a dialkyl disulfide ligand. This type of product often has, predictably, a rather low stability to ligand loss and when this is so decomposition of this product is the direct consequence.

The formation and properties of metal complexes having disulfide ligands is an interesting subject. We defer a discussion of this chemistry to a subsequent paper.

One additional result merits comment, in that it portends some further interesting study. This concerns the reaction between $[W(MeSSMe)(CO)_3(\eta\text{-}C_5H_5)]BF_4$ and $PPN[W(CO)_3(\eta\text{-}C_5H_5)]$ which occurs according to 7. The

$$[W(MeSSMe)(CO)_3(\eta\text{-}C_5H_5)]BF_4 + PPN[W(CO)_3(\eta\text{-}C_5H_5)] \rightarrow 2W(SMe)(CO)_3(\eta\text{-}C_5H_5) + [PPN]BF_4 \quad (7)$$

rapid formation of the product must come about from nucleophilic attack on the coordinated disulfide ligand. Two alternative reactions, displacement of a ligand in the cation by the nucleophilic anion or electron transfer, do not appear to be a significant factor since $[W(CO)_3(\eta\text{-}C_5H_5)]_2$ is not seen as a product. Significantly the reaction is much faster (complete upon mixing) than the reaction of $PPN[W(CO)_3(\eta\text{-}C_5H_5)]$ and MeSSMe (34 h for completion). In effect, coordination of the metal group to the disulfide has caused the ligand to be much more susceptible to nucleophilic cleavage; or if one prefers, the $W(SMe)(CO)_3(\eta\text{-}C_5H_5)$ group is a better leaving group than SMe^-. Enhanced rates of nucleophilic cleavage upon coordination of a metal ion to a disulfide is a known phenomenon in the biochemical area; metal ions such as Hg^{2+}, Ag^+, and $MeHg^+$ greatly enhance rates of cleavage of disulfide linkages.[20] A similar result was recently documented in cobalt(III) coordination chemistry.[21] It seems desirable to look further at this interesting reaction of a coordinated ligand.

Registry No. $PPN[W(CO)_3(\eta\text{-}C_5H_5)]$, 100312-14-9; $W(SPh)(CO)_3(\eta\text{-}C_5H_5)]$, 12110-93-9; $W(SCF_3)(CO)_3(\eta\text{-}C_5H_5)]$, 35828-05-8; $W(SMe)(CO)_3(\eta\text{-}C_5H_5)$, 12108-26-8; $PPN[Mo(CO)_3(\eta\text{-}C_5H_5)]$, 67486-18-4; $Mo(SPh)(CO)_3(\eta\text{-}C_5H_5)$, 100312-15-0; $[Mo(\mu\text{-}SPh)(CO)_2(\eta\text{-}C_5H_5)]_2$, 12115-34-3; $Mo(SCF_3(CO)_3(\eta\text{-}C_5H_5)$, 35828-04-7; $Mo(SMe)(CO)_3(\eta\text{-}C_5H_5)$, 12108-24-6; $[Mo(M\text{-}SMe)(CO)_2(\eta\text{-}C_5H_5)]_2$, 12112-22-0; $PPN[Mn(CO)_5]$, 52542-59-3; $PPN[Mn_2(\mu\text{-}SPh)_3(CO)_6]$, 100334-04-1; $Mn(SPh)(CO)_5$, 100312-16-1; $Mn_2(\mu\text{-}SPh)_2(CO)_8$, 21240-14-2; $Mn(SCF_3)(CO)_5$, 50979-57-2; $PPN[Mn(SCF_3)_2(CO)_4]$, 100312-18-3; $PPN[Mn_2(\mu\text{-}SCF_3)_3(CO)_6]$, 100312-20-7; $PPN[Mn_2(\mu\text{-}SMe)_3(CO)_6]$, 100312-21-8; $[W(MeSSMe)(CO)_3(\eta\text{-}C_5H_5)]BF_4$, 100312-23-0; $[Mo(MeSSMe)(CO)_3(\eta\text{-}C_5H_5)]BF_4$, 100312-25-2; $Mn_2(\mu\text{-}SMe)_2(CO)_8$, 21321-38-0; $Mn(SMe)(CO)_5$, 66672-68-2; $Mn(CO)_5(MeSSMe)]BF_4$, 100312-27-4; PhSSPh, 882-33-7; CF_3SSCF_3, 372-64-5; MeSSMe, 624-92-0; $[Me_2SSMe]BF_4$, 5799-67-7.

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(20) Bach, R. D.; Rajan, S. J. *J. Am. Chem. Soc.* **1980**, *101*, 3113 and cited references.

(21) Ishimura, A.; Nosco, D. L.; Deutsch, E. *J. Am. Chem. Soc.* **1983**, *105*, 844.

Synthesis, Structure, and Reactivity of Some (σ-Allenyl)- and (σ-Prop-2-ynyl)palladium(II) Complexes

C. J. Elsevier,† H. Kleijn, J. Boersma,* and P. Vermeer

Department of Organic Chemistry, State University at Utrecht, Croesestraat 79,
3522 AD Utrecht, The Netherlands

Received July 30, 1985

Prop-2-ynylic halides, $R^1R^2CXC{\equiv}CR^3$ (1, X = Cl, Br), react with $Pd[PPh_3]_4$ to yield pure *trans*-(σ-allenyl)bis(triphenylphosphine)palladium(II) halides, $R^1R^2C{=}C{=}CR^3Pd[PPh_3]_2X$ (3), when R^3 is hydrogen. The acetylenic isomers *trans*-$R^3C{\equiv}CCR^1R^2Pd[PPh_3]_2X$ (4) are obtained pure when R^3 is a bulky group, e.g., $t\text{-}C_4H_9$ and $(CH_3)_3Si$, and R^1 and R^2 are both hydrogen. A mixture of both isomers is formed when R^3 is methyl and R^1 and R^2 are both hydrogen. Prop-2-ynylic acetates, $R^1R^2CXC{\equiv}CR^3$ (1, X = OAc), can also be used to prepare the palladium(II) complexes, but salts like zinc or lithium chloride must be present to let the conversion proceed. The formation of 3 from 1 takes place with anti stereoselectivity. In a number of cases adducts 3 have been prepared by reaction of allenic halides, $R^1R^2C{=}C{=}CR^3X$ (2, X = Cl, Br), with $Pd[PPh_3]_4$. This reaction occurs with inversion of configuration of the allenyl moiety. The reactivity of adducts 3 and 4 was studied by reacting them with organozinc compounds, R^4ZnX'. The reactions preferentially lead to allenes, $R^1R^2C{=}C{=}CR^3R^4$. The acetylenic isomers arise when the R^3 group is very bulky.

Introduction

In a series of investigations we and others have shown that prop-2-ynylic halides and esters and α-acetylenic oxirans as well as 1-haloallenes are converted smoothly into substituted allenes, $-\overset{|}{C}{=}C{=}\overset{|}{C}-R$, in which R is an unsaturated group, by reaction with an appropriate organometallic reagent, R–M, in the presence of $Pd[PPh_3]_4$ as a catalyst.[1] In this way allenes could be prepared, in which the R group is aryl, 1-alkenyl, 1,2-alkadienyl, 1-alkynyl, and 1,3-alkadiynyl.

It has been assumed that (σ-allenyl)palladium(II) complexes are intermediates in these reactions, an assumption which is not unreasonable as such complexes are known,

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† Present address: Vakgroep Anorganische Chemie, Universiteit van Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands.

(1) (a) Jeffery-Luong, T.; Linstrumelle, G. *Tetrahedron Lett.* **1980**, *21*, 5019. (b) Ruitenberg, K.; Kleijn, H.; Elsevier, C. J.; Meijer, J.; Vermeer, P. *Ibid.* **1981**, *22*, 1451. (c) Kleijn, H.; Meijer, J.; Overbeek, G. C.; Vermeer, P. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 97. (d) Ruitenberg, K.; Kleijn, H.; Westmijze, H.; Meijer, J.; Vermeer, P. *Ibid.* **1982**, *101*, 405.

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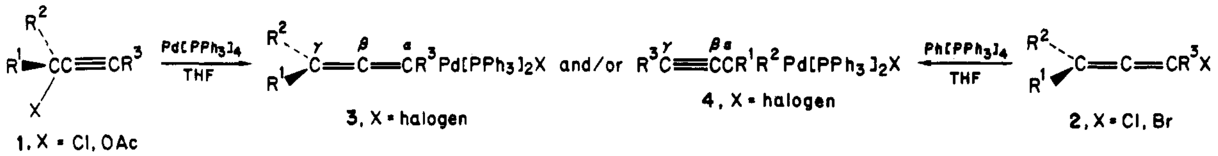
Scheme I



1, X = Cl, OAc

3, X = halogen

4, X = halogen

2, X = Cl, Br

1-4	R^1	R^2	R^3	X
1a, 2a, 3a	CH_3	CH_3	H	Cl[a]
1b, 3b	C_5H_{10}		H	Cl
2c, 3c	t-C_4H_9	CH_3	H	Cl
1d, 3d	C_6H_5	H	H	Cl[a]
2e, 3e	t-C_4H_9	H	H	Br
1f, 3f	CH_3	H	CH_3	Cl
1g, 4g	H	H	t-C_4H_9	Cl
1h, 4h	H	H	$Si(CH_3)_3$	Cl

[a] In the case of 1 as starting compound, both the chloride and the acetate (+ LiCl) were used.

e.g., Rh, Ir, and Pt.[2] Evidence for the occurrence of (σ-allenyl)palladium(II) species is, however, lacking in the literature. It was therefore of interest to attempt their preparation.[3] Also from a stereochemical point of view it was important to study their formation. The fact is that the conversion of prop-2-ynylic esters by phenylzinc compounds in the presence of the catalyst $Pd[PPh_3]_4$ proceeds anti.[4] The question is how this anti stereochemistry is reached. It was assumed that the oxidative addition reaction leading to the (σ-allenyl)palladium(II) species occurs anti (cf. ref 4).

In this context it was worthwhile to attempt the preparation, isolation, and identification of the proposed (σ-allenyl)palladium(II) intermediates and to study the stereochemistry of their formation as well as their behavior toward organozinc compounds in order to substantiate (or modify) mechanistic proposals in the literature.

Results and Discussion

Preparation and Properties. The intermediates were prepared by stirring a small excess of the prop-2-ynylic chlorides and acetates 1 or the 1-haloallenes 2 with the complex $Pd[PPh_3]_4$ (solvent THF). Acetates 1 as such did not react; they could be activated, however, by adding an equimolar amount of zinc chloride or lithium chloride. From the literature it is known that also allylic acetates are highly unreactive toward $Pd[PPh_3]_4$ solely.[5]

Spectroscopic evidence (vide infra) showed that indeed (σ-allenyl)palladium(II) compounds 3 are formed from 1 and 2 when the R^3 group is not too bulky. Thus, compounds **3a–f** in Scheme I were obtained with over 95% regioselectivity (by ^1H NMR) from the indicated starting compounds. On the other hand, (σ-prop-2-ynyl)palladium(II) complexes 4 were obtained with over 95% regioselectivity (by ^1H NMR) in the case of bulky R^3 groups, viz., t-C_4H_9 and Me_3Si (compounds **4g** and **4h** in Scheme I). In one case a mixture of both regioisomers was obtained, viz., upon reaction of $MeC{\equiv}CCH_2Cl$ with $Pd[PPh_3]_4$ (ratio 3:4 ≃ 20:80; not recorded in Scheme I). The relative size of the R^{1-3} groups is apparently important for the regiochemistry. It should be mentioned that, starting from 1 (X = OAc), no acetate group was present in complex 3 or 4 as it was easily seen in the ^1H and ^{13}C NMR spectra. Instead of the acetate group, chloride was present, being delivered by the zinc or lithium chloride which we had added to realize the conversion of 1 for X = OAc (vide supra).

The palladium(II) compounds 3 and 4 are bright yellow powders; they decompose at their (rather sharp) melting points. The species are very prone to oxidation by air in the solute state, but in the solid state they are fairly stable toward air. Their solubility in polar solvents (water, acetonitrile, dioxane, methanol, etc.) as well as in highly apolar solvents (n-pentane and n-hexane) is very low; it is somewhat better in diethyl ether and excellent in solvents like benzene, toluene, tetrahydrofuran, acetone, methylene chloride, and chloroform.

Compounds 3 and 4 are monomeric in THF (by ebulliometry). Also microanalytical data are consistent with the formation of the indicated compounds. Unfortunately, attempts to grow suitably sized single crystals for X-ray analysis failed. Nevertheless, the spectroscopic data given in the next section do correspond well with the proposed structures. Stereochemical features were studied by reacting optically active 1 and 2 with $Pd[PPh_3]_4$.

Spectroscopic Results. IR (KBr). The (σ-allenyl)palladium(II) complexes 3 all showed a weak to very weak absorption for the (asymmetric) stretching vibration of the allenyl moiety in the region around 1900 cm^{-1}. Generally, allenic hydrocarbons absorb in the region around 1950 cm^{-1}. Our value is in good agreement, however, with values reported for σ-allenyl complexes derived from other transition metals.[2] In the case of the (σ-prop-2-ynyl)palladium(II) compounds **4g** and **4h** a medium to weak stretching vibration for the acetylenic moiety was found at ≃2150 cm^{-1}.

^{1}H NMR. These spectra were determined by using Varian EM-390 and Bruker WP-200 spectrometers. The integration data were in perfect agreement with the presence of two triphenylphosphine groups in the oxidative addition products 3 and 4. Homonuclear proton decoupling experiments for 3 resulted in the appearance of a pure triplet ($J \simeq 6.0$–9.0 Hz) for the allenic α-H atom (R^3 = H). The triplet pattern is due to $^3J(P,H)$ coupling and points to the presence of two equivalent triphenylphosphine groups. The δ values for the α-H atom in 3 are somewhat lower than those generally observed for allenes; also the α-H atoms in adducts 4 are found at relatively high field ($\delta \simeq 1.3$). These observations are consistent with data reported for other (σ-allenyl)- and (σ-prop-2-ynyl)metal compounds (cf. ref 2).

^{13}C NMR. The spectra were recorded on a Brucker WP-200 spectrometer. In the case of adducts 3 a signal

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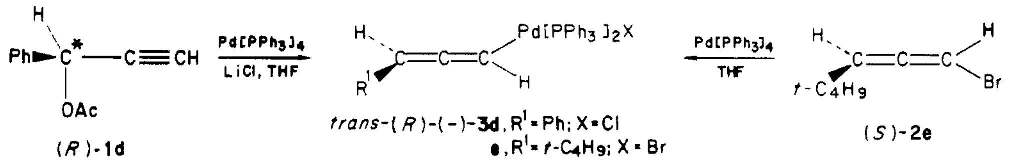
[2] (a) Collman, J. P.; Cawse, J. N.; Kang, J. W. *Inorg. Chem.* **1969**, *8*, 2574. (b) Mann, B. E.; Shaw, B. L.; Tucker, N. I. *J. Chem. Soc. A* **1971**, 2667. (c) See also: Jacobs, T. L. In ref 12b, Vol. 2, p 334.

[3] For a preliminary communication see: Elsevier, C. J.; Kleijn, H.; Ruitenberg, K.; Vermeer, P. *J. Chem. Soc., Chem. Commun.* **1983**, 1529.

[4] Elsevier, C. J.; Stehouwer, P. M.; Westmijze, H.; Vermeer, P. *J. Org. Chem.* **1983**, *48*, 1103.

[5] Yamomoto, T.; Saito, O.; Yamomoto, A. *J. Am. Chem. Soc.* **1981**, *103*, 5600.

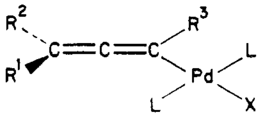
Scheme II



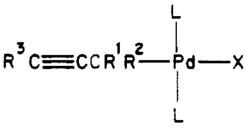
of low intensity was found in the region around δ 195. The signal is characteristic for the sp-hybridized allenic carbon atom. The α-C atoms in 3 and 4 do not couple measurably with the ^{31}P nuclei. This points to a P–Pd–C angle of ≃90° as it is known for (σ-allyl)palladium(II) complexes that ^2J(P–Pd–C) is ≃0 Hz when the angle P–Pd–C is ca. 90° and ≃125 Hz when it is ca. 180°.[6]

^{31}P NMR. The $^{31}P\{^1H\}$ NMR spectra were determined on a Bruker WP-200 spectrometer using Na_3PO_4 as external standard. In all cases only one sharp P signal ($w_{1/2}$ = 3–4 Hz) was observed in the region around δ 20 (at 298 K). Similar to the ^1H NMR evidence, this points to two magnetically equivalent ^{31}P nuclei.

Structure. The spectroscopic, ebulliometric, and microanalytical data provide good evidence for a structure in which an allenyl or prop-2-ynyl moiety is σ-bounded to a $Pd[PPh_3]_2X$ group. The two triphenylphosphine ligands in the square-planar complexes 3 and 4 will be trans oriented as then the two phosphine ligands are magnetically equivalent. The trans geometry is generally observed for the oxidative addition products of late transition metals with organic halides.[7]



trans-**3**



trans-**4**

L = PPh_3

Stereochemical Results. In order to study stereochemical features, we treated optically pure **1d** (R^1 = Ph; $R^2 = R^3$ = H; X = OAc) as well as optically active allenic halide **2e** (R^1 = t-C_4H_9; $R^2 = R^3$ = H; X = Br) with the complex $Pd[PPh_3]_4$. In the case of 1 we used the acetate, as the compound can be readily prepared from the optically active alcohol without racemization. Use of the corresponding chloride was less attractive as its preparation from the alcohol is accompanied by extensive racemization.[8] It was already mentioned that in the case of prop-2-ynylic acetates a halide source must be present. We used for our purpose lithium chloride. In separate experiments it was established that, under the conditions of the reaction, lithium chloride does not racemize acetate **1d** nor converts it into a halide.

Thus, treatment of optically pure (*R*)-**1d**[9] gave *levorotatory* (σ-allenyl)palladium(II) chloride **3d** ($[\alpha]^{20}_D$ −720° (c 0.40, in $CHCl_3$)). Similarly, *levorotatory* **3e** ($[a]^{20}_D$ −40° (c 0.50, $CHCl_3$)) was obtained by reacting (*S*)-(+)-1-bromo-4,4-dimethyl-1,2-pentadiene (**2e**; $[\alpha]_D$ +140° (c 0.80, EtOH), ee 61%)[10] with $Pd[PPh_3]_4$. The stereochemical course of the two reactions is therefore as depicted (Scheme II). To levorotatory **3d** and **3e** the *R* absolute configuration must be assigned on the basis of Lowe–Brewster rules[11] and the chirality functions approach as developed by Ruch and Runge.[12] As a consequence, the conversion of **1d** into **3d** proceeds anti. Anti 1,3-substitution reactions were also observed for organocopper(I)-induced formations of allenes from prop-2-ynylic substrates.[13]

The overall anti stereochemistry as reported for the conversion of prop-2-ynylic esters by organozinc reagents using catalytic amounts of $Pd[PPh_3]_4$[4] will therefore most likely be brought about as follows. The first step of the reaction sequence will be the formation of **3** in an anti fashion as indicated. In the second step the halogen X in **3** will be replaced by R^4 by reaction with the organozinc compound. This step and the following one involving reductive elimination of the allene $R^1R^2C{=}C{=}CR^3R^4$ both will proceed with retention of configuration of the allenyl moiety, in analogy with what has been observed for alkenes;[14] see, however, the next section.

The conversion of (*S*)-**2e** into (*R*)-**3e** implies the occurrence of *inversion* of configuration in the allenyl moiety. Apparently, the preferred process is not a direct insertion of palladium(0) in the C–Br bond of **2e**, as in that case the configuration would not change, but an anti S_N2'-like displacement of bromide followed by attachment of bromide to palladium leading to (*R*)-$HC{\equiv}CCH(t\text{-}C_4H_9)$-$Pd[PPh_3]_2Br$ does occur. A suprafacial 1,3 shift of the group $Pd[PPh_3]_2Br$ then gives (*R*)-**3**. A similar process has been proposed for the conversion of an allenic bromide into a substituted allene by an organocuprate.[15]

Conversion by Organozinc Compounds. For the catalytic conversion of **1** and **2** by organozinc reagents adducts **3** were the intermediates proposed.[1b-d] Having these compounds now available, it was of interest to treat them with organozinc compounds and to see what would happen.

Our first experiments concerned the behavior of adduct **3a** ($R^1 = R^2$ = Me; R^3 = H; X = Cl). The complex appeared to react smoothly with some selected organozinc

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[6] (a) Schick, K.-P. Ph.D. Dissertation, Ruhr-Universität at Bochum, 1982. (b) Buch, H. M.; Binger, P.; Benn, R.; Krüger, C.; Rufinška, A. *Angew. Chem.* **1983**, *95*, 814.

[7] For instance, see: (a) Kochi, J. K. "Organometallic Mechanisms and Catalysis", Academic Press: London, 1978. (b) Maitlis, P. M.; Espinet, P.; Russell, M. J. H. "Comprehensive Organometallic Chemistry"; Pergamon Press: Oxford, 1982; Vol. 6, pp 243, 279.

[8] Muscio, O. J.; Jun, Y.; Philips, J. B. *Tetrahedron Lett.* **1978**, 2379.

[9] For its preparation see: ref 4. The required optically pure alcohol (*R*)-(−)-1-phenyl-2-propyn-1-ol, $[\alpha]^{20}_D$ −20.8° (dioxane, c 4.3), was obtained following our procedure: ref 13c.

[10] For its preparation see: Elsevier, C. J.; Vermeer, P.; Gedanken, A.; Runge, W. *J. Org. Chem.* **1985**, *50*, 364.

[11] (a) Lowe, G. *Chem. Commun.* **1965**, 411. (b) Brewster, J. H. *Top. Stereochem.* **1967**, *2*, 1. (c) Note that we assume a higher polarizability for $Pd[PPh_3]_2X$ over hydrogen. This is very reasonable and is supported by CD measurements for (−)-**3d** which will be reported elsewhere.

[12] (a) Runge, W. In "The Chemistry of Ketenes, Allenes and related Compounds"; Patai, S., Ed.; Wiley: Chichester, 1980; Part 1. (b) Runge, W. In "The Chemistry of the Allenes"; Landor, S. R., Ed.; Academic Press: London, 1982; Vol. 3.

[13] For instance see: (a) Rona, P.; Crabbé, P. *J. Am. Chem. Soc.* **1969**, *91*, 3289. (b) Luche, J. L.; Barreiro, E.; Dollat, J.-M.; Crabbé, P. *Tetrahedron Lett.* **1975**, 4615. (c) Tadema, G.; Everhardus, R. H.; Westmijze, H.; Vermeer, P. *Ibid.* **1978**, 3935. (d) Pirkle, W. H.; Boeder, C. W. *J. Org. Chem.* **1978**, *43*, 1950. (e) Olsson, L.-I.; Claesson, A. *Acta Chem. Scand., Ser. B* **1979**, *B33*, 679. (f) Elsevier, C. J.; Meijer, J.; Westmijze, H.; Vermeer, P.; Van Dijck, L. A. *J. Chem. Soc., Chem. Commun.* **1982**, 84. (g) Haces, A.; Van Kruchten, E. M. G. A.; Okamura, W. H. *Tetrahedron Lett.* **1982**, *23*, 2707. (h) Elsevier, C. J. Ph.D. Dissertation, State University at Utrecht, 1984.

[14] For instance see: (a) ref 7. (b) Loar, M. K.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4174.

[15] Corey, E. J.; Boaz, N. W. *Tetrahedron Lett.* **1984**, *25*, 3059, 3063.

reagents, R^4ZnX', viz., "PhZnCl", Ph_2Zn, and $Me_3SiC{\equiv}CZnCl$, to give pure allenes $(CH_3)_2C{=}C{=}CHR^4$ in 76–85% yield (solvent THF). The tendency to form allenes is high. For instance, reaction of the mixture consisting of $CH_3C{\equiv}CCH_2Pd[PPh_3]_2Cl$ (80 relative %) and $H_2C{=}C{=}C(CH_3)Pd[PPh_3]_2Cl$ (20 relative %) with Ph_2Zn gave *pure* $H_2C{=}C{=}C(Me)Ph$ (yield 87%). These results are completely in line with those reported for the catalytic reaction.[1d] Only when the R^3 group is very bulky and R^1 and R^2 are small, the acetylenic product will arise too. This is the case starting from pure $Me_3SiC{\equiv}CCH_2Pd[PPh_3]_2Cl$ (**4h**): reaction of **4h** with Ph_2Zn produced a mixture of $H_2C{=}C{=}C(SiMe_3)Ph$ and $Me_3SiC{\equiv}CCH_2Ph$ in the ratio 27:73. The attempted isolation of intermediates of the type $R^1R^2C{=}C{=}CR^3Pd[PPh_3]_2R^4$ (or $R^3C{\equiv}CCR^1R^2Pd[PPh_3]_2R^4$) failed because the reductive elimination of the allenes $R^1R^2C{=}C{=}CR^3R^4$ (or the acetylenes $R^3C{\equiv}CCR^1R^2R^4$) is too rapid.

As a logical extension of the stereochemical study, also an optically active complex **3**, viz., **3d** (R^1 = Ph; R^2 = R^3 = H; X = Cl), was allowed to react with PhZnCl and Ph_2Zn. Unfortunately, the 1,3-diphenylpropadiene produced showed no optical rotation at all. The catalytic reaction proceeds in a high optical yield (cf. ref 4). This could mean that either the catalytic reaction does not follow a route in which **3** occurs or that the allene produced initially is optically active but racemizes rapidly with the complex $Pd[PPh_3]_2$ which is liberated in an equimolar amount. For the time being, we believe that the second suggestion is the most likely reason for the zero rotation of 1,3-diphenylpropadiene. Allenes may form complexes with palladium(0).[16] The bond order of the complexed double bond will be substantially lower than when it is uncomplexed (cf. ref 16). One could therefore imagine that through such complexes racemization may occur. In some separate experiments it was found that optically active 1,3-diphenylpropadiene suffers from substantial racemization when treated with 10 mol % of $Pd[PPh_3]_4$. It is therefore highly likely that equimolar amounts of $Pd[PPh_3]_2$ are capable of racemizing 1,3-diphenylpropadiene completely. It is also conceivable that addition of 2–5 molar equiv of triphenylphosphine to **3d** prior to the phenylzinc compound gave no improvement of the $[\alpha]_D$ value. In the catalytic reaction only a few mole percent of $Pd[PPh_3]_4$ were used (cf. ref 1) so that subsequent racemization of the produced allene was not important. In this sense the conversion of isolated **3** and **4** by an equimolar amount of R^4ZnX' is not a good model for the catalytic reaction.

Conclusion

From the presented work it can be concluded that (σ-allenyl)palladium(II) species **3** are the most likely candidates to be intermediates in the $Pd[PPh_3]_4$-catalyzed conversion of compounds **1** and **2** by organozinc compounds into the allenes $R^1R^2C{=}C{=}CR^3R^4$. One should realize, however, that also (σ-prop-2-ynyl)palladium(II) halides **4** may be precursors for the allenes $R^1R^2C{=}C{=}CR^3R^4$ as the $CH_3C{\equiv}CCH_2Pd[PPh_3]_2Cl$ example indicates. From a stereochemical point of view it will not make much difference whether the reaction proceeds through **3** or **4**, as in both cases the intermediates will be formed in an anti fashion.[17]

Experimental Section

General Comments. All reactions and other manipulations were performed under an atmosphere of pure nitrogen. Standard syringe techniques were used to transfer organometallic and other air-sensitive compounds. Elemental analyses were carried out by G. J. Rotscheid, ITC/TNO, Zeist, The Netherlands. Melting points were obtained by using a melting point microscope and are uncorrected. Ebulliometric measurements on THF solutions of the palladium(II) species were carried out with a Gallenkamp ebulliometer. Infrared spectra were recorded on a Perkin-Elmer 457 IR spectrophotometer. NMR spectra were recorded on Varian-EM-390 and Brucker WP-200 spectrometers. All reported ^{13}C and ^1H chemical shifts are relative to Me_4Si. ^{31}P NMR chemical shifts are relative to Na_3PO_4 (saturated solution in D_2O) with downfield chemical shifts reported as positive. Optical rotations were measured at 20 °C with a Perkin-Elmer 241 polarimeter and standard cuvettes (l = 1 dm). The relative error in $[\alpha]_D$ is $\leq 2\%$.

Materials. Tetrahydrofuran was distilled from $LiAlH_4$. The complex $Pd[PPh_3]_4$ was prepared according to the procedure of Coulson;[18] it was used as a 0.02 M solution in THF. Lithium and zinc chlorides (purchased from Merck) were dried at 200 °C in high vacuum and used as a 0.6 and 1.0 M solution in THF, respectively; *n*-butyllithium was purchased from Metallgesellschaft A. G. (Frankfurt am Main) as a 1.5 M solution in *n*-hexane. Diphenylzinc was obtained following the procedure of Hofstee.[19] "Phenylzinc chloride" was prepared in situ (solvent THF) by mixing equimolar amounts of PhMgBr and zinc chloride; [(trimethylsilyl)ethynyl]zinc chloride was obtained by sequential treatment of (trimethylsilyl)acetylene with equimolar amounts of *n*-butyllithium and zinc chloride (solvent THF). The starting compounds **1** and **2** were prepared according to known procedures.[20] Optically pure (*R*)-**1d** and optically enriched (*S*)-**2e** (ee 61%) were obtained from (*R*)-1-phenylprop-2-yn-1-ol[9] and (*R*)-4,4-dimethylpent-1-yn-3-ol,[10] respectively.

General Procedure for Reactions of Compounds 1 and 2 with $Pd[PPh_3]_4$. (a) Halides. Compound **1** or **2** (1.0–1.5 mmol) was added at once to $Pd[PPh_3]_4$ (1.0 mmol) in THF (50 mL) at 20 °C. The mixture was stirred for 15 min at 20 °C, and then half the volume of solvent was evaporated at reduced pressure, distilled *n*-pentane (50–75 mL) was added, and the yellow precipitate was collected on a fritted funnel (designed for manipulating under nitrogen atmosphere). The precipitate was washed with diethyl ether (20 mL) and *n*-pentane (25 mL) and freed from solvent in vacuo (20 °C (0.02 mmHg) for 3 h). Adducts **3** and **4** were isolated in 82–95% yield; they were stored under nitrogen. In the case of optically active (*R*)-**3e** all manipulations were carried out in a black apparatus to prevent racemization by light.

(b) Acetates. A solution of (racemic) acetate **1** (1.1 mmol) in THF (0.5 mL) was added at once to $Pd[PPh_3]_4$ (1.0 mmol) in THF (50 mL) at 20 °C. Then a solution of zinc chloride (1.1 mmol) in THF (1.1 mL) was added, and the mixture was stirred for 10–15 min at 20 °C. The palladium(II) compound was precipitated by addition of water (50–75 mL) and collected on a fritted funnel. It was washed with diethyl ether (2 × 20 mL) and *n*-pentane (1 × 20 mL) and dried at 20 °C (0.02 mmHg) for 3 h (yield 80–85%). In the case of the optically active acetate (*R*)-**1d**, lithium chloride (1.2 mmol, 0.58 M solution in THF) instead of zinc chloride was used (yield of **3d**, 83%). To prevent racemization by light, all manipulations were carried out in a black apparatus.

Spectral[21] and Physical Data. 3a: mp 137 °C dec; IR (KBr) 1903 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 7.6–7.9 (m, 12 H, aromatic ortho protons), 7.2–7.6 (m, 18 H, aromatic meta and para protons), 4.65 (m, 1 H, $=C{=}CH$, $J_{P,H}$ = 8.3 Hz), 0.80 (s (br), 6 H, 2 × CH_3);

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[16] Okamoto, K.; Kai, Y.; Yasuoka, N.; Kasai, N. *J. Organomet. Chem.* **1974**, *65*, 427.

[17] Optically active α-phenethyl bromide, for instance, adds oxidatively to $Pd[PPh_3]_4$ with inversion of configuration at carbon in 95% ee: Lau, K. S. Y.; Wong, P. K.; Stille, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 5832.

[18] Coulson D. R. "Inorganic Syntheses"; McGraw-Hill: New York, 1972; Vol. 13, p 121.

[19] Hofstee, H. K. Ph.D. Dissertation, State University at Utrecht, 1978.

[20] (a) Brandsma, L. "Preparative Acetylenic Chemistry"; Elsevier: Amsterdam, 1971. (b) Brandsma, L.; Verkruijsse, H. D. "Synthesis of Acetylenes, Allenes and Cumulenes"; Elsevier: Amsterdam, 1981. (c) Reference 10.

[21] The ^{13}C signals for C_{ipso}, C_{ortho}, and C_{meta} of the triphenylphosphine ligands appeared as triplets. Similar observations have been reported for the compounds $PdX_2(PPh_3)_2$ (X = Cl, N_3): MacDougall, J. J.; Nelson, J. H. *Inorg. Nucl. Chem. Lett.* **1979**, *15*, 315.

^{13}C NMR ($CDCl_3$) δ 194.6 (=C=), 135.1 (C_{ortho}), 131.6 (C_{ipso}), 130.1 (C_{para}), 128.1 (C_{meta}), 91.4 (=CR^1R^2), 84.3 (=CR^3), 19.9 (CH_3); ^{31}P NMR ($CDCl_3$) δ 15.7 (s). Anal. Calcd for $C_{41}H_{37}ClP_2Pd$: C, 67.13; H, 5.08; Cl, 4.83; P, 8.44; Pd, 14.50. Found: C, 66.47; H, 4.94; Cl, 4.66; P, 8.05; Pd, 14.3. Molecular weight by ebulliometry (THF): 772 (calcd 734).

3b: mp 119–120 °C dec; IR (KBr) 1890 cm^{-1} (w); ^{1}H NMR ($CDCl_3$) δ 7.5–7.9 (m, 12 H, aromatic ortho protons), 7.1–7.5 (m, 18 H, aromatic meta and para protons), 4.67 (m, 1 H, =C=CH; $J_{P,H}$ = 8.4 Hz), 0.9–1.4 (m, 10 H, pentamethylene group); ^{13}C NMR ($CDCl_3$) δ 191.1 (=C=), 135.0 (C_{ortho}), 131.6 (C_{ipso}), 129.9 (C_{para}), 128.0 (C_{meta}), 99.0 (=CR^1R^2), 84.7 (=CR^3), 30.7 (CH_2C=), 27.0 (CH_2CC=), 26.2 (CH_2CCC=); ^{31}P NMR ($CDCl_3$) δ 15.5 (s). Anal. Calcd for $C_{44}H_{42}ClP_2Pd$: C, 68.31; H, 5.34; Cl, 4.58; P, 8.01. Found: C, 67.90; H, 5.45; Cl, 4.59; P, 7.75. Molecular weight by ebulliometry (THF): 758 (calcd 774).

3c: mp 118 °C dec; IR (KBr) 1895 cm^{-1} (w); ^{1}H NMR (CD_2Cl_2) δ 7.6–7.9 (m, 12 H, aromatic ortho protons), 7.3–7.6 (m, 18 H, aromatic meta and para protons), 4.76 (m, 1 H, =C=CH, $J_{P,H}$ = 9.0 Hz), 0.62 (s, 9 H, $(CH_3)_3C$), 0.50 (d, 3 H, CH_3); ^{13}C NMR (CD_2Cl_2) δ 192.5 (=C=), 135.7 (C_{ortho}), 132.2 (C_{ipso}) 130.8 (C_{para}), 128.7 (C_{meta}), 106.5 (=CR^1R^2), 86.6 (=CR^3), 34.3 ($C(CH_3)_3$), 29.4 ($(CH_3)_3C$), 14.6 (CH_3C=); ^{31}P NMR (CD_2Cl_2) δ 18.2 (s). Anal. Calcd for $C_{44}H_{43}ClP_2Pd$: C, 68.06; H, 5.58; Cl, 4.66; P, 7.98. Found: C, 67.70; H, 5.71; Cl, 4.21; P, 7.84. Molecular weight by ebulliometry (THF): 860 (calcd 776).

3d: mp 138–140 °C dec; IR (KBr) 1903 cm^{-1} (w); ^{1}H NMR ($CDCl_3$) δ 7.5–7.8 (m, 12 H, aromatic ortho protons), 7.2–7.5 (m, 18 H, aromatic meta and para protons), 6.7–7.0 + 6.4–6.6 (m, 5 H, C_6H_5C=), 5.30 (dt, 1 H, =C=CH, $^4J_{H,H}$ = −6.0 Hz, $J_{P,H}$ = 6.0 Hz), 4.43 (dt, 1 H, =C=CH, $J_{P,H}$ = 1.7 Hz); ^{13}C NMR ($CDCl_3$) δ 195.3 (=C=), 135.2, 130.3, 128.0, and 126.1 (C_{ipso}, C_{meta}, C_{para}, and C_{ortho} for the group $R^1 = C_6H_5$), 135.0, 131.1, 130.1, and 128.1 (C_{ortho}, C_{ipso}, C_{para}, and C_{meta} for the phenyl groups in the triphenylphosphine ligands), 88.7 (=CPh), 77.2 (=CR^3); ^{31}P NMR ($CDCl_3$) δ 17.1 (s). Anal. Calcd for $C_{45}H_{37}ClP_2Pd$: C, 69.15; H, 4.77; Cl, 4.53; P, 7.92; Pd, 13.61. Found: C, 68.75; H, 4.84; Cl, 4.53; P, 7.73; Pd, 13.6. Molecular weight by ebulliometry (THF): 778 (calcd 782). When **3d** was prepared from optically pure (*R*)-**1d** (X = OAc), its $[\alpha]^{20}_D$ value amounted to −720° (*c* 0.35, $CHCl_3$).

3e: mp 122–123 °C dec; IR (KBr) 1910 cm^{-1} (w); ^{1}H NMR ($CDCl_3$) δ 7.5–7.9 (m, 12 H, aromatic ortho protons), 7.2–7.5 (m, 18 H, aromatic meta and para protons), 4.83 (dt, 1 H, =C=CH; $^4J_{H,H}$ = −5.7 Hz, $J_{P,H}$ = 8.1 Hz); 3.43 (d, 1 H, =C=CH), 0.60 (s, 9 H, $(CH_3)_3C$); ^{13}C NMR ($CDCl_3$) δ 193.2 (=C=), 135.2 (C_{ortho}), 131.6 (C_{ipso}), 130.0 (C_{para}), 128.0 (C_{meta}), 98.5 (=CR^1R^2), 90.9 (=CR^3), 31.6 ($C(CH_3)_3$), 30.1 ($(CH_3)_3C$); ^{31}P NMR ($CDCl_3$) δ 18.9 (s). Anal. Calcd for $C_{43}H_{41}BrP_2Pd$: C, 64.07; H, 5.13; Br, 9.91; P, 7.69. Found: C, 63.43; H, 5.21; Br, 10.17; P, 7.49. When **3e** was prepared from (*S*)-**2e** (ee 61%), a $[\alpha]^{20}_D$ value of −40° (c 0.50, $CHCl_3$) was measured for the compound.

3f: mp 138–140 °C dec; IR (KBr) 1905 cm^{-1} (?, vw); ^{1}H NMR ($CDCl_3$) δ 7.6–7.9 (m, 12 H, aromatic ortho protons), 7.2–7.4 (m, 18 H, aromatic meta and para protons), 3.6–3.9 (m, 1 H, =C=CH), 0.7–1.0 (m, 6 H, 2 × CH_3); ^{13}C NMR (CD_2Cl_2)[22] δ 134.3 (C_{ortho}), 131.4 (C_{ipso}), 129.8 (C_{para}), 128.0 (C_{meta}), 96.7 (=CR^3), 79.3 (=CR^1R^2), 20.7 (CH_3), 12.7 (CH_3). ^{31}P NMR ($CDCl_3$) δ 16.4 (s). Anal. Calcd for $C_{41}H_{37}ClP_2Pd$: C, 67.13; H, 5.08; Cl, 4.83; P, 8.44. Found: C, 67.37; H, 5.39; Cl, 4.62; P, 8.17.

4g: mp 142 °C dec; IR (KBr) 2180 cm^{-1} (w); ^{1}H NMR (CD_2Cl_2) δ 7.6–7.9 (m, 12 H, aromatic ortho protons), 7.2–7.6 (m, 18 H, aromatic meta and para protons), 1.28 (s (br), 2 H, CH_2Pd), 0.98 (s, 9 H, $(CH_3)_3C$); ^{13}C NMR (CD_2Cl_2) δ 135.0 (C_{ortho}), 131.9 (C_{ipso}), 129.9 (C_{para}), 128.4 (C_{meta}), 81.5 (≡CR^3), 67.9 (≡CCH_2), 30.9 ($(CH_3)_3C$), 30.6 ($C(CH_3)_3$), 7.9 (CH_2Pd); ^{31}P NMR (CD_2Cl_2) δ 22.9 (s). Anal. Calcd for $C_{43}H_{41}ClP_2Pd$: C, 67.81; H, 5.43; Cl, 4.66; P, 8.13. Found: C, 67.95; H, 6.20; Cl, 4.35; P, 7.19.

4h: mp 148–149 °C dec; IR (KBr) 2135 cm^{-1} (w); ^{1}H NMR ($CDCl_3$) δ 7.6–7.8 (m, 12 H, aromatic ortho protons), 7.3–7.6 (m, 18 H, aromatic meta and para protons), 1.30 (s (br), 2 H, CH_2Pd), 0.00 (s, 9 H, $(CH_3)_3Si$); ^{13}C NMR ($CDCl_3$) δ 135.0 (C_{ortho}), 131.0 (C_{ipso}), 130.2 (C_{para}), 128.1 (C_{meta}), 88.7 (≡CR^3), 77.1 (≡CCH_2), 6.7 (CH_2Pd), 0.0 ($(CH_3)_3Si$); ^{31}P NMR ($CDCl_3$) δ 20.6 (s). Anal. Calcd for $C_{42}H_{41}ClP_2SiPd$: C, 64.87; H, 5.31; Cl, 4.56; P, 7.97. Found: C, 65.12; H, 6.00; Cl, 4.42; P, 7.17. Molecular weight by ebulliometry (THF): 762 (calcd 778).

Reactions of 3 and 4 with Selected Organozinc Compounds. The palladium(II) compound (0.50 mmol) was added at once to a stirred solution of the organozinc reagent (0.55 mmol) in THF (20 mL) at 0 °C. The temperature was kept at 20 °C for 15–30 min. The product was isolated by pouring the resulting mixture onto an aqueous NH_4Cl solution (100 mL) and extracting with *n*-pentane (2 × 25 mL). The combined extracts were washed with water and dried with K_2CO_3. The solvent was evaporated in vacuo. The crude compounds were purified over silica (eluent, *n*-pentane) and were analyzed by ^{1}H NMR, IR, and GLC. In this way, $(CH_3)_2C{=}C{=}CHPh$ was obtained from **3a** in 85% yield by using Ph_2Zn and in 81% yield by using "PhZnCl"; $(CH_3)_2C{=}C{=}CH\text{-}C{\equiv}CSi(CH_3)_3$ was isolated in 76% yield. The allenes were pure and their spectroscopic data were identical with those already described.[1d,23] Pure $PhC(CH_3){=}C{=}CH_2$ was obtained by treatment of the mixture consisting of $H_2C{=}C{=}C(CH_3)Pd(PPh_3)_2Cl$ and $CH_3C{\equiv}CCH_2Pd(PPh_3)_2Cl$ with Ph_2Zn; yield (after purification over silica) 87%; the allene was identical with a sample of the known compound.[24] Compound **4h** was allowed to react with "PhZnCl" and Ph_2Zn; in both cases a mixture of $(CH_3)_3SiC{\equiv}CCH_2Ph$ and $H_2C{=}C{=}C(Ph)Si(CH_3)_3$ (ratio 73:27) was obtained which was not further purified.

Acknowledgment. We are indebted to A. V. E. George and D. Seijkens for recording the NMR spectra. This work was supported in part (C.J.E.) by The Netherlands Foundation for Chemical Research (SON) with financial aid from The Netherlands Organization for the Advancement of Pure Research (ZWO).

Registry No. 1 ($R^1 = R^2$ = H, $R^3 = CH_3$, X = Cl), 3355-17-7; **1a** (X = Cl), 1111-97-3; **1a** (X = OAc), 1604-29-1; **1b**, 50284-86-1; **1d** (X = Cl), 33992-53-9; **1d** (X = OAc), 16169-88-3; (*R*)-**1d**, 84681-19-6; **1f**, 27301-53-7; **1g**, 55683-00-6; **1h**, 18135-82-5; **2a**, 27822-67-9; **2c**, 16487-13-1; **2e**, 100207-07-6; (*S*)-**2e**, 100207-08-7; 3 ($R^1 = R^2$ = H, $R^3 = CH_3$, X = Cl), 100228-93-1; **3a**, 89184-49-6; **3b**, 100228-88-4; **3c**, 100228-89-5; **3d**, 100228-90-8; (*R*)-(−)-**3d**, 100296-41-1; **3e**, 100296-40-0; (*R*)-(−)-**3e**, 100296-42-2; **3f**, 100243-53-6; 4 ($R^1 = R^2$ = H, $R^3 = CH_3$, X = Cl), 100228-94-2; **4g**, 100228-91-9; **4h**, 100228-92-0; $Pd[PPh_3]_4$, 14221-01-3; PhZnCl, 28557-00-8; Ph_2Zn, 1078-58-6; $Me_3SiC{\equiv}CZnCl$, 78389-87-4; $(CH_3)_2C{=}C{=}CHPh$, 21020-31-5; $(CH_3)_2C{=}C{=}CHC{\equiv}CSiMe_3$, 78389-99-8; $H_2C{=}C{=}c(Me)Ph$, 22433-39-2; $H_2C{=}C{=}C(SiMe_3)Ph$, 71321-00-1; $Me_3SiC{\equiv}CCH_2Ph$, 31683-47-3; $PhCH{=}C{=}CHPh$, 19753-98-1.

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(22) Several attempts to make the C sp signal visible failed due to decomposition of the complex.

(23) Ruitenberg, K.; Kleijn, H.; Meijer, J.; Oostveen, E. A.; Vermeer, P. *J. Organomet. Chem.* **1982**, *224*, 399.

(24) Vermeer, P.; Meijer, J.; Brandsma, L. *Recl. Trav. Chim. Pays-Bas* **1975**, *94*, 12.