

*Journal of Organometallic Chemistry*, 378 (1989) 115–124  
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands  
JOM 20211

## Chiral induction in the synthesis of 4,4-dimethyl-1-phenylpenta-1,2-diene (1-Ph-3-t-Bu-allene) catalyzed by chiral phosphine complexes of palladium

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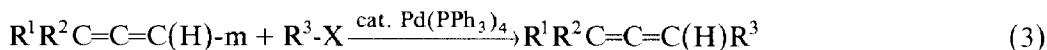
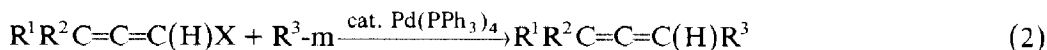
(Received June 26th, 1989)

### Abstract

4,4-Dimethyl-1-phenylpenta-1,2-diene (1-phenyl-3-t-butylallene) (**2**) has been prepared by a palladium-catalyzed cross-coupling reaction between either in situ prepared 4,4-dimethylpenta-1,2-dienylzinc chloride and iodobenzene (Route A) or 1-bromo-4,4-dimethylpenta-1,2-diene and phenylzinc chloride (Route B). Several palladium complexes with known chiral phosphine, phosphine-amine and diphosphine ligands were used as chiral catalysts. The highest enantiomeric excess (25% ee) was obtained via route A with catalysis by the 1/1 complex of palladium chloride and (*R,R*)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane, {(*R,R*)-diop}. The enantiomeric excess (19% ee) when the complex Pd{(*R,R*)-diop}<sub>2</sub> was used appeared to be independent of the temperature, the amount of catalyst, and the ratio of the reagents. However, when a magnesium or copper reagent was used instead of the zinc reagent, the configuration was reversed (3–10% ee). The suggested intermediate PdIPh{(*R,R*)-diop} was prepared by treating one equivalent of (*R,R*)-diop with PdIPh(tmeda) (tmeda = *N,N,N',N'*-tetramethylethanediamine) and studied by <sup>31</sup>P NMR spectroscopy. PdIPh{(*R,R*)-diop} appeared to be present in solution as an equilibrium mixture of *cis*-chelating and *trans*-monodentate bonded species, with the ratio depending upon the concentration and the palladium/diphosphine ratio. Reaction of a slight excess of 4,4-dimethyl-1,2-pentadienyl-zinc chloride or -magnesium chloride with PdIPh{(*R,R*)-diop} gave 1-phenyl-3-t-butylallene **2** with the same configuration, though with a slightly smaller ee than that from the reactions catalyzed by PdCl<sub>2</sub>{(*R,R*)-diop} or Pd{(*R,R*)-diop}<sub>2</sub>. The results strongly suggest that reaction of the organometallic reagent with the palladium(II) intermediate PdIPh{(*R,R*)-diop} is the enantiodifferentiating step in the catalytic cycle.

## Introduction

The synthesis of allenes is well documented [1] and there are numerous examples of their use in organic synthesis [2]. Effective methods for the synthesis of allenes employing palladium-catalyzed cross-coupling reactions have been devised. These rely on substitutions of propynylic esters or halides (eq. 1) or halogenoallenes (eq. 2) by use of organo-magnesium or -zinc reagents [3]. Also, allenylmetal reagents may be used in combination with, e.g., alkenyl, alkynyl or aryl halides (eq. 3) [4].



(m = ZnCl, MgCl, Cu)

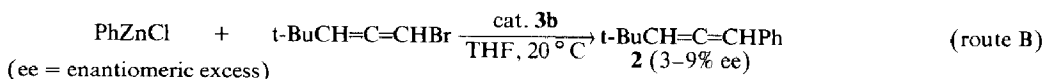
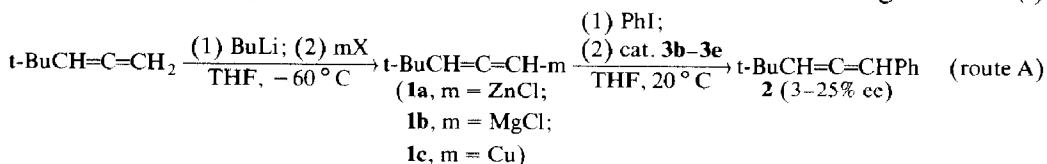
(X = halogen, Y = X, OAc, OSO<sub>2</sub>Me)

Enantiomerically-enriched allenes have previously been obtained with excellent stereoselectivities from enantiomerically pure (or enriched) propynylic esters by 1,3-substitution reactions with modified aluminumhydrides [5], organocopper reagents [6], or palladium-catalyzed coupling reactions [7]. Recently, stereoselective copper- [8], nickel- [9] and palladium-mediated [10] conversions enantiomerically enriched halogenoallenes were also shown to be effective for the synthesis of optically active allenes. These approaches rely on the availability of enantiomerically pure (or enriched) precursors in stoichiometric amounts.

The alternative approach, i.e. use of racemic or achiral reagents in combination with a catalytic amount of an enantiomerically-pure chiral metal catalyst, has been employed in, e.g., hydrogenation of alkenes [11] and reactions of vinylic halides with Grignard reagents [12], but this method has not previously been applied to the enantioselective synthesis of axially dissymmetric 1,3-substituted allenes. The above-mentioned enantiodifferentiating reactions involve the creation or kinetic resolution of chiral tetrahedral carbon sites. As the factors governing the extent of helical chirality associated with chiral allenes and the ways of inducing and transferring this type of chirality are still not well known, a study intended to extend knowledge of this subject was deemed to be of interest. We report here our results on the chiral induction in the synthesis of a selected allene.

## Approach

The reaction of 1-metallio-4,4-dimethylpenta-1,2-diene (**1a–1c**) with iodobenzene (Scheme 1; route A) was chosen as a model reaction for the following reasons: (i)



Scheme 1. Two routes for the synthesis of t-BuCH=C=CHPh (**2**).

**1a–1c** are readily obtained from 4,4-dimethyl-1,2-pentadiene; (ii) a reasonable stereoselection in diastereomeric intermediates could be expected, since the difference between the t-Bu and H substituents on the allenyl C(3) atom is large; (iii) the reaction with iodobenzene proceeds readily in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub>; (iv) the specific rotation, viz.  $[\alpha]_D^{20} +370^\circ\text{C}$ , is known for the product (*S*)-t-BuCH=C=CHPh (**2**) [6d].

Several palladium complexes of chiral monophosphine, bis(phosphine) and phosphine-amine ligands (Fig. 1) were tested for their effectiveness as catalysts for the synthesis of enantiomerically enriched allene **2**. For one specific catalyst, several parameters (reagent/substrate ratio, amount of catalyst, temperature, metal in reagent **1a–1c**) were varied in order to optimize chiral induction. For comparison, the alternative route (Scheme 1; route B) employing a phenylzinc reagent and 1-bromo-4,4-dimethylpenta-1,2-diene as the substrate, was also examined. The latter reaction will also yield the allene **2**, but probably via a complementary sequence of oxidative addition and transmetalation reactions. A comparison of the amount and sense of induced chirality in the product **2** obtained by these two routes may provide information about the reaction sequence and the diastereoselective step.

## Results and discussion

### Catalytic reactions (Route A).

Treatment of 4,4-dimethylpenta-1,2-diene (t-Bu-allene) with BuLi in THF at  $-60^\circ\text{C}$  results in selective deprotonation at the 1-position [13]. Subsequent metathesis with ZnCl<sub>2</sub> gives the zinc reagent **1a** in solution.

The results of the reactions of **1a** with iodobenzene to yield **2** are listed in Table 1. In the absence of a catalyst no reaction occurred and iodobenzene was recovered quantitatively. When 0.4 to 3.0 mol% of the palladium complexes of various ligands (see Fig. 1) were used, the conversion was generally reasonable to good.

The ee's were moderate and varied between 4 and 25%. The highest ee (25%) was obtained with PdCl<sub>2</sub>{(*R,R*)-diop} (**3c**) as (pre)catalyst, which also brought about a quantitative conversion under mild conditions. The palladium(0) complex, Pd{(*R,R*)-diop}<sub>2</sub> (**3b**), used either as the pure solid or prepared in situ by mixing Pd(PPh<sub>3</sub>)<sub>4</sub> with 2 equivalents of (*R,R*)-diop, gave a somewhat lower ee (Table 1,

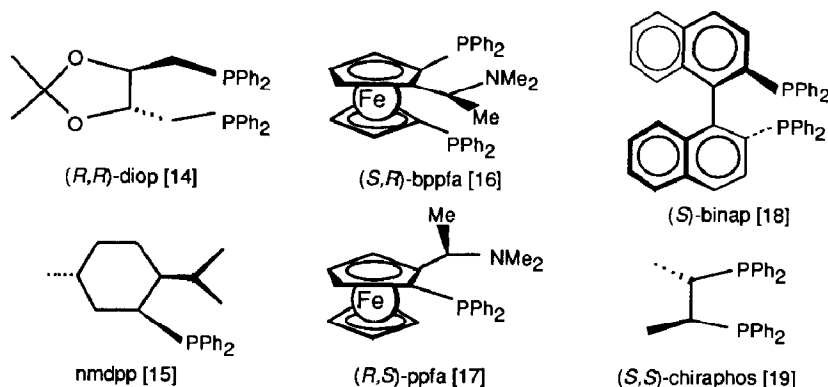


Fig. 1. Chiral phosphine ligands and their abbreviations.

Table 1

Chiral induction in the formation of *t*-BuCH=C=CHPh (**2**) from *t*-BuCH=C=CHm (**1a–1c**) and PhI <sup>a</sup> catalyzed by chiral palladium complexes

Entry	Catalyst	(mol%)	m	Temperature (°C)	Time (h)	Conversion <sup>b</sup> (%)	[ $\alpha$ ] <sub>D</sub> <sup>c</sup> (deg.)	ee <sup>d</sup> (%)	Configuration
1	Pd(PPh) <sub>4</sub> ( <b>3a</b> )	2.0	ZnCl	20	1	95	–	–	–
2	Pd{(R,R)-diop} <sub>2</sub> ( <b>3b</b> )	1.0	ZnCl	20	17	60	+79	21	<i>S</i>
3	PdCl <sub>2</sub> {(R,R)-diop} ( <b>3c</b> )	0.6	ZnCl	20	1	100	+93	25	<i>S</i>
4	PdIPh{(R,R)-diop} ( <b>3d</b> )	1.0	ZnCl	20	2	100	+92	25	<i>S</i>
5	PdCl <sub>2</sub> (nmdpp) <sub>2</sub> ( <b>3e</b> )	1.2	ZnCl	20	17	87	+71	19	<i>S</i>
6	PdCl <sub>2</sub> {(S,R)-bppfa} ( <b>3f</b> )	0.4	ZnCl	20	17	88	–78	21	<i>R</i>
7	PdCl <sub>2</sub> {(R,S)-ppfa} ( <b>3g</b> )	0.7	ZnCl	20	2	33	+17	5	<i>S</i>
8	PdCl <sub>2</sub> {(S)-binap} ( <b>3h</b> )	0.4	ZnCl	20	42	78	+22	6	<i>S</i>
9	PdCl <sub>2</sub> {(S,S)-chiraphos} ( <b>3i</b> )	1.0	ZnCl	50	24	60	+12	5	<i>S</i>
10	PdCl <sub>2</sub> {(R,R)-diop}	1.0	ZnI	20	2	100	+98	26	<i>S</i>
11	Pd{(R,R)-diop} <sub>2</sub>	3.0	Mg <sub>1/2</sub>	60	2.5	100	–23	6	<i>R</i>
12	PdCl <sub>2</sub> {(R,R)-diop}	0.1	MgCl	20	1.5	45	–12	3	<i>R</i>
13	Pd{(R,R)-diop} <sub>2</sub>	4.0	Cu	50	0.5	100	–38	10	<i>R</i>

<sup>a</sup> 5.5 mmol *t*-Bu-CH=C=CH-m was reacted with 5.0 mmol PhI. <sup>b</sup> Degree of conversion determined from the *t*-Bu-CH=C=CH-Ph/PhI(*o*-H) ratio in the <sup>1</sup>H NMR spectrum of the product mixture. <sup>c</sup> [ $\alpha$ ]<sub>D</sub> (*c* = 0.5–2, ethanol) was corrected for the presence of some PhI when conversion was incomplete. <sup>d</sup> Enantiomeric excess and configuration based on [ $\alpha$ ]<sub>D</sub><sup>20</sup> = +370 °C for (*S*)-*t*-Bu-CH=C=CH-Ph [6d].

entry 2). PdCl<sub>2</sub>(nmdpp)<sub>2</sub> (**3e**), a complex of a chiral monodentate phosphine, derived from (–)-menthol, surprisingly showed an almost as effective chiral induction as that found for the (*R,R*)-diop complexes.

It is noteworthy that the palladium dichloride complexes of (*S,R*)-bppfa and (*R,S*)-ppfa, both of which gave good chiral inductions (up to 65%) in the reaction of 1-phenylethylmagnesium chloride with vinyl bromide [12], are quite ineffective in this reaction (Table 1, entries 6,7). The bis(fosfine)-amine complex PdCl<sub>2</sub>{(*S,R*)-bppfa} (**3f**) gave (*R*)-**2** in 21% ee, a value which is comparable to that for catalysts **3a,3b** and **3c**. PdCl<sub>2</sub>{(*R,S*)-ppfa} (**3g**) gave (*S*)-**2** in only 5% ee. Palladium

Table 2

Chiral induction in the Pd{(R,R)-diop}<sub>2</sub>-catalyzed formation of *t*-BuCH=C=CHPh (**2**) from *t*-BuCH=C=CH-ZnCl (**1a**) and PhI

Entry	Rm (mmol)	PhI (mmol)	cat. (mol%)	Temperature (°C)	Time (h)	Conversion <sup>a</sup> (%)	[ $\alpha$ ] <sub>D</sub> <sup>b</sup> (deg.)	ee <sup>c</sup> (%)	Configuration
1	5.0	4.0	12.5	60	2	70	+65	18	<i>S</i>
2	5.0	4.0	2	60	2	50	+65	18	<i>S</i>
3	5.0	4.5	2	20	100	50	+65	18	<i>S</i>
4	10.0	5.0	4	50	4	100	+70	19	<i>S</i>
5	10.0	5.0	4	0	24	100	+70	19	<i>S</i>
6	25.0	2.5	4	50	4	100	+70	19	<i>S</i>

<sup>a</sup> Degree of conversion determined from the *t*-BuCH=C=CHPh/PhI(*o*-H) ratio in the <sup>1</sup>H NMR spectrum of the product mixture. <sup>b</sup> [ $\alpha$ ]<sub>D</sub> (*c* = 0.5–2, ethanol) was corrected for the presence of some PhI when conversion was incomplete. <sup>c</sup> Enantiomeric excess and configuration based on [ $\alpha$ ]<sub>D</sub><sup>20</sup> +370 °C for (*S*)-*t*-BuCH=C=CHPh [6d].

dichloride complexes with rigid bis(phosphine) ligands like (*S*)-binap and (*S,S*)-chiraphos (Table 1, entry 8,9) gave both low conversions and low ee's.

The Pd{(*R,R*)-diop}<sub>2</sub> (**3b**) catalyzed reaction (Table 2) was studied in more detail by varying several parameters that might affect the enantiomeric excess of allene **2**. It became evident that it made little or no difference whether **3b** was used as pure complex or prepared in situ. Also, higher catalyst concentrations and changes in the ratio **1a**/PhI had no influence on the enantiomeric excess of **2**; this indicates that the enantiomeric forms of the zinc reagent **1a** undergo interconversion at a rate which is much higher than that of the irreversible C–C coupling. This absence of dependence on the organometallic reagent/substrate ratio has been observed by Kumada et al. [12] and by Consiglio et al. [20] for the nickel-catalyzed cross-coupling of vinyl and aryl halides with secondary-alkyl Grignard reagents.

Variation of the reaction temperature between 0 and 50 °C did not affect the enantiomeric excess. According to Izumi [21] absence of dependence on the temperature points to a small enthalpy or a large entropy term in the stereodifferentiating step of the reaction.

A reaction of iodobenzene with *t*-BuCH=C=CHZnI instead of the corresponding chloride (**1a**) was carried out in order to examine the influence of the nature of the halide on the reaction. It appeared that there was no significant effect (comp. Table 1, entry 10).

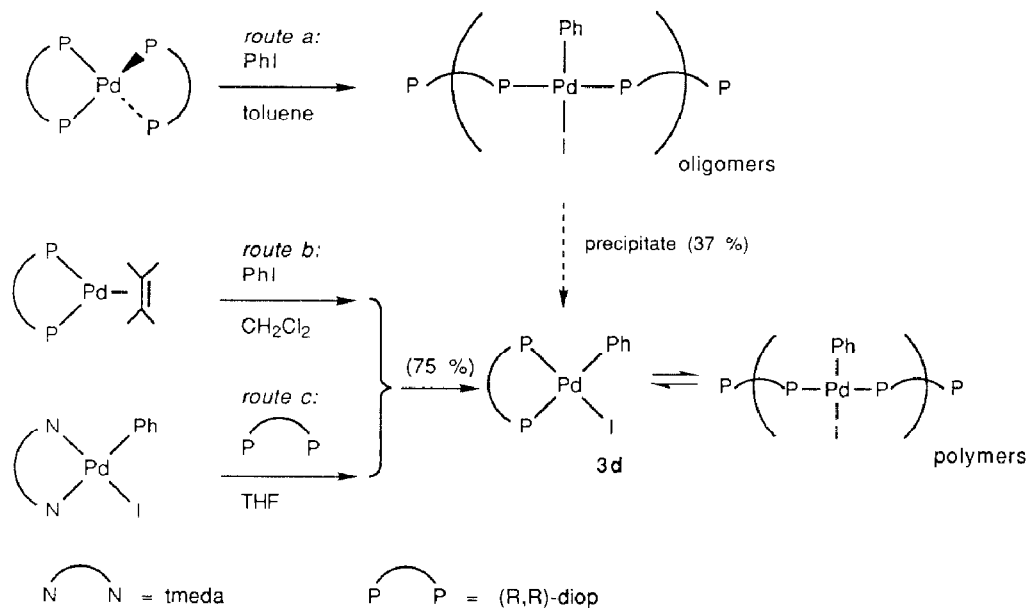
However, change of the metal of the organometallic reagent (**1a**–**1c**) used in the enantiodifferentiating synthesis of **2** had a pronounced influence on the stereochemical outcome of the reaction. The copper and magnesium reagents (**1b** and **1c**) were prepared by metathesis of 4,4-dimethyl-1-lithiopenta-1,2-diene with LiCuBr<sub>2</sub> or MgCl<sub>2</sub> and subsequently treated with iodobenzene in the presence of **3b** as catalyst (Table 1, entry 11,13). The enantiomeric excesses of **2** obtained from these reagents (**1b** and **1c**) are lower than those obtained from the reaction with the zinc reagent, **1a**, but intriguingly the configuration is reversed. A similar reversal of stereoselectivity was observed by Cross and Kellogg [22] and by Posner et al. [23] in their studies of the asymmetric cross-coupling reactions of Grignard reagents on the one hand and organozinc or organocopper reagents on the other. The reason for this reversal is unknown.

#### *Catalytic reactions (Route B)*

The synthesis of **2** via route B, starting from PhZnCl and *t*-BuCH=C=CHBr catalyzed by Pd{(*R,R*)-diop}<sub>2</sub> (**3b**), gave quantitative conversions but very low enantiomeric excesses (Scheme 1; route B). The configuration of the product is opposite to that obtained by route A (Table 1, entry 2). Furthermore, the enantiomeric excess depends on the reaction temperature. These different stereochemical results cannot be easily explained since more than one pair of diastereomeric intermediates (e.g. PdBr(CH=C=CH-*t*-Bu){(*R,R*)-diop}, or PdPh(CH=C=CH-*t*-Bu){(*R,R*)-diop}), formed and consumed at different rates, may be involved in the reaction sequence.

#### *Preparation of the suggested intermediate PdIPh{(R,R)-diop}*

The results with different metal reagents (Scheme 1, route A) suggest that transfer of the allenyl moiety from the metal reagents (**1a**–**1c**) to palladium may be the enantiodifferentiating step. Recently, PdIPh{(*R,R*)-diop} (**3d**), which should be



Scheme 2. Syntheses and possible structures of PdIPh{(R,R)-diop} (**3d**).

an intermediate in the reaction of **1a** with PhI catalyzed by the palladium{(R,R)-diop} complexes (**3b,3c**), was prepared by reaction of Pd(CH<sub>2</sub>=CH<sub>2</sub>){(R,R)-diop} with iodobenzene (Scheme 2; route b) [24]. It was characterized by means of its <sup>31</sup>P spectrum, which showed an AX pattern for the two inequivalent phosphorus atoms on palladium. We found, however, that Pd{(R,R)-diop}<sub>2</sub> (**3b**), reacted with iodobenzene in toluene to give a different complex. Its <sup>31</sup>P NMR spectrum is consistent with a coordination oligomer with non-chelating bridging and terminal bis(phosphine) ligands (Scheme 2; route a). In an attempt to isolate the compound, an oil, which was not further studied, and a yellowish-brown precipitate (37%) were obtained. According to its <sup>31</sup>P NMR spectrum in dilute solution, this precipitate appeared to be the chelate-bonded complex **3d**, and the analytical data (C, H, I) were in agreement with the formula PdIPh{(R,R)-diop}.

In order to perform stoichiometric reactions with pure **3d** it was necessary to have access to the compound in larger amounts. We prepared PdIPh{(R,R)-diop} (**3d**) in high yield (75%) through a convenient alternative route involving ligand substitution of PdIPh(tmeda) (tmeda = *N,N,N',N'*-tetramethylethanediamine) [25] with one equivalent of (R,R)-diop (Scheme 2; route c). The elemental analyses for compound **3d** prepared in this way were correct, but its <sup>31</sup>P NMR spectrum showed a small broad signal at +17 to 18 ppm, the intensity of which was dependent on the concentration. At high dilution (< 5 mg/ml) the expected AX spectrum (peaks at δ -4 and +12 ppm; *J*(P,P) 41 Hz) of monomeric PdIPh{(R,R)-diop} (**3d**) was observed. Furthermore, a signal at ca. +18 ppm was always present, even at high dilution. The latter signal, which becomes the main signal at a concentration of ca. 40 mg/ml, attributed to a coordination polymer of the formula [trans-PdIPh{(R,R)-diop}]<sub>n</sub>. The (broadened) AX pattern diminishes considerably compared with the signal at +18 ppm but does not disappear completely. This observation suggests that the polymer and the monomer are in a concentration

dependent equilibrium; at low concentration ( $< 4$  mg/ml) the equilibrium shifts to the monomer, and at high concentration it shifts to the polymer. The formation of such polymers has also been observed for (acyl)(chloro){1,4-bis(diphenylphosphino)butane}platinum complexes [26]. Probably the high *trans*-influence of the organic ligand (Ph, acyl) tends to direct the weakest ligand (halogen) to the *trans*-position and disfavours the formation of a chelate ring.

#### *Stoichiometric reactions with PdIPh{(R,R)-diop}*

The reaction of *t*-Bu-CH=C=CHZnCl (**1a**) with PhI catalyzed by PdIPh{(R,R)-diop} (**3d**) gave (*S*)-**2** in 25% ee, as did the reaction catalyzed by PdCl<sub>2</sub>{(R,R)-diop} (**3c**) (Table 1, entries 3,4). This supports the view that PdIPh{(R,R)-diop} (**3d**) is involved in the catalytic cycle. In order to substantiate the idea that reaction of the organometallic reagent with **3d** is the enantiodifferentiating step, stoichiometric reactions with the reagents **1a** and **1b** were performed; this reaction can now be performed since **3d** has become readily available. Reaction of **3d** with zinc reagent **1a** afforded (*S*)-**2** in 17–19% ee. However, reaction of **3d** with magnesium reagent **1b** afforded (*R*)-**2** in only 2% ee. The configurations and ee's of **2** formed in these stoichiometric reactions correspond with those in the corresponding catalytic reactions (Table 1, entries 3, 12). These observations support the view that the metathesis of the palladium-iodine bond in **3d** by the organometallic reagents, **1a** or **1b**, is the enantiodifferentiating step. The question remains of the form in which **3d** is involved in this reaction because the concentration of **3d** at the moment of the stoichiometric reaction was ca. 40 mg/ml, consistent with most of **3d** being present in the polymeric *trans*-form, and in the catalytic reaction, the concentration of **3d** is so low ( $< 5$  mg/ml) that most of the **3d** should be in the monomeric *cis*-form.

## Experimental

All reactions were conducted under dry nitrogen. Work-up and manipulations were carried out in air unless otherwise noted. THF was distilled from LiAlH<sub>4</sub> or Na/benzophenone. Optical rotations were measured with a Perkin–Elmer 241 Polarimeter. Routine <sup>1</sup>H NMR spectra were recorded on a Varian EM-360 spectrometer. <sup>31</sup>P NMR spectra were recorded on Bruker WP-200 and AC-200 spectrometers with 85% H<sub>3</sub>PO<sub>4</sub> as external standard; shifts to higher frequencies are positive.

*Starting materials.* The ligands, (*R,R*)-diop [14] and (*R,S*)-ppfa [17], we made by published procedures. Other ligands were obtained from Strem Chemicals. 4,4-Dimethyl-1,2-pentadiene [27] and 1-bromo-4,4-dimethyl-1,2-pentadiene [28] were made by published procedures. The PdCl<sub>2</sub> complexes were prepared by treating PdCl<sub>2</sub>(MeCN)<sub>2</sub> in benzene with a stoichiometric amount of the ligand or, in the case of (*R,R*)-diop and neomenthyldiphenylphosphine, by treating a stoichiometric amount of the ligand in ethanol with Li<sub>2</sub>PdCl<sub>4</sub> in water. Yields were almost quantitative.

Pd(PPh<sub>4</sub>)<sub>4</sub> [29], Pd{(R,R)-diop}<sub>2</sub> [30] and PdIPh(tmeda) [25] were prepared by published procedures.

*Procedure for the reactions of allenylmetal reagents with iodobenzene.* A solution of 4,4-dimethyl-1,2-pentadiene (0.60 g; 6.0 mmol) in 10 ml of THF was cooled to  $-60^{\circ}\text{C}$  (CO<sub>2</sub>/acetone) and 3.5 ml of a 1.55 *M* solution of BuLi (5.5 mmol) was

added dropwise, the temperature being kept below  $-55^{\circ}\text{C}$ . After 0.5 h stirring at  $-60^{\circ}\text{C}$ , 6.0 ml of a 1.0 *M* solution of  $\text{ZnCl}_2$  in THF was added ( $< -40^{\circ}\text{C}$ ), to give reagent **1a**. Similarly, 20 ml of a 0.3 *M* solution of  $\text{MgCl}_2$  was added to give reagent **1b**. For reagent **1c**, a different procedure was used: 0.80 g of  $\text{CuBr}$  was dissolved in 5 ml of THF containing 1.5 mmol of  $\text{LiBr}$ . This solution was added dropwise to a solution of lithiated 4,4-dimethyl-1,2-pentadiene, the temperature being kept below  $-50^{\circ}\text{C}$ , and then 1.0 g. of  $\text{PhI}$  (5 mmol) and the catalyst were added.

Except for  $\text{Pd}(\text{PPh}_3)_4$  and  $\text{Pd}\{(R,R)\text{-diop}\}_2$ , which were added as 0.02 *M* solutions in THF, the catalysts were added as solids in the amounts stated in Table 1. The temperature was then allowed to rise to room temperature and the mixture stirred under the conditions given in Table 1.

Work-up was performed by shaking the reaction mixture with a saturated solution of  $\text{NH}_4\text{Cl}$  in water, separating the organic layer, drying it over  $\text{MgSO}_4$ , and concentrating it in vacuo. The residue was chromatographed over a short column (20 cm,  $\varnothing$  1 cm) charged with alumina (deactivated with 5%  $\text{H}_2\text{O}$ ), and eluted with diethyl ether/pentane (1/1, v/v). Yield 0.75–0.90 g of a light-yellow oil.  $^1\text{H}$  NMR data for the allene **2** were identical with those in the literature. In the cases in which a mixture of **2** and  $\text{PhI}$  was obtained, their ratio was determined from the relative integrals of the signals from the *o*-hydrogen atoms of  $\text{PhI}$  and the allenic hydrogen atoms of **2**.

*Preparation and determination of the monomer-polymer equilibrium of PdIPh}\{(R,R)\text{-diop}\} (3d).* The  $^{31}\text{P}$  chemical shifts of  $(R,R)\text{-diop}$  ( $\delta -22.0$  ppm) and  $\text{Pd}\{(R,R)\text{-diop}\}_2$  ( $\delta +1.5$  ppm) were determined in toluene- $d_8$  as solvent.

A 10 mm NMR-tube was charged with a solution of  $\text{Pd}\{(R,R)\text{-diop}\}_2$  (about 100 mg) in toluene (2.5 ml).  $\text{PhI}$  (0.2 g) and toluene- $d_8$  (0.5 ml, deuterium lock) were added. The tube was kept at  $50^{\circ}\text{C}$  for 15 minutes, then  $^{31}\text{P}$  NMR spectra were recorded as the temperature of the sample was raised from 178 to 318 K in 20 K steps. Typical results:  $\delta$  (298 K)  $-20.9$  (br. s);  $+20.0$  (br. s).  $\delta$  (218 K)  $-22.0$  (s);  $-21.0$  (br. s);  $+20.5$  (br. s);  $+21.4$  (br. s).

*Preparation of PdIPh}\{(R,R)\text{-diop}\} (3d) (Scheme 2; route a).*  $\text{PhI}$  (0.45 g; 2.25 mmol) was added to a solution of  $\text{Pd}\{(R,R)\text{-diop}\}_2$  (0.52 g; 0.5 mmol) in 5 ml of benzene and the mixture was kept at  $50^{\circ}\text{C}$  for 15 min. The solution was then concentrated to about 2 ml under reduced pressure and treated with 10 ml of an 1/1 diethyl ether/pentane mixture. An oil and a white precipitate were formed. The white precipitate was dissolved in 2 ml of benzene and the procedure was repeated to give a very pale yellow precipitate, which was filtered off. Yield 0.14 g (36%). M.p. 170–173 (dec.). Anal.: Found: C, 54.88; H, 4.67; I, 15.58.  $\text{C}_{37}\text{H}_{37}\text{IO}_2\text{P}_2\text{Pd}$  calcd.: C, 54.93; H, 4.61; I, 15.69%.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta -4.2$  (d,  $J(\text{P},\text{P}')$  41 Hz);  $+11.9$  (d,  $J(\text{P},\text{P}')$  41 Hz);  $+18.5$  ppm (br. s).

*Preparation of PdIPh}\{(R,R)\text{-diop}\} (3d) (Scheme 2; route c).*  $(R,R)\text{-Diop}$  (0.5 g; 1.0 mmol) was added to a solution of  $\text{PdIPh}(\text{tmeda})$  (0.42 g; 1.0 mmol) in THF (20 ml) to give a clear solution. Diethyl ether/pentane (1/1; 30 ml) was added, and this produced a pale yellow precipitate, which was filtered off and dried in vacuo. Yield 0.6 g (75%). M.p. 165–170 $^{\circ}\text{C}$  (dec.). Anal.: Found: C, 54.46; H, 4.83; I, 15.63.  $\text{C}_{37}\text{H}_{37}\text{IO}_2\text{P}_2\text{Pd}$  calcd.: C, 54.93; H, 4.61; I, 15.69%.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta -4.2$  (d,  $J(\text{P},\text{P}')$  41 Hz);  $+6.1$  (s);  $+11.9$  (d,  $J(\text{P},\text{P}')$  41 Hz);  $+17.5$  ppm (br. s, major peak);  $+21.3$  (s);  $+31.4$  ppm (s).



*Reaction of PdIPh{(R,R)-diop} (3d) with t-BuCH=C=CHZnCl (1a) and t-BuCH=C=CHMgCl (1b).* The PdIPh{(R,R)-diop} (3d) used in this section was prepared from PdIPh(tmeda) by ligand exchange with (R,R)-diop (Scheme 2; route c). The organometallic reagents 1a and 1b were prepared as described above on a 1.5 mmol scale. A solution of PdIPh{(R,R)-diop} (3d) (0.82 g; 1.0 mmol) in THF (20 ml) was added dropwise with the temperature maintained at  $-60^{\circ}\text{C}$ . The mixture was then allowed to warm to room temperature, and stirred for 15 min at this temperature, and dimethyl maleate (0.25 ml; 1.5 mmol) was then added. Work-up was as described for the catalytic reactions. Yield 0.16 g (90%). The product 2 was characterized by  $^1\text{H}$  NMR. The  $[\alpha]_{\text{D}}$  was  $+72^{\circ}$ , corresponding to an ee of 19.5%.

The experiment was repeated with 0.40 g (0.48 mmol) of PdIPh{(R,R)-diop} to give 67 mg (80%) of 2. The product 2 was characterized by  $^1\text{H}$  NMR. The  $[\alpha]_{\text{D}}$  was  $+64^{\circ}$ , corresponding to an ee of 17%.

The experiment was repeated with 0.20 g (0.24 mmol) of PdIPh{(R,R)-diop}. Instead of zinc reagent 1a, the magnesium reagent 1b was used. The yield of 2 was 24 mg (70%). The product was characterized by  $^1\text{H}$  NMR spectroscopy. The value of  $[\alpha]_{\text{D}}$  was  $-7.5^{\circ}$ , corresponding with an ee of 2%.

## Acknowledgment

This work was supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

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