Chirality Transfer from Optically Active Allylsilanes to π-Allylpalladium Complexes

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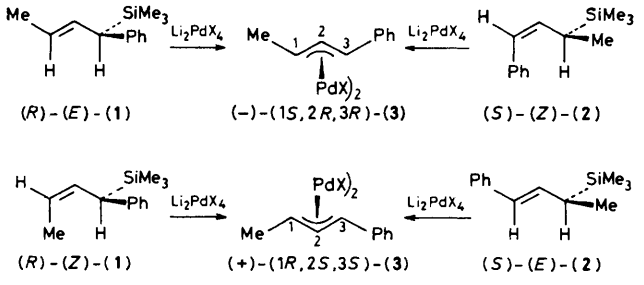
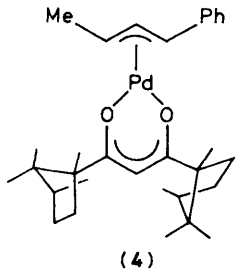
The reaction of lithium palladates with the optically active allylsilanes, (*E*)- and (*Z*)-1-phenyl-1-trimethylsilylbut-2-ene and (*E*)- and (*Z*)-1-phenyl-3-trimethylsilylbut-1-ene proceeds stereospecifically [*anti* attack of palladium(II) with respect to the leaving silyl group] to give optically active π-allylpalladium complexes containing the η^3-(1-methyl-3-phenylallyl) group in high yields.

In spite of increasing interest in π-allylpalladium complexes for organic synthesis,[1] only a few examples have so far been reported of optically active complexes whose chirality is due to unsymmetrical substitution at the co-ordinated π-allyl group.[2] We report here the first general procedure for the preparation of optically active π-allyl complexes by chirality transfer from allylsilanes.

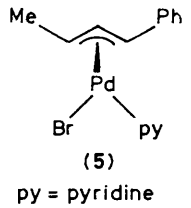
The optically active allylsilanes, (*E*)- and (*Z*)-1-phenyl-1-trimethylsilylbut-2-ene (**1**)[3] and (*E*)- and (*Z*)-1-phenyl-3-trimethylsilylbut-1-ene (**2**),† all of which have definite absolute configuration and enantiomeric purity, could be obtained in large quantities by asymmetric Grignard cross-coupling in the presence of a chiral ferrocenylphosphine–palladium catalyst. The allylsilane with the *E* double bond, (*R*)-(*E*)-(**1**) (77% e.e.), was allowed to react with a slight excess of lithium chloropalladate in methanol[4] to give, in 84% yield, di-μ-chloro-bis(1-methyl-3-phenyl-π-allyl)dipalladium (**3a**) [m.p. 161—163 °C (decomp.)] where both methyl and phenyl substituents are located in the *syn* positions with respect to the central hydrogen (Scheme 1). The π-allylpalladium complex (**3a**) has a large negative specific rotation, $[\alpha]_D^{20}$ −579° ($CHCl_3$), and did not racemize in solution at room temperature even after several days (entry 1, Table 1). Allowing the complex (−)-(**3a**) to react with the sodium enolate of di-(+)-camphorylmethane[5] [H(dcm)] gave a π-allylpalladium complex (**4**), with the dcm ligand, in quantitative yield. The ^{1}H n.m.r. spectrum of the dcm complex showed the presence of two diastereoisomeric isomers in the ratio 91 : 9.‡ It follows that the enantiomeric purity of the π-allylpalladium complex (−)-(**3a**) is 82%. A similar result was obtained from palladation with lithium bromopalladate (entry 3, Table 1). In the reaction of the *Z* allylsilane (*R*)-(*Z*)-(**1**) (24% e.e.) with lithium chloropalladate



Scheme 1



(**4**)



(**5**)

py = pyridine

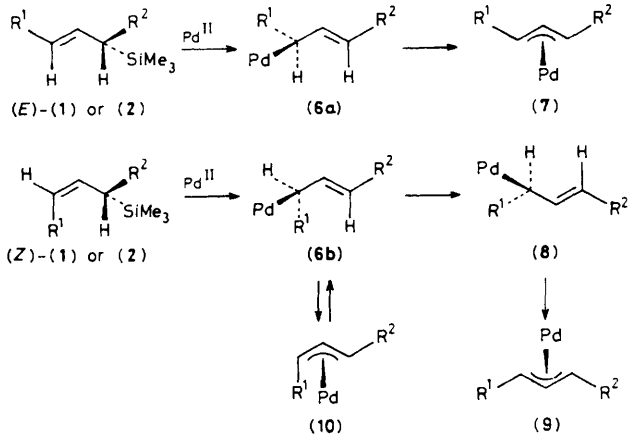
† The allylsilanes (*E*)-(**2**) and (*Z*)-(**2**) were prepared by asymmetric cross-coupling of 1-trimethylsilylethylmagnesium chloride with (*E*)- and (*Z*)-β-bromostyrene, respectively, in the presence of dichloro[(*R*)-*N*,*N*-dimethyl-1-{(*S*)-2-(diphenylphosphino)ferrocenyl}ethylamine]palladium(II). Full details will be reported elsewhere.

‡ The ^{1}H n.m.r. resonances attributable to methine at C-3 (δ 4.21 and 4.25) and one of the dcm methyls at the highest field (δ 0.31 and 0.40) were used for the determination of the enantiomeric purity.

Table 1. Reaction of allylsilanes (**1**) and (**2**) with lithium palladates.[a]

Entry	Allylsilane	(% e.e.)	Palladate	Product[b] (yield, %)	$[\alpha]_D^{20}$/°[c]	% e.e. (configuration)
1	(*R*)-(*E*)-(**1**)	(77)	Li_2PdCl_4	(**3a**) (84)	−579	82[d] (1*S*,2*R*,3*R*)
2	(*R*)-(*E*)-(**1**)	(81)	Li_2PdCl_4	(**3a**) (83)	−603	85[e] (1*S*,2*R*,3*R*)
3	(*R*)-(*E*)-(**1**)	(77)	Li_2PdBr_4	(**3b**) (82)[f]	−572	80[d] (1*S*,2*R*,3*R*)
4	(*R*)-(*Z*)-(**1**)	(24)	Li_2PdCl_4	(**3a**) (100)	+163	26[d] (1*R*,2*S*,3*S*)
5	(*S*)-(*E*)-(**2**)	(71)	Li_2PdCl_4	(**3a**) (79)	+493	70[e] (1*R*,2*S*,3*S*)
6	(*S*)-(*Z*)-(**2**)	(59)	Li_2PdCl_4	(**3a**) (76)	−416	59[e] (1*S*,2*R*,3*R*)

[a] To a solution of the lithium palladate (5.0 mmol) in methanol (10 ml) was added the allylsilane (4.6 mol), and the mixture was stirred at 0 °C for 3 h. The yellow precipitates formed were collected on a glass-filter, washed with cold methanol, and dried under reduced pressure. [b] (**3a**): m.p. 161—163 °C (decomp.); ^{1}H n.m.r. ($CDCl_3$): δ 1.27 (d, *J* 7 Hz, 3H), 3.92 (double q, *J* 11 and 7 Hz, 1H), 4.40 (d, *J* 11 Hz, 1H), 5.62 (t, *J* 11 Hz, 1H), and 7.06—7.65 (m, 5H). (**3b**): m.p. 167—170 °C; ^{1}H n.m.r. ($CDCl_3$): δ 1.44 (d, *J* 7 Hz, 3H), 4.01 (double q, *J* 11.5 and 7 Hz, 1H), 4.51 (d, *J* 11.5 Hz, 1H), 5.69 (t, *J* 11.5 Hz, 1H), and 7.10—7.65 (m, 5H). [c] *c* 0.7—1.2, $CHCl_3$. [d] Determined from the ^{1}H n.m.r. spectrum of the diastereoisomeric dcm complex (see text). [e] Determined from the optical rotation. The maximum rotation of (**3a**) was calculated to be ±706° based on the data in entry 1. [f] Reaction for 18 h.



Scheme 2

the π-allylpalladium complex (**3a**) was again formed with both the methyl and phenyl *syn*. A positive rotation, $[\alpha]_D^{20}$ +163° ($CHCl_3$) was obtained, indicating the formation of the π-allyl complex with opposite configuration to that from (*R*)-(*E*)-(**1**) (entry 4, Table 1). The enantiomeric purity was determined to be 26% from the ^{1}H n.m.r. spectrum of the dcm derivative.‡ The reaction of (**2**) also proceeded in a similar manner (entries 5 and 6, Table 1). Thus, (*S*)-(*E*)-(**2**) (71% e.e.) led to (+)-(**3a**) (70% e.e.) while (*S*)-(*Z*)-(**2**) (59% e.e.) led to (−)-(**3a**) (59% e.e.). These results demonstrate that the chirality transfer is completely stereospecific, the enantiomeric excess of all the products being essentially identical, within experimental error, with that of the starting allylsilanes.

The absolute configuration of (−)-(**3**) has been determined to be 1*S*,2*R*,3*R* by the *X*-ray crystal structure analysis of bromo(1-methyl-3-phenyl-π-allyl)(pyridine)palladium (**5**).§ The S_E' reaction of allylsilanes has been shown to proceed with *anti* stereochemistry with several kinds of electrophiles,[3,6] as does the palladation reported here. Scheme 2 illustrates a mechanism to explain the stereochemical results. Thus, the palladium(II) attacks the double bond of the allylsilane from the side opposite to the leaving trimethylsilyl group (*anti* attack) to produce the σ-allylpalladium intermediate (**6**). The intermediate (**6a**) formed from (*E*)-allylsilane rearranges to the π-allylpalladium complex (**7**) with the two substituents *syn*. In the reaction of the (*Z*)-allylsilane, the σ-allyl intermediate (**6b**) undergoes rotation of the alkenyl group by 180° and the resulting intermediate (**8**) leads to the π-allylpalladium complex (**9**) which is an enantiomer of (**7**).[7] Other π-allyl species such as (**10**) with the two substituents *syn* and *anti* may be involved during the formation of (**9**).[8]

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7 It has been reported that the 1,3-disubstituted π-allylpalladium complexes have a strong tendency to adopt both substituents *syn* for steric reasons. See for example references 2a and 2b and B. M. Trost, P. E. Strege, L. Weber, T. J. Fullerton, and T. J. Dietsche, *J. Am. Chem. Soc.*, 1978, **100**, 3407.

8 The 1,3-unsymmetrically substituted π-allyl system does not racemize *via* the π-allyl–σ-allyl rearrangement. References 2a and 2b; B. Bosnich and P. B. Mackenzie, *Pure Appl. Chem.*, 1982, **54**, 189.

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