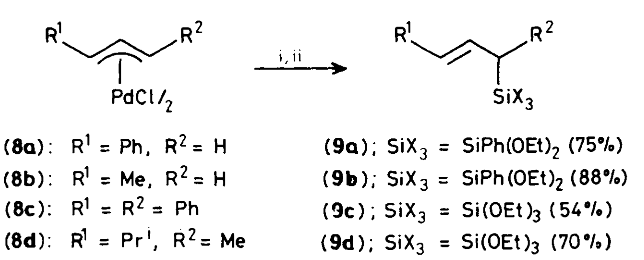
Of other disilanes, $Cl_2PhSiSiMe_3$[6] (**2b**) was the most reactive to give (0 °C, 40 h) a 96% yield of a mixture of the allylsilanes (**3b**) and (**4b**) in a ratio of 5 : 1. At higher temperature (40 °C), $Cl_2MeSiSiMe_3$ (**2c**) gave a 54% yield of allylsilanes [(**3c**) : (**4c**) 6 : 1], but only a trace (<5% yield) of silylation products was formed with $ClMe_2SiSiMe_3$, $Me_3SiSiMe_3$, $ClMe_2SiSiMe_2Cl$, and $Cl_2MeSiSiMe_2Cl$.‡ It seems that



Scheme 2. *Reagents:* i, MCPBA (1.1 equiv.), KHF_2 (20 equiv.), DMF, 24 h at room temp., 66% yield; ii, $PdCl_2(MeCN)_2$ (1.2 equiv.), MeOH, 14 h at room temp., 98% yield.



Scheme 3. *Reagents:* i, (**2b**), PPh_3 (5 equiv.), THF, 1 h at 0 °C, then MeMgBr–Et_2O (6 equiv.), 72% yield; ii, $PdCl_2(MeCN)_2$ (1.3 equiv.), MeOH, 53% yield.



Scheme 4. *Reagents:* i, for (**8a,b**), (**2b**), PPh_3 (5 equiv.), THF, 0 °C; for (**8c**), (**2a**), 1,2-bis(diphenylphosphino)ethane (1 equiv.), THF, 0 °C; for (**8d,e**), (**2a**), PPh_3 (5 equiv.), THF, 20 °C; ii, EtOH, Et_3N.

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† Similar stereochemistry has been reported in the palladium-catalysed silylation of an allyl acetate though the selectivity is not always high.[2b]

‡ Although an 80% yield of silylation product (**3a**) was obtained with $Cl_3SiSiCl_3$, it turned out that this disilane is effective only for the silylation of (**1**). Its reaction with other π-allylpalladium complexes such as (**8b**—**e**) failed to give any silylation products.

the unsymmetrical disilanes are more reactive than symmetrical ones and polarization of the silicon–silicon bond facilitates transfer of the silyl group from silicon to palladium. Use of triphenylsilyl-lithium (Ph_3SiLi)[7] and the silyl–aluminium reagent $Ph_3SiAlEt_2$[8] for the reaction with (**1**) resulted in low yields (45 and 35%, respectively) of the triphenyl(allyl)silane (**3d**)[9] with low stereoselectivity (14 and 57% e.e., respectively).

The retention of stereochemistry in the silylation was also demonstrated in the reaction of the optically active π-allylpalladium complex (**6**)[9] (Scheme 3). Treatment of (+)-(**6**) {$[\alpha]_D^{20}$ +20.3° (chloroform)} with (**2b**) in the presence of triphenylphosphine at 0 °C for 1 h followed by methylation with MeMgBr gave a 72% yield of the (*R*)-phenyldimethylsilane (**7**) whose configuration was determined by palladation to give (−)-(**6**) {$[\alpha]_D^{20}$ −17.8° (chloroform)}. High reactivity of the disilanes (**2a**) or (**2b**) was also observed in reactions with several π-allylpalladium complexes (**8a—e**) (Scheme 4). Silylation took place at the less substituted π-allyl carbon atom to give the corresponding (*E*)-allylsilanes (**9**) in high yields.

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