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Stereochemistry and mechanism of the ligand-coupling reaction of an optically active acetylacetonato(π-allyl)palladium complex

Tamio Hayashi *, Akihiro Yamamoto, and Yoshihiko Ito*

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606 (Japan)

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Abstract

The reaction of optically active acetylacetonato(1-methyl-3-phenyl-π-allyl)palladium(II) with triphenylphosphine in THF gave [1-((*E*)-styryl)ethyl]acetylacetone with inversion of configuration, which indicates that the acetylacetonate anion attacked the π-allyl carbon of a cationic phosphine complex from the side opposite to palladium.

Introduction

Acetylacetonato(π-allyl)palladium(II) complexes undergo ligand coupling to give allylacetylacetones by reaction with carbon monoxide [1], and the mechanism of the coupling has attracted attention [2] in connection with the reaction of nucleophiles with π-allylpalladium complexes [3], which proceeds either with inversion or retention depending on the nature of the nucleophile [4]. Here we report the stereochemical results of ligand coupling in an optically active acetylacetonato(π-allyl)palladium complex, which demonstrates the external attack of the acetylacetonate anion at the π-allyl carbon.

Results and discussion

The optically active complex, di-μ-chlorobis(1-methyl-3-phenyl-π-allyl)dipalladium(II) (**1**) ($[\alpha]_D^{20}$ −586° (chloroform), 83% ee (1*S*,2*R*,3*R*)) [5], by treatment with one equivalent of sodium acetylacetonate in THF at 0°C, was converted quantitatively into acetylacetonato(1-methyl-3-phenyl-π-allyl)palladium(II) (**2**) ($[\alpha]_D^{20}$ −342° (*c* 0.98, chloroform)) which should have the same configuration and enantiomeric purity as **1** (Scheme 1). Treatment of the complex **2** with carbon monoxide by a published procedure [1,2] gave only a small amount (< 10%) of coupling product. We have found that a high yield of the product can be obtained when an excess of triphenylphosphine is used instead of carbon monoxide. Thus, the

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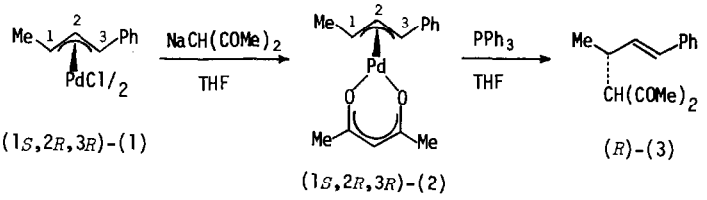
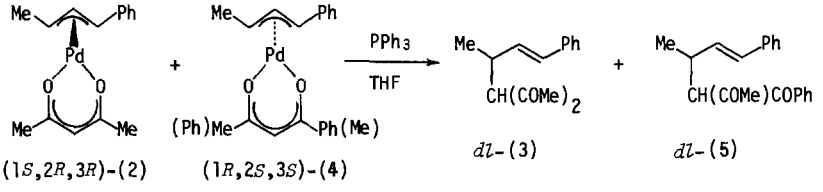


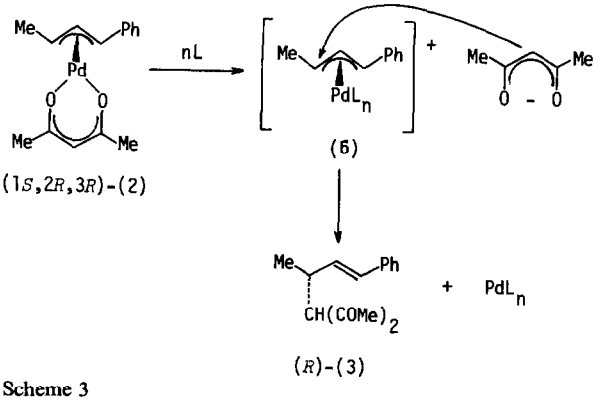
Scheme 1

acetylacetonate complex (1*S*,2*R*,3*R*)-**2** (83% ee) was allowed to react with five equivalents of triphenylphosphine in THF at room temperature for 50 min to give (*R*)-[1-((*E*)-styryl)ethyl]acetylacetone (**3**) [6] ($[\alpha]_D^{20}$ +115° (*c* 0.95, chloroform), 87% ee)) in 94% yield, which was accompanied by the formation of tetrakis(triphenylphosphine)palladium(0). The stereospecific formation of (*R*)-**3** from (1*S*,2*R*,3*R*)-**2** indicates that the coupling reaction proceeds selectively with inversion of configuration with respect to the C(1) carbon of the π-allyl. The reaction of (1*S*,2*R*,3*R*)-**2** with one equivalent of triphenylphosphine proceeded slowly to give (*R*)-**3** of 31% ee in low yield (30–40%).

Benzoylacetonate complex (1*R*,2*S*,3*S*)-**4** (79% ee), which consists of *cis* and *trans* isomers in a ratio of 6/4 (see Experimental), was also prepared by treatment of (1*R*,2*S*,3*S*)-**1** (79% ee) with sodium benzoylacetonate. Addition of an excess of triphenylphosphine to a mixture of equimolecular amounts of the acetylacetonate complex (1*S*,2*R*,3*R*)-**2** (83% ee) and its enantiomeric benzoylacetonate complex



Scheme 2



Scheme 3

(1*R*,2*S*,3*S*)-**4** (79% ee), gave **3** ($[\alpha]_D^{20}$ +1° (chloroform)) and its benzoylacetone analogue **5** ($[\alpha]_D^{20}$ ±0° (chloroform)), in 79% and 93% yields, respectively (Scheme 2). The formation of the racemic products demonstrates that the present reaction is intermolecular to give the crossover products.

The stereochemical results can be visualized by the mechanism shown in Scheme 3. The acetylacetonate ligand dissociates from the palladium atom upon addition of triphenylphosphine to leave a cationic π-allylpalladium bearing phosphine ligands **6**, and the acetylacetonate anion intermolecularly attacks the π-allyl carbon of the cationic complex **6** from the side opposite to palladium to give the allylacetylacetone (*R*)-**3** with inversion of configuration. A similar dissociation mechanism has been proposed for the alkylation of π- and σ-allylplatinum(II) complexes [7].

Experimental

(1S,2R,3R)-Acetylacetonato(1-methyl-3-phenyl-π-allyl)palladium (2)

To a yellow suspension of 170 mg (0.62 mmol) of the optically active complex, (1*S*,2*R*,3*R*)-di-μ-chlorobis(1-methyl-3-phenyl-π-allyl)dipalladium(II) (**1**) ($[\alpha]_D^{20}$ −586° (chloroform), 83% ee) [5] in 5 ml of THF was added a white suspension of sodium acetylacetonate in THF (at 0°C), which had been prepared by the slow addition of 62 mg (0.62 mmol) of acetylacetone to a suspension of 15 mg (0.63 mmol) of sodium hydride in 3 ml of THF at 0°C. The resulting clear yellow solution was stirred at 0°C for 10 min, then hydrolyzed with water, and extracted with ether. The ether extracts were washed with water, dried over anhydrous magnesium sulfate, and stripped of solvent to give 210 mg (100% yield) of (1*S*,2*R*,3*R*)-acetylacetonato(1-methyl-3-phenyl-π-allyl)palladium(II) (**2**) ($[\alpha]_D^{20}$ −342° (*c* 0.98, chloroform)). ^{1}H NMR ($CDCl_3$): δ 1.37 (d, 3H, *J* 7 Hz), 1.80 and 1.95 (a pair of s, 6H), 3.73 (dq, 1H, *J* 11 and 7 Hz), 4.23 (d, 1H, *J* 11 Hz), 5.23 (s, 1H), 5.60 (t, 1H, *J* 11 Hz), and 7.1–7.6 (m, 5H). Found: C, 53.09; H, 5.30. $C_{15}H_{18}O_2Pd$ calc: C, 53.51; H, 5.39%.

Reaction of (1S,2R,3R)-2 with triphenylphosphine

To a pale yellow solution of 81 mg (0.24 mmol) of the acetylacetonato complex (1*S*,2*R*,3*R*)-**2** (83% ee) in 5 ml of THF was added 314 mg (1.20 mmol) of crystalline triphenylphosphine in one portion at room temperature. In 10 min, the yellow precipitate of tetrakis(triphenylphosphine)palladium(0) appeared. The mixture was stirred at room temperature for 50 min, and preparative TLC on silica gel (hexane/ethyl acetate = 5/1) gave 52 mg (94% yield) of [1-((*E*)-styryl)ethyl] acetylacetone (**3**) ($[\alpha]_D^{20}$ +115° (*c* 0.95, chloroform)). (lit. [6] (*S*)-**3**; $[\alpha]_D^{20}$ −132° (chloroform)).

(1R,2S,3S)-Benzoylacetonato(1-methyl-3-phenyl-π-allyl)palladium (4)

In a similar manner to the preparation of (1*S*,2*R*,3*R*)-**2**, 164 mg (0.60 mmol) of (1*R*,2*S*,3*S*)-**1** ($[\alpha]_D^{20}$ +553° (chloroform), 79% ee) [5] was treated with 0.60 mmol of sodium benzoylacetonate in THF at room temperature for 30 min to give 240 mg (100% yield) of (1*R*,2*S*,3*S*)-**4** ($[\alpha]_D^{20}$ +277°C (*c* 1.0, chloroform)). Variable-temperature ^{1}H NMR studies showed that the complex **4** consisted of regioisomers in a 6/4 ratio below about 25°C and they interconvert at higher temperature. ^{1}H NMR ($CDCl_3$ at −24°C): δ 1.43 and 1.45 (a pair of *d*, *J* 6 Hz, 3H), 1.94 and 2.11 (a pair

of s, 3H), 3.64–4.01 (m, 1H), 4.26 and 4.35 (a pair of d, *J* 11 Hz, 1H), 5.68 and 5.74 (a pair of t, *J* 11 Hz, 1H), 5.94 (s, 1H), 7.06–7.94 (m, 10H). ^{1}H NMR ($CDCl_3$ at 39 °C): δ 1.42 (d, *J* 6 Hz, 3H), 2.06 (broad s, 3H), 3.85 (dq, *J* 11 and 6 Hz, 1H), 4.34 (d, *J* 11 Hz, 1H), 5.71 (t, *J* 11 Hz, 1H), 5.93 (s, 1H), 7.03–7.98 (m, 10H). An analytically pure sample could not be obtained owing to the difficulty in purification.

Reaction of a mixture of (1S,2R,3R)-2 and (1R,2S,3S)-4 with triphenylphosphine

To a solution of 202 mg (0.60 mmol) of (1*S*,2*R*,3*R*)-**2** (83% ee) and 239 mg (0.60 mmol) of (1*R*,2*S*,3*S*)-**4** (79% ee) in 24 ml of THF was added 1.574 g (6.0 mmol) of triphenylphosphine at room temperature. The mixture was stirred for 40 min and stripped of solvent. Preparative TLC on silica gel (hexane/ethyl acetate = 5/1) yielded 109 mg (79% yield) of **3** ($[\alpha]_D^{20}$ +1° (*c* 1.1, chloroform)) and 163 mg (93% yield) of [1-((*E*)-styryl)ethyl]benzoylacetone (**5**) ($[\alpha]_D^{20}$ ±0° (*c* 1.0, chloroform)). The benzoylacetone **5** was shown by ^{1}H NMR to be a mixture of diastereomeric isomers in a ratio of 57/43. ^{1}H NMR ($CDCl_3$) of major isomer: δ 1.07 (d, *J* 7 Hz, 3H), 2.04 (s, 3H), 3.16–3.64 (m, 1H), 4.39 (d, *J* 10 Hz, 1H), 6.04 (dd, *J* 15 and 8 Hz, 1H), 6.49 (d, *J* 15 Hz, 1H), 7.04–8.20 (m, 10H). ^{1}H NMR ($CDCl_3$) of minor isomer: δ 1.14 (d, *J* 7 Hz, 3H), 2.11 (s, 3H), 3.16–3.64 (m, 1H), 4.43 (d, *J* 10 Hz, 1H), 5.94 (dd, *J* 15 and 8 Hz, 1H), 6.36 (d, *J* 15 Hz, 1H), 7.04–8.20 (m, 10H). Found: C, 82.23; H, 6.84. $C_{20}H_{20}O_2$ calc: C, 82.16; H, 6.89%.

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