Stereochemistry of the Palladium(0)-Catalyzed Phenylation of 1-Halogenoallenes

Cornelis J. Elsevier and Peter Vermeer*

Department of Organic Chemistry, State University at Utrecht, 3522 AD Utrecht, The Netherlands

Received December 6, 1984

The stereochemistry of the $Pd[PPh_3]_4$-catalyzed phenylation of the 1-halogenoallenes RCH=C=CHX (R = Ph, *t*-Bu; X = Cl, Br, or I) with phenylzinc reagents has been elucidated by using optically active 1-halogenoallenes. The products RCH=C=CHPh were obtained with a moderate to high degree of inversion of configuration around the allenyl moiety when X was Cl and Br. When X was I, retention of configuration was observed. A rationalization of the results is given on the basis of two competing processes, viz., insertion of palladium in the C–X bond (oxidative addition) to give $RCH{=}C{=}CH(Pd[PPh_3]_2X)$ with retention of configuration and a $Pd[PPh_3]_2$-induced anti-S_N2'-like reaction followed by a suprafacial [1,3]-shift of the $Pd[PPh_3]_2$ group leading to $RCH{=}C{=}CH(Pd[PPh_3]_2X)$ with inversion of the configuration. For the latter reaction mode, such an allenyl palladium(0) intermediate was isolated and its absolute configuration determined.

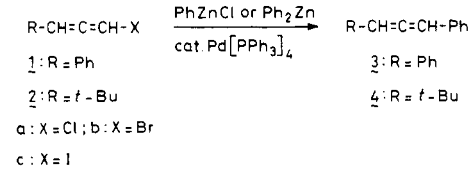
The synthesis of allenes is well documented.[1] An interesting topic in this field is the stereochemical course of transition-metal-mediated allene synthesis from 1-halogenoallenes. The stereochemistry of the organocuprate-induced formation of optically active allenes from 1-bromoallenes was recently investigated.[2] It was shown that the reaction proceeds with retention of configuration in the allenyl moiety.[2b]

We and others[3] showed that 1-halogenoallenes can also be converted into allenic products by palladium(0)-catalyzed reactions with organozinc and organomagnesium reagents. As palladium(0)-catalyzed reactions of vinylic halides with organometallic species are known to occur with retention of configuration around the double bond,[4] it could be expected that Pd(0)-catalyzed conversions of 1-halogenoallenes into other allenes also proceed with retention of configuration. It will be shown in the paper that our results are more complicated.[5]

Results and Discussion

General Remarks. We have focussed our attention on Pd(0)-catalyzed conversions of the optically active 1-halogenoallenes **1** and **2** by phenylzinc reagents into the phenyl substituted allenes **3** and **4**. The allenes **1** and **2** are readily accessible in optically active form[6] and are smoothly converted by the phenylzinc reagents into allenes **3** and **4** when $Pd[PPh_3]_4$ is used as catalyst (conversion >98%); see Scheme I. The use of phenylzinc reagents is also attractive because the absolute rotations of the produced allenes **3** and **4** are known with a high degree of certitude, viz., $[\alpha]^{20}_D$ 1137° ($CHCl_3$ or EtOH) for **3**[7] and 370° (EtOH) for **4**.[8] Therefore, reasonable estimations of optical purities of the products can be made and insight in the stereoselectivity of the reactions can be obtained.

Scheme I



Conversion of 1 and 2. The results of our experiments are collected in Table I. The obtained allenes **3** and **4** contained less than 2% of 1,3-substitution products; the regioselectivity of the reactions is therefore good. It is noteworthy in this connection that organocyanocuprates generally convert 1-bromoallenes predominantly or even exclusively into alkynes.[2] On the other hand, alkylallenes are obtained upon treatment of 1-bromoallenes with lithium diorganocuprates.[9]

The yields of **3** and **4** amounted to 70–85% after isolation and purification. Table I shows that the stereoselectivity of our reactions was generally reasonable to good. A number of factors appeared to influence the stereoselectivity, viz., the origin and type of phenylzinc reagent, the amount of catalyst, and the nature of the halogen.

Phenylzinc Reagent. When PhZnCl was used, it was prepared in situ from PhMgBr and an equimolar amount of $ZnCl_2$ in THF as the solvent. The resulting mixture is heterogeneous under the conditions used for the reactions (see Table I). Ph_2Zn was prepared in situ in THF from PhMgBr and half the amount of $ZnCl_2$ or it was used as a pure compound in THF (homogeneous solutions). The conversions of **1a**, **1b**, and **2b** showed the highest stereoselectivities when pure Ph_2Zn was applied (entries 3, 6, and 11), although the difference with PhZnCl is not very pronounced (see entries 1, 4, and 10). The reagent Ph_2Zn being prepared in situ gave in these cases inferior results (entries 2 and 5). Initially it was thought that starting compounds and/or products could racemize under the influence of magnesium halides or species like PhMgX and Ph_2Mg. Treatment of starting compounds and products

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(6) The $[\alpha]^{20}_D$ values for optically pure **1a**, **1b**, and **1c** are assumed to amount to 610°, 1235° and 1550°, respectively, being the highest values known for these compounds. Elsevier, C. J.; Meijer, J.; Tadema, G.; Stehouwer, P. M.; Bos, H. J. T.; Vermeer, P.; Runge, W. *J. Org. Chem.* **1982**, *47*, 2194. The $[\alpha]^{20}_D$ values for optically pure **2b** and **2c** are assumed to amount to 230° and 314°, respectively, being the highest values known for these two allenes. Elsevier, C. J.; Vermeer, P.; Gedanken, A.; Runge, W. *Ibid.* **1985**, *50*, 364.

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Table I. Preparation, Configuration, and Specific Rotation for the Allenes RCH=C=CHPh (3, R = Ph; 4, R = *t*-Bu)

entry	substrate[a]	reagent[b]	conditions		product[c]	$[\alpha]^{20}_{D}$,[d] deg	ee,[e] %
			T, °C	min			
1	(*R*)-**1a**	PhZnCl	−60→0	5	(*S*)-**3**	+705	62
2	(*R*)-**1a**	Ph_2Zn	−60→0	5	(*S*)-**3**	+410	36
3	(*R*)-**1a**	Ph_2Zn	−60→0	5	(*S*)-**3**	+760	67
4	(*R*)-**1b**	PhZnCl	−60→0	5	(*S*)-**3**	+900	80
5	(*R*)-**1b**	Ph_2Zn	−60→0	5	(*S*)-**3**	+525	52
6	(*R*)-**1b**	Ph_2Zn	−60→0	5	(*S*)-**3**	+985	87
7	(*R*)-**1c**	PhZnCl	0	60	(*R*)-**3**	−135	12
8	(*R*)-**1c**	Ph_2Zn	0	60	(*R*)-**3**	−64	6
9	(*R*)-**1c**	Ph_2Zn	0	60	(*R*)-**3**	−60	6
10	(*R*)-**2b**	PhZnCl	−60→20	15	(*S*)-**4**	+244	67
11	(*R*)-**2b**	Ph_2Zn	−60→20	15	(*S*)-**4**	+268	73
12	(*R*)-**2c**	PhZnCl	20	30	(*R*)-**4**	−268	73
13	(*R*)-**2c**	Ph_2Zn	20	30	(*R*)-**4**	−251	68

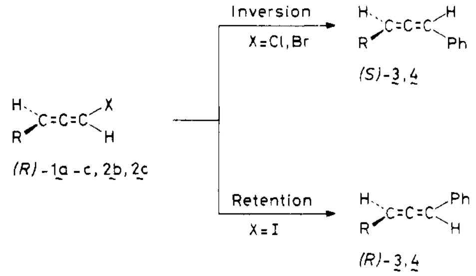
[a] Levorotatory compounds (ref 6). The ee values for **1a**, **1b**, **1c**, **2b**, and **2c** used in the experiments amounted to 75%, 95%, 25%, 38%, and 38%, respectively. [b] Prepared in situ from PhMgBr and $ZnCl_2$ except in entries 3, 6, 9, 11, and 13 where pure Ph_2Zn was used. The Ph_2Zn solutions were homogeneous, the PhZnCl solutions a suspension in the solvent THF. [c] Chemical yields, 70–85% (after purification). [d] Measured in abs. EtOH; the $[\alpha]_D$ values refer to the use of "optically pure" (cf. ref 6) 1-halogenoallenes and are therefore extrapolated values (see note *a*). [e] Calculated from $[\alpha]_D$ −1137° (EtOH) and $[\alpha]_D$ −370° (EtOH) for optically pure (*R*)-**3** and (*R*)-**4**, respectively.[7,8]

with these species under the conditions of the reaction gave no racemization, however. It could be that the inferior results obtained for Ph_2Zn being prepared in situ are due to a competing reaction of the initially formed allenylpalladium(II) intermediates (see below) with free PhMgBr, but we have not proven that.

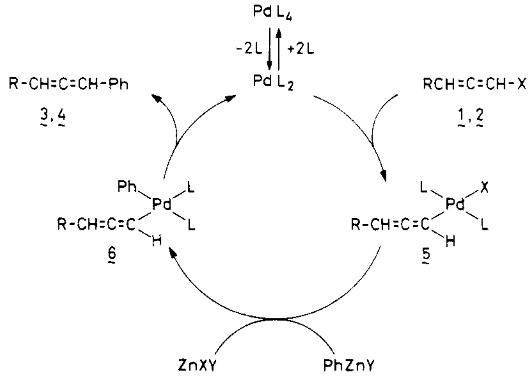
Catalyst. When the amount of catalyst was varied from 2–10 mol %, the optical yield was only slightly influenced. The lower stereoselectivities with increasing amounts of catalyst pointed to partial racemization of either starting allene or product by the catalyst. Treatment of allenes **3** and **4** with 5 mol % of the catalyst under the conditions of the reactions gave no detectable racemization of these allenes. However, when **1a** and **1b** were reacted with 5 mol % of the catalyst in THF, while allowing the temperature of the mixture to rise from −60 to 0 °C and thus imitating the conditions used to convert **1** and **2** into **3** and **4**, 10–20% racemization of **1a** and **1b** was observed. The mechanism of the racemization of **1a** and **1b** by the catalyst is not clear. From the literature it is known that allene itself gives the relatively stable bis(triphenylphosphine)-allene–palladium complex.[10] The allene moiety is no longer linear, the C(1)–C(2)–C(3) angle being 148.3°. The coordinated double bond is 1.4011 Å long, in free allene 1.304 Å. This lengthening suggests a decrease of bond order resulting from a ligand-to-metal charge transfer as well as an electron transfer from the metal to antibonding orbitals of the allene ligand (cf. 10). It could be that formation of such a complex between palladium and allene **1** is responsible for the occurrence of some racemization. Cis–trans isomerization of a halogen-substituted double bond through a Pt(0) complex is known,[11] so that a similar process cannot be excluded here. One could also think of a reversible oxidative addition/reductive elimination process. In the case of chiral cyclohexenyl acetates it was found that $Pd[PPh_3]_4$ causes racemization in that way.[12] The observation that **3** and **4** are configurationally stable toward the catalyst under the conditions of the reactions seems to be in favor of the last mentioned racemization mode but definite conclusions cannot be drawn.

Nature of Halogen. Starting from levorotatory 1-chloro- and 1-bromoallenes (compounds **1a**, **1b**, and **2b**) the dextrorotatory allenes **3** and **4** were obtained. The stereoselectivity appeared to be high when PhZnCl or pure Ph_2Zn were used as reagents (see Table I). On the other hand, starting from the levorotatory 1-iodoallenes **1c** and **2c** the levorotatory allenes **3** and **4** were formed (Table I, entries 7–9, 12, and 13). The stereoselectivity was very poor starting from **1c** but good starting from **2c** (Scheme II). As our levorotatory 1-halogenoallenes **1** and **2** as well as the levorotatory allenes **3** and **4** are of *R* absolute configuration,[13] the following net stereochemistry can be inferred from our experiments: inversion of configuration in the allenyl moiety for X is Cl and Br and retention for X is I.

Scheme II



Scheme III



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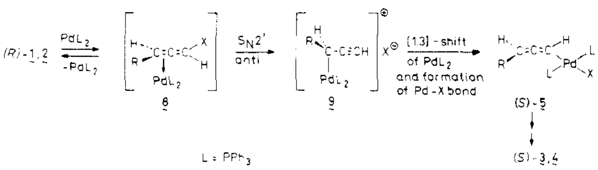
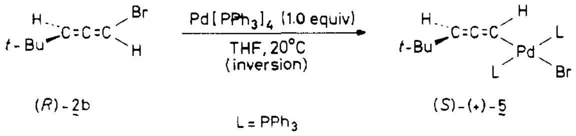
(12) Trost, B. M.; Verhoeven, T. R.; Fortunak, J. M. *Tetrahedron Lett.* **1979**, 2301.

(13) The absolute configuration of **3** was determined by CD measurements. Mason, S. F.; Vane, G. W. *Tetrahedron Lett.* **1965**, 1593. CD spectroscopy was also used to determine the absolute configurations of **1**, **2**, and **4**.[8] In the case of acyclic 1,3-disubstituted chiral allenes Lowe-Brewster rules can be used to predict the absolute configuration of the allenes from the sign of the optical rotation. Ref. 6 and Lowe, G. *Chem. Commun.* **1965**, 411.

Scheme IV



Scheme V

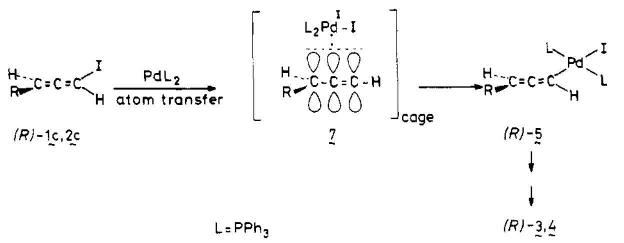


Mechanism. In view of what is known for transition-metal-catalyzed substitution of vinylic halides by organometallic species,[14] a catalytic cycle as depicted in Scheme III seems to a reasonable rationale for our reactions. The cycle involves the conversion of **1** and **2** into the allenylpalladium(II) complexes **5** and subsequent conversion of **5** by the organozinc reagent into the allenylpalladium(II) complexes **6** followed by reductive elimination of allenes **3** and **4** from **6**. In analogy with similar reactions for vinylic halides,[14] the conversions of **5** into **6** and **6** into **3** and **4** both will proceed with retention of configuration in the allenyl moiety, irrespective of the nature of X. The different stereochemical outcome depending on X must therefore be due to a formation of **5** from **1** and **2** in which stereochemistry, viz., retention or inversion, is determined by X.

To explain the anti stereochemistry observed when X is Cl or Br, one could imagine that in these cases, after the formation of the π-complex **7**, the catalyst preferentially induces an anti-S_N2'-like displacement of X to give the 2-propynylic palladium(II) intermediate **8**, from which by a suprafacial [1,3]-shift of PdL_2 and subsequent attachment of X complex **5** is obtained (Scheme IV). The anti stereochemistry for the formation of **8** is not unlikely in view of the fact that cuprates also induce anti-S_N2'-like reactions in 1-bromoallenes;[2] furthermore, several Pd(O)-catalyzed conversions of allylic compounds have been found to proceed through allylpalladium(II) complexes formed by anti substitution.[15] Strong support for this route was obtained by the following experiment. As shown in Scheme V, treatment of the 1-bromoallene (*R*)-(–)-**2b** ($[\alpha]^{20}_D$ –140° (EtOH); 60% ee) with an equimolar amount of the catalyst produced the corresponding palladium(II) intermediate **5** (R = *t*-Bu) in 90% yield. The complex appeared to be *dextrorotatory* ($[\alpha]^{20}_D$ +40°), so that in view of Lowe–Brewster rules the absolute configuration of the allene is *S*.[16] Its formation, therefore, took place with predominant inversion of configuration.

The following line of reasoning could be put forward to explain the results obtained for the 1-iodoallenes **1c** and **2c**. From the literature it is well-known that the ability of vinylic halides to add oxidatively to transition metals like Pd decreases in the order I > Br > Cl.[14] The heavier group VIII elements especially show a high affinity to the heavy halogens. One could therefore expect that the "indirect" oxidative addition mentioned above is largely accompanied by a direct oxidative addition of the 1-halogenoallene when X is I. The latter reaction will proceed with retention.[14] Starting from **1c**, both routes should then be almost equally important. The high amount of retention observed for the conversion of **2c** could then be due to steric reasons; the bulky *tert*-butyl group makes the "indirect" oxidative addition route much less attractive.

Scheme VI



In the case of the iodides **1c** and **2c**, we cannot exclude a mechanism involving the formation of an allenyl radical–L_2PdI complex by inner-sphere atom transfer (cf. 14). Such a reaction will proceed with a high degree of retention in the allenyl moiety when the recombination step is so fast that rotation in the allenyl radical is unimportant. However, when the allenyl radical is relatively stable, and that will be the case when R is Ph, it has time to rotate before it recombines with the group L_2PdI. In this way, the extensive racemization during the conversion of **1c** also becomes conceivable (Scheme VI). Attempts to convert **2c** into the corresponding allenylpalladium(II) intermediate **5**, as was done for **2b**, failed to give discrete products. We have therefore not been able to check the stereochemistry of the formation of **5** in the case of the 1-iodoallenes.

Finally, further interesting from a mechanistic point of view is that the 1-chloro- and 1-bromoallenes are converted faster into the allenes **3** and **4** than the 1-iodo compounds. It is not clear why the difference in reactivity is in that order. We suppose that in the "indirect" oxidative addition route (see above) it is not necessary that intermediate **8** gives first **5** by attachment of X and then the palladium(II) derivative **6**, but it can also react directly with the organometallic reagent to give **6** at once. In that case the "indirect" route could be faster than the "direct" one, because in the latter route an additional substitution step is involved, viz., the conversion of **5** into **6**.

Conclusion. The stereochemistry of the palladium(0)-catalyzed conversion of 1-halogenoallenes into other allenes resembles that of vinylic halides only when the halogen in the allene is iodine, viz., retention of configuration. In the case of chlorine and bromine the displacements preferentially proceed with inversion of configuration in the allenyl moieties. This unexpected result is most likely due to a participation by the $\Delta^{2,3}$-double bond of the allenic system in the reaction so that a $Pd[PPh_3]_2$-induced anti-S_N2' displacement of halogen can occur in the first stage of the substitution reaction.

Experimental Section

General Methods. All reactions were carried out in an inert atmosphere of dry nitrogen. Standard syringe techniques were applied for transfer of organometallic compounds and other air- or moisture-sensitive materials.

IR spectra were recorded on a Perkin-Elmer 457 IR spectrometer. ^1H NMR spectra were recorded on Varian EM-390 and Bruker WP-200 spectrometers, using CCl_4 or $CDCl_3$ as solvent

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[14] See, for instance: Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: London, 1978; Chapters 7 and 14.

[15] Hayashi, T.; Hagihara, T.; Konishi, M.; Kumada, M. *J. Am. Chem. Soc.* **1983**, *105*, 7767 and references cited therein. It is not clear why the optical yield of the conversion of **1b** is somewhat better than that starting from **1a**. It could be that in the latter case the racemization of the 1-halogenoallene by the catalyst (see text) is somewhat more pronounced.

[16] A requirement for this configurational assignment is that the group PdL_2Br is more polarizable than hydrogen. This is undoubtedly the case. In a CD study it was found, for instance, that (+)-PhCH=C=CHPd$(PPh_3)_2$X is of *S* absolute configuration which indicates a higher polarizability of Pd$(PPh_3)_2$X (X is halogen) over hydrogen.[8]

and Me_4Si as internal standard. ^{13}C NMR spectra were recorded on Varian CFT-20 and Bruker WP-200 spectrometers in $CDCl_3$, using Me_4Si as internal standard. The ^{31}P NMR spectrum was recorded on a Bruker WP-200 spectrometer using a saturated Na_3PO_4 solution in D_2O as external reference. Mass spectra were recorded on a Kratos MS 80 spectrometer. Optical rotations were measured in a Perkin-Elmer 241 polarimeter, using standard cuvettes (l = 1 dm) at 20 °C. The relative error in α_D and $[\alpha]_D$ amounts to ca. 2%.

Materials. THF was distilled from $LiAlH_4$ prior to use. Diphenylzinc was prepared according to the literature.[17] Zinc chloride (Merck–Darmstadt) was used as a standard 1.0 M solution in THF. $Pd[PPh_3]_4$ was prepared according to the procedure of Coulson[18] and has been applied as a 0.02 M solution in THF. Optically active halogenoallenes **1** and **2** were synthesized following our procedure.[6]

Phenylation of the 1-Halogenoallenes 1 and 2. The phenylzinc reagents were prepared in situ by stirring PhMgBr (4.0 mmol) in THF (15 mL) with $ZnCl_2$ (4.0 mmol to obtain PhZnCl, 2.0 mmol to obtain Ph_2Zn) for 15 min at 25 °C. When salt-free Ph_2Zn was used (Table I), the solid Ph_2Zn (2.0 mmol) was dissolved in THF (18 mL). At –60 °C, the $Pd[PPh_3]_4$ catalyst (6 mL of a 0.02 M THF solution) was added to the zinc reagent followed by solutions of **1** or **2** (3.0 mmol in case of the 1-chloro- and 1-bromoallenes, 2.0 mmol in case of the 1-iodoallenes) in THF (2 mL). Further reaction conditions are given in Table I.

The products **3** and **4** were isolated by pouring the reaction mixtures into an aqueous NH_4Cl solution (100 mL) and extracting with n-pentane (2 × 50 mL), washing the combined extracts with water (5 × 200 mL), drying the extracts over Na_2SO_4, and evaporating the solvent in vacuo.

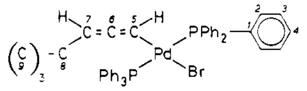
The chemical purity of crude 1,3-diphenylallene **3** was determined by ^1H NMR by adding a known amount of t-BuC(O)C≡CSiMe$_3$ as internal standard and comparing the integration data for the signals of the allenic hydrogens of **3** with those of the t-Bu and $SiMe_3$ group. Crude **3** generally contained 10–20% of biphenyl, a contaminant of the applied Grignard reagent. Purification of **3** over silica yielded the pure allene which had the same specific rotation as that of the crude allene after correction for the contaminant biphenyl. Crude **4** was almost chemically pure; it was further purified by column chromatography over neutral alumina (Woelm; deactivated with 5% H_2O) using n-pentane as the eluent. The optical purity of the applied starting allenes **1** and **2** amounted to 25–95% ee (cf. ref 6); the specific rotations and ee values for the products **3** and **4** given in Table I refer to the use of optically pure (cf. ref 6) **1** and **2** are therefore extrapolated values. Furthermore, the ee values for **3** and **4** as indicated in Table I were calculated by assuming that the rotational data for optically pure **3** and **4** are those given in note e under Table I. Physical constants and spectroscopic data for **3** and **4** are as follows.

1,3-Diphenylpropadiene (3): IR (neat) 1940 cm^{-1} (C=C=C); ^1H NMR (CCl_4) δ 7.10–7.35 (m, 10 H, aromatic protons), 6.50 (s, 2 H, =C=CH); ^{13}C NMR ($CDCl_3$) δ 207.9 (=C=), 133.6 + 128.8 + 127.4 + 127.0 (aromatic ring C-atoms), 98.5 (2 × =CPh); mass spectrum, m/z 192 (M^+).

4,4-Dimethyl-1-phenyl-1,2-pentadiene (4): bp 102 °C (15 mmHg); $n^{20}{}_D$ 1.5395; IR (neat) 1950 cm^{-1} (C=C=C); ^1H NMR (CCl_4) δ 7.18 (m (br),5 H, aromatic protons), 6.09 (d, 1 H, =C*H*Ph), 5.48 (d, 1 H, =C*H*-*t*-Bu), 1.10 (s, 9 H, $(CH_3)_3C$), ^4J(HC=C=CH) –6.45 Hz; ^{13}C NMR ($CDCl_3$) δ 202.4 (=C=), 135.2 + 128.5 + 126.5 + 126.3 (aromatic ring C-atoms), 106.7 (=*C*-*t*-Bu), 96.2 (=*C*Ph), 32.6 ((CH_3)*C*), 30.2 (3 × CH_3); mass spectrum, m/z 172 (M^+).

Preparation of *trans*-(*S*)-5 (R = *t*-Bu) from (*R*)-2b. To a solution of $Pd[PPh_3]_4$ (1.0 mmol) in THF (50 mL) was added, at 20 °C, the 1-bromoallene (*R*)-**2b** (60% ee, 1.2 mmol). The mixture was stirred for 15 min at 20 °C. Half of the volume of THF was then evaporated at reduced pressure while the temperature of the solution was kept at 20 °C. To the resulting concentrated solution was added n-pentane (50 mL). Adduct **5** was precipitated as a yellow compound and was collected on a fritted funnel (G3 filter) which was designed for manipulation under exclusion of air. The compound was washed with pentane (3 × 20 mL). Small amounts of solvent in **5** were removed at 20 °C at 0.02 mmHg (evacuation time: 2 h). Adduct **5** was obtained in 90% yield and showed $[\alpha]^{20}{}_D$ +40° ($CHCl_3$, c 0.5). The trans configuration around Pd in **5** was assigned on the basis of the ^1H and ^{13}C NMR data given below.[19] For the configuration of the allenyl moiety, see the text.

***trans*-(4,4-Dimethyl-1,2-pentadienyl)bis(triphenylphosphine)palladium(II) bromide:** mp 135.5 °C dec; IR (KBr) 1910 cm^{-1} (C=C=C); ^1H NMR ($CDCl_3$) δ 7.5–7.9 (m, 12 H, aromatic protons), 7.2–7.5 (m, 18 H, aromatic protons), 4.83 (dt, 1 H, =CHPd), ^4J(*H*C=C=C*H*) –5.7 Hz, ^3J(*P*PdC*H*) 8.1 Hz, 3.43 (d (br), 1 H, =C*H*-*t*-Bu), 0.60 (s, 9 H, $(CH_3)_3C$); ^{13}C NMR ($CDCl_3$)[20] δ 193.2 (C_6), 135.2 (C_2, t, J(P,C) 5.9 Hz), 131.6 (C_1, t, J(P,C) 22.3 Hz), 130.0 (C_4), 128.0 (C_3, t, J(P,C) 4.3 Hz), 98.5 (C_7), 90.9 (C_5), 31.8 (C_8), 30.1 (C_9). ^{31}P NMR ($CDCl_3$) δ 18.9 (s).



Acknowledgment. This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

Registry No. (*R*)-**1a**, 68276-38-0; (*R*)-**1b**, 89178-58-5; (*R*)-**1c**, 97042-97-2; (*R*)-**2b**, 94137-72-1; (*R*)-**2c**, 94137-73-2; (*S*)-**3**, 3780-00-5; (*R*)-**3**, 49768-13-0; (*S*)-**4**, 94137-70-9; (*R*)-**4**, 97042-98-3; *trans*-(*S*)-**5** (R = *t*-Bu), 97059-52-4; PhZnCl, 28557-00-8; Ph_2Zn, 1078-58-6; $Pd[PPh_3]_4$, 14221-01-3.

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(20) The triplet patterns for C_1, C_2, and C_3 indicate that the coupling constants for these C atoms with both phosphorus nuclei are (almost) identical.