

Synthesis, Structure, and Reactivity of (1,2,3- η^3 -Butadien-3-yl)palladium Complexes

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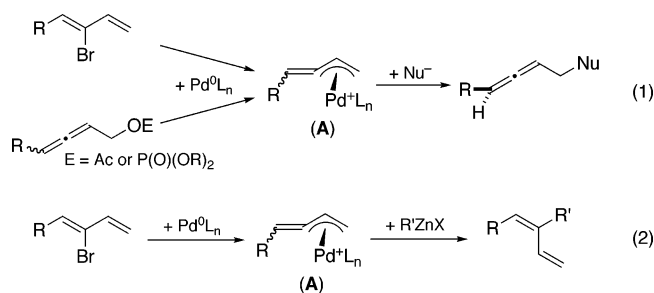
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The cationic *exo*-isopropylidene- π -allylpalladium complex [Pd(η^3 -CH₂CMeC=Me₂)(dppb)]BAR^F₄ (**1**; Ar^F = C₆H₃-3,5-(CF₃)₂), was prepared, and its solid-state structure was determined by X-ray crystallography. The CMe₂ plane of the *exo*-isopropylidene moiety and the η^3 -CH₂CMeC plane are not coplanar, with a dihedral angle of 66.06°. A reaction between **1** and a stabilized nucleophile, Na[CMe(CO₂Me)₂], took place at the terminal methylene carbon of η^3 -CH₂CMeC to give the corresponding allene exclusively. On the other hand, a reaction of **1** with a Grignard reagent proceeded via an initial nucleophilic attack at the Pd center to give a conjugated diene. Complex **1** showed good catalytic activity in the reactions between 2-bromo-1,3-dienes and stabilized nucleophiles, and a variety of allenes were obtained in good yields. The dynamic process of forming the alkylidene- π -allylpalladium complexes from 2-bromo-1,3-dienes and Pd(0) was also examined.

Introduction

Recently, we reported Pd-catalyzed enantioselective synthesis of axially chiral allenes from 2-bromo-1,3-dienes and stabilized nucleophiles (eq 1, top),¹ which proceeds via a (1,2,3- η^3 -butadien-3-yl)palladium (alkylidene- π -allylpalladium) intermediate (species **A**).^{1,2} The intermediary alkylidene- π -allylpalladium species can be generated by oxidative addition of an alka-2,3-dienyl ester to a Pd(0) species,^{3,4} and the route was utilized for dynamic kinetic resolution of the racemic allenic esters⁴ (eq 1, bottom). Another reaction via an alkylidene- π -allylpalladium intermediate is Pd-catalyzed cross-coupling of 2-bromo-1,3-

dienes, which takes place with clean inversion of the double-bond configuration (eq 2).⁵



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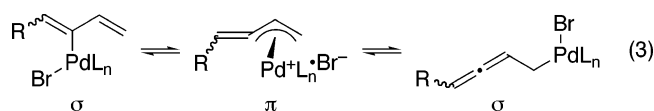
(1) (a) Ogasawara, M.; Ikeda, H.; Nagano, T.; Hayashi, T. *J. Am. Chem. Soc.* **2001**, *123*, 2089. (b) Ogasawara, M.; Ueyama, K.; Nagano, T.; Mizuhata, Y.; Hayashi, T. *Org. Lett.* **2003**, *5*, 217. (c) Ogasawara, M.; Nagano, T.; Hayashi, T. *J. Org. Chem.* **2005**, *70*, 5764. (d) Ogasawara, M.; Ngo, H. L.; Sakamoto, T.; Takahashi, T.; Lin, W. *Org. Lett.* **2005**, *7*, 2881.

(2) (a) Ogasawara, M.; Ikeda, H.; Hayashi, T. *Angew. Chem., Int. Ed.* **2000**, *39*, 1042. (b) Ogasawara, M.; Ikeda, H.; Nagano, T.; Hayashi, T. *Org. Lett.* **2001**, *3*, 2615. (c) Ogasawara, M.; Ge, Y.; Uetake, K.; Fan, L.; Takahashi, T. *J. Org. Chem.* **2005**, *70*, 3871. (d) Ogasawara, M.; Ge, Y.; Uetake, K.; Takahashi, T. *Org. Lett.* **2005**, *7*, 5697. (e) Ogasawara, M.; Fan, L.; Ge, Y.; Takahashi, T. *Org. Lett.* **2006**, *8*, 5409.

(3) For examples of Pd-catalyzed reactions involving alkylidene- π -allylpalladium intermediates, see: (a) Kleijn, H.; Westmijze, H.; Meijer, J.; Vermeer, P. *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 378. (b) Djahanbini, D.; Cazes, B.; Gore, J. *Tetrahedron Lett.* **1984**, *25*, 203. (c) Djahanbini, D.; Cazes, B.; Gore, J. *Tetrahedron* **1985**, *41*, 867. (d) Djahanbini, D.; Cazes, B.; Gore, J. *Tetrahedron* **1987**, *43*, 3441. (e) Trost, B. M.; Tour, J. M. *J. Org. Chem.* **1989**, *54*, 484. (f) Nokami, J.; Maihara, A.; Tsuji, J. *Tetrahedron Lett.* **1990**, *31*, 5629. (g) Piotti, M. E.; Alper, H. *J. Org. Chem.* **1994**, *59*, 1956. (h) Imada, Y.; Vasapollo, G.; Alper, H. *J. Org. Chem.* **1996**, *61*, 7982.

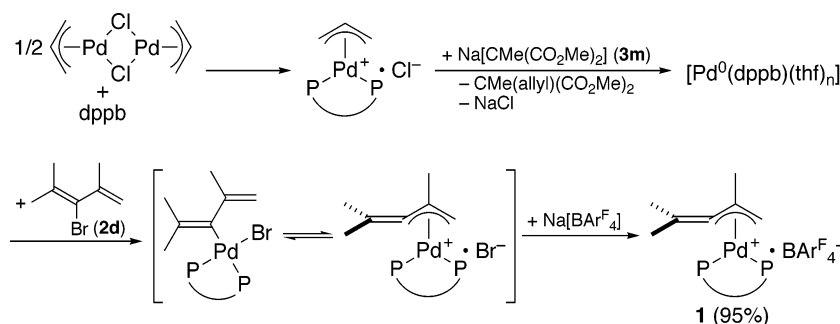
(4) (a) Imada, Y.; Ueno, K.; Kutsuwa, K.; Murahashi, S. *Chem. Lett.* **2002**, 140. (b) Imada, Y.; Nishida, M.; Kutsuwa, K.; Murahashi, S.; Naota, T. *Org. Lett.* **2005**, *7*, 5837. (c) Trost, B. M.; Fandrick, D. R.; Dinh, D. C. *J. Am. Chem. Soc.* **2005**, *127*, 14186.

Apparently, dynamic behavior and three-dimensional structures of the intermediate **A** play important roles for determining enantioselectivity of the asymmetric allene synthesis (eq 1) as well as *E/Z* selectivity of the 1,3-diene synthesis (eq 2). In a previous report, we studied the dynamic behavior of alkylidene- π -allylpalladium species and clarified that they were in equilibrium with two σ -allylpalladium species (eq 3).^{2e} On the other hand, three-dimensional structures of alkylidene- π -allylpalladium species have been rarely studied. Although isolation and NMR characterization of several such complexes were reported so far,^{1a,2a,6} their X-ray crystal structures have not been reported to date. In the stereoselective reactions shown in eq 1 and 2, the configuration of the two substituents/atoms at the *exo*-alkylidene carbon in **A** is especially important.

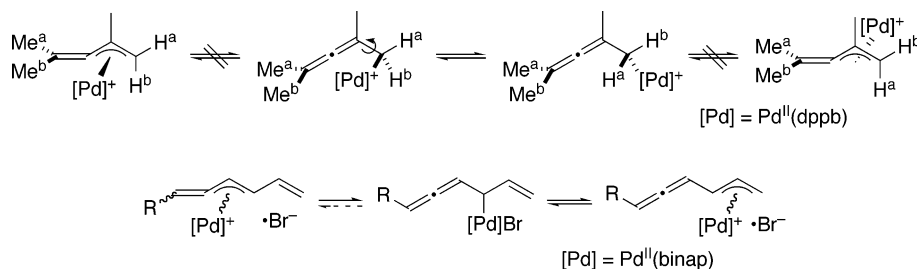


(5) (a) Zeng, X.; Hu, Q.; Qian, M.; Negishi, E. *J. Am. Chem. Soc.* **2003**, *125*, 13636. (b) Zeng, X.; Qian, M.; Hu, Q.; Negishi, E. *Angew. Chem., Int. Ed.* **2004**, *43*, 2259.

Scheme 1



Scheme 2



In this report, the first crystal structural study on a (1,2,3- η^3 -butadien-3-yl)palladium complex, $[\text{Pd}(\eta^3\text{-CH}_2\text{CMeC=CM}_2\text{)}(\text{dppb})]\text{BAr}^{\text{F}}_4$, is described. Application of the palladium complex in stoichiometric reactions as well as in catalytic reactions is also examined in detail.

Results and Discussion

Preparation of $[\text{Pd}(\eta^3\text{-CH}_2\text{CMeC=CM}_2\text{)}(\text{dppb})]\text{BAr}^{\text{F}}_4$ (1). The cationic palladium complex **1** was prepared as depicted in Scheme 1. A mixture of $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{dppb})]\text{Cl}$, which was generated in situ from $[\text{PdCl}(\eta^3\text{-C}_3\text{H}_5)]_2$ and dppb, and $\text{Na}[\text{CMe}(\text{CO}_2\text{Me})_2]$ (**3m**; 1.05 equiv to the Pd complex) was stirred for ca. 20 min in THF at room temperature to give a dark orange solution. The dark color indicates formation of a coordinatively unsaturated Pd(0) species. The Pd(0) species was metastable (probably solvated by THF) and decomposed to palladium black during prolonged stirring. Addition of stoichiometric $\text{Me}_2\text{C=CH-Br}$ (**2d**)⁷ to this solution and stirring for a few hours at room temperature lightened the dark color and a pale yellow mixture was obtained. After removal of an insoluble precipitate by filtration, the filtrate was evaporated to dryness under vacuum. Treatment of the residue with a stoichiometric amount of $\text{NaBAr}^{\text{F}}_4$ ($\text{Ar}^{\text{F}} = \text{-C}_6\text{H}_3\text{-3,5-(CF}_3)_2$)⁸ in dichloromethane afforded the cationic palladium complex $[\text{Pd}(\eta^3\text{-CH}_2\text{CMeC=CM}_2\text{)}(\text{dppb})]\text{BAr}^{\text{F}}_4$ (**1**). The complex is air- and moisture-insensitive and can be purified by silica gel chromatography (with CHCl_3 as an eluent) under air. The complex was obtained in 95% yield as a highly viscous oil, which slowly solidified on standing.

The solution behavior of **1** was studied in a noncoordinating solvent (CDCl_3 or toluene- d_8). In the NMR spectra of **1** in CDCl_3 , no (or very slow) exchange was observed between the two methyl groups in the isopropylidene moiety (Me^a and Me^b in Scheme 2, top) as well as the two terminal CH_2 -hydrogens

in the η^3 -allyl moiety (H^a and H^b in Scheme 2, top). They were detected as clearly separated sharp resonances at and above room temperature, and no line-broadening was observed even at 100 °C in toluene- d_8 . In accordance with this, the Pd complex **1** showed a pair of well-resolved doublets at δ 15.3 and 30.7 with $^2J_{\text{PP}} = 46.3$ Hz between 23 and 100 °C in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra in toluene- d_8 . These indicate that a π - σ - π process involving a (σ -allenylmethyl)palladium species is not effectively operative in **1** (Scheme 2, top). This is a clear contrast to the dynamic behavior of analogous (hexatrienyl)palladium complexes (Scheme 2, bottom).^{2e} The π -to- σ isomerization in **1** is not preferable, because the palladium center becomes more electron deficient ($16e^-$ to $14e^-$) upon isomerization due to the noncoordinating character of the $\text{BAr}^{\text{F}}_4^-$ anion. On the other hand, the anion in the (hexatrienyl)palladium species is bromide, and simultaneous isomerization and bromide coordination/dissociation maintain the 16-electron count of the palladium center in the π - σ - π process.

X-ray Crystal Structure Study of 1. Slow diffusion of pentane into a concentrated Et_2O solution of **1** grew prismatic colorless crystals, and the solid-state structure was determined by single-crystal X-ray crystallography (Figure 1).⁹ Selected bond lengths and angles are listed in Table 1. The overall molecular structure of the complex is distorted four-coordinate square planar. The Pd(1)–P(2) bond is longer than the Pd(1)–P(1) bond, which can be attributed to a stronger *trans* influence from C(3) than that from C(1). The *exo*-alkylidene C(3)–C(4) bond length is 1.292(10) Å, which is in a typical range for olefinic C=C double bonds. The CMe_2 plane of the *exo*-isopropylidene moiety and the η^3 -CCMeCH $_2$ plane are not coplanar, with a dihedral angle of 66.06°. No bonding interac-

(6) Benyunes, S. A.; Brandt, L.; Fries, A.; Green, M.; Mahon, M. F.; Papworth, T. M. *J. Chem. Soc., Dalton Trans.* **1993**, 3785.

(7) Magnus, P.; Westwood, N.; Spyvee, M.; Frost, C.; Linnane, P.; Tavares, F.; Lynch, V. *Tetrahedron* **1999**, 55, 6435.

(8) Brookhart, M.; Grant, B.; Volper, Jr., A. F. *Organometallics* **1992**, 11, 3920.

(9) Crystallographic data for $\text{C}_{67}\text{H}_{51}\text{BF}_4\text{P}_2\text{Pd}$: MW = 1491.28; triclinic; space group $P1$; $a = 12.9774(11)$ Å, $b = 21.5134(17)$ Å, $c = 12.9372(7)$ Å, $\alpha = 104.254(4)^\circ$, $\beta = 90.176(3)^\circ$, $\gamma = 77.2712(11)^\circ$; $V = 3409.7(4)$ Å³; $Z = 2$; $d = 1.452$ g/cm³; $\mu = 4.24$ cm⁻¹; crystal dimensions 0.40 × 0.30 × 0.20 mm; $R1 = 0.0792$ ($I > 2\sigma(I)$); $R = 0.1058$ (all reflections); $wR2 = 0.2757$ (all reflections); maximum/minimum residual density 1.22/−0.72 e/Å³. Data were collected on a Rigaku PAXIS-RAPID imaging plate diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.7107$ Å). Full details of the crystallographic analysis are described in the Supporting Information.

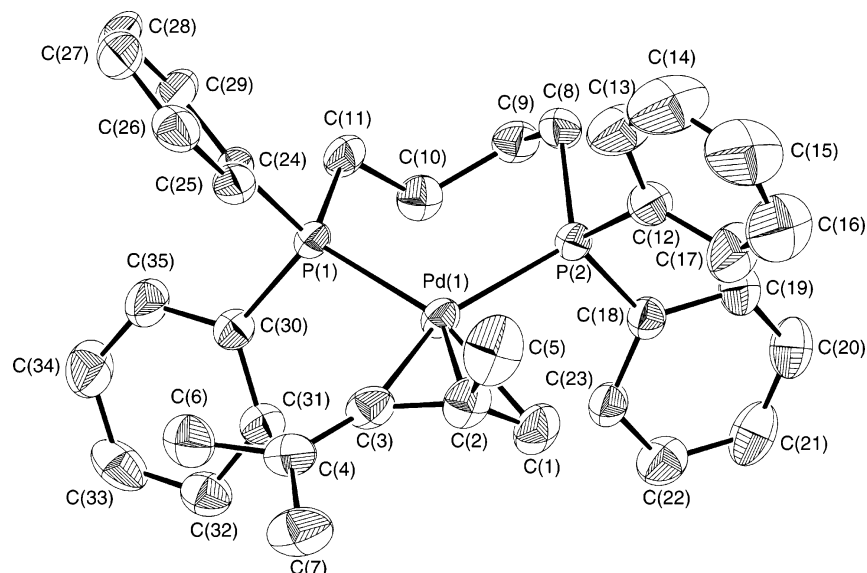


Figure 1. ORTEP drawing of the cation in $[\text{Pd}(\eta^3\text{-CH}_2\text{CMeC=Me}_2)(\text{dppb})]\text{BARF}_4$ (**1**) with 30% thermal ellipsoids. The BARF_4^- anion and all hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances and Angles for **1**

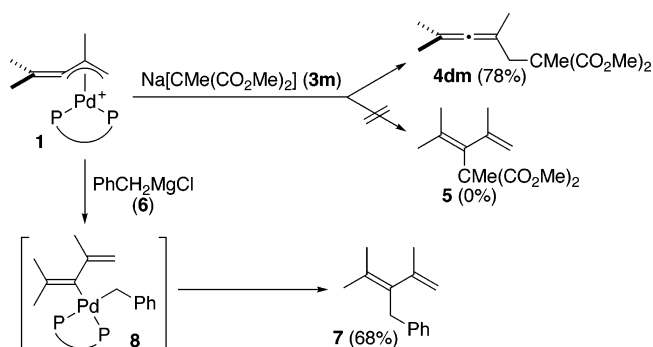
Bond Distances (Å)			
Pd(1)–P(1)	2.2973(11)	Pd(1)–P(2)	2.3322(16)
Pd(1)–C(1)	2.205(7)	Pd(1)–C(2)	2.195(7)
Pd(1)–C(3)	2.127(7)	C(1)–C(2)	1.388(12)
C(2)–C(3)	1.445(9)	C(3)–C(4)	1.292(10)
C(2)–C(5)	1.520(12)	C(4)–C(6)	1.509(9)
C(4)–C(7)	1.502(11)		
Bond Angles (deg)			
P(1)–Pd(1)–P(2)	101.42(4)	P(1)–Pd(1)–C(3)	102.16(16)
C(1)–Pd(1)–C(3)	67.5(3)	P(2)–Pd(1)–C(1)	90.2(2)
C(1)–Pd(1)–C(2)	36.8(3)	C(2)–Pd(1)–C(3)	39.0(2)
C(1)–C(2)–C(3)	116.4(7)	C(1)–C(2)–C(5)	122.4(8)
C(3)–C(2)–C(5)	120.3(7)	Pd(1)–C(2)–C(5)	121.2(6)
C(3)–C(4)–C(6)	124.5(6)	C(3)–C(4)–C(7)	119.7(6)
C(2)–C(3)–C(4)	136.3(6)	C(6)–C(4)–C(7)	115.8(7)

tions are observed between the cationic palladium moiety and the BARF_4^- anion.

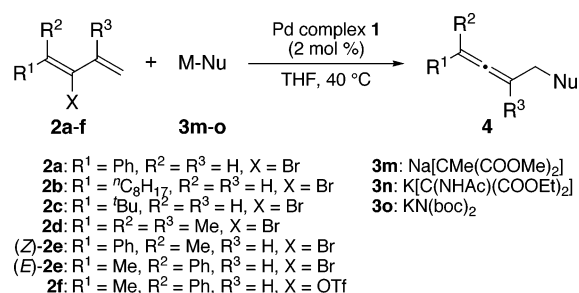
Reactions of **1 with Nucleophiles.** Alkylidene- π -allylpalladium species have been suggested as probable intermediates in several Pd-catalyzed nucleophilic substitution reactions to give either allenes or conjugated dienes selectively depending on the nature (stabilized or nonstabilized) of the nucleophiles.³ Accordingly, reactions of the Pd complex **1** with a couple of nucleophiles were examined. A reaction of **1** with the stabilized nucleophile, $\text{Na}[\text{CMe}(\text{CO}_2\text{Me})_2]$ (**3m**), proceeded cleanly to give the allenic product **4dm** in 78% isolated yield. The nucleophilic attack was highly regioselective at the CH_2 carbon of the η^3 -allylic moiety (C(1) in Figure 1), and the conjugated diene **5**, which was an expected product from a nucleophilic attack at C(3), was not detected at all. On the other hand, a reaction with a nonstabilized nucleophile, PhCH_2MgCl (**6**), afforded the conjugated diene **7** in 68% yield exclusively (Scheme 3).

In the η^3 -butadienyl ligand in **1**, the tricoordinate C(3) atom should be a better π -acceptor than the tetracoordinate C(1). And thus, the former becomes more electron-rich than the latter; that is, C(1) is more electrophilic than C(3). The stabilized nucleophile **3m** attacks C(1) from the opposite side of Pd(1) with respect to the η^3 -allyl plane to produce the allene **4dm** selectively. The reaction with **6** takes place in a different manner, and a plausible route to the formation of the conjugated diene **7** could be explained as follows. The nonstabilized nucleophile **6** attacks the Pd center instead of the η^3 -butadienyl ligand to

Scheme 3



Scheme 4



form the (σ -butadienyl)benzylpalladium intermediate **8** and following reductive elimination gives **7**. The nucleophile-dependent allene/1,3-diene selectivity shown in Scheme 3 was previously predicted by a theoretical study¹⁰ and is consistent with the results of several catalytic reactions.³

Application of **1 as a Catalyst Precursor in Allene Synthesis Reaction.** The palladium complex **1** can be regarded as an isolable intermediate of the Pd-catalyzed allene synthesis reaction, and thus it should function as a catalyst precursor in the reaction. The palladium complex **1** was applied to reactions of 2-bromo-1,3-dienes (or a 1,3-dien-2-yl triflate) **2** with stabilized nucleophiles **3**, and the results are summarized in Scheme 4 and Table 2. In all the cases examined here, the reactions proceeded cleanly and di- (entries 1–5), tri- (entries 7–10), and tetrasubstituted (entry 6) allenes **4** were obtained

(10) Bigot, B.; Delbecq, F. *New J. Chem.* **1990**, *14*, 659.

Table 2. Preparation of Allenes **4** Catalyzed by Pd Complex **1**^a

entry	diene 2	nucleophile 3	time (h)	yield of 4 ^b (%)
1	2a	3m	18	84 (4am)
2	2a	3n	24	88 (4an)
3	2a	3o	24	70 (4ao)
4	2b	3o	24	79 (4bo)
5	2c	3o	36	76 (4co)
6	2d	3m	4	91 (4dm)
7	(<i>Z</i>)- 2e	3m	24	95 (4em)
8	(<i>E</i>)- 2e	3n	72	35 (4en) ^c
9	(<i>Z</i>)- 2e	3n	36	29 (4en)
10	2f	3n	6	90 (4en)

^a Reaction was carried out with **2** (1.0 mmol) and **3** (1.1 mmol) in THF in the presence of **1** (0.02 mmol; 2 mol %). ^b Isolated yield by silica gel chromatography. ^c Remaining substrate (*E*)-**2e** was recovered in 44% yield.

exclusively; no conjugated dienes were detected. In our original report of the reaction,^{2a} it was found that the choice of phosphine ancillary ligand was important to gain high activity of the palladium catalyst. The best choice was the triarylphosphine dppb,¹¹ and a Pd species with dppb, which is the phosphine ligand in **1**, showed poor performance. As a consequence, the catalyst **1** showed lower catalytic activity, and relatively higher temperature and longer time were required for the reactions in Table 2.

A reaction between (*E*)-**2e** and **3n** was especially sluggish and was incomplete even after 72 h (entry 8). An analogous reaction with the isomeric (*Z*)-**2e** was also slow (entry 9). On the other hand, the triflate **2f**, which is isostructural to (*E*)-**2e**, was much more reactive, and a reaction with **3n** was complete within 6 h (entry 10). Oxidative addition of either **2e** or **2f** to a Pd(0) species gives an equilibrium mixture of the σ -dienylpalladium **9** and the *exo*-alkylidene- π -allylpalladium **10** (Scheme 5). Triflate anion is a weaker σ -donor than bromide, and thus replacement of the anion in the Pd intermediates from bromide to triflate should drive the equilibrium toward **10**. This may be the origin of the different reactivity between **2e** and **2f**. Because a nucleophile attacks **10** (not **9**) to give an allene in the final step of the catalytic process, the triflate substrate **2f** is more reactive than the bromide substrate **2e**.

Preparation of [Pd(η^3 -CH₂CHC=CM₂Ph)(dppb)]BAR^F₄ (11**).** Another alkylidene- π -allylpalladium complex, [Pd(η^3 -CH₂-CHC=CM₂Ph)(dppb)]BAR^F₄ (**11**), was prepared as a pale yellow, viscous oil from 3-bromo-4-phenyl-1,3-pentadiene (**2e**) by the method shown in Scheme 1. Since complex **11** possesses two different substituents on the *exo*-alkylidene carbon, it exists as a mixture of two isomers (see Scheme 6). Complex **11** prepared from (*E*)-**2e** consists of *anti*- and *syn*-isomers in a 95:5 molar ratio. No exchange was detected between the two isomers. It was found that the relative configuration of the PhMeC=C moiety in **2e** did not affect formation of **11**; that is, (*Z*)-**2e** also afforded **11** with the identical isomeric distribution (*anti*-**11**/*syn*-**11** = 95:5). Apparently, there is a rapid exchange process between *syn*- and *anti*-intermediates **12**, which have a bromide counteranion, and they reach thermodynamic equilibrium prior to termination of the exchange by NaBAR^F₄ treatment.

The observations shown in Scheme 6 imply that the difference between *E*- and *Z*-isomers of the bromodiene substrate might show no influence in the alkylidene- π -allylpalladium-mediated asymmetric allene synthesis. A reaction of (*E*)-**2e** with Cs-[C(NHAc)(CO₂Et)₂] (**3n'**) at 30 °C in the presence of a Pd(*R*)-

binap catalyst gave the axially chiral allene (*R*)-**4en**¹² of 57% ee in 56% yield (Scheme 7). On the assumption that there is no exchange process between *anti*-**12** and *syn*-**12**, the reaction of (*Z*)-**2e** with **3n'** catalyzed by Pd(*R*)-binap should form (*S*)-**4en**, in which the relative positions of the Ph group and the Me group on the allenic terminal carbon are reversed compared with the allenic product from (*E*)-**2e**. As predicted from Scheme 6, however, the product from (*Z*)-**2e** was also (*R*)-**4en** with nearly identical enantiopurity (58% ee, 61% yield).

Conclusions

In summary, we have determined a solid-state structure of an alkylidene- π -allylpalladium complex for the first time. While the Pd complex reacts with a stabilized nucleophile at the unsubstituted terminal of the η^3 -allylic moiety to give an allene, a Grignard reagent attacks at the Pd center to give a conjugated diene. The nucleophile-dependent selectivity is consistent with previously reported allene versus diene selectivity in alkylidene- π -allylpalladium-mediated reactions. The Pd complex was found to be a good catalyst precursor for the reactions between 2-bromo-1,3-dienes and stabilized nucleophiles, giving allenes. The dynamic process of forming the alkylidene- π -allylpalladium complexes from 2-bromo-1,3-dienes and Pd(0) was also clarified.

Experimental Section

General Procedures. All anaerobic and/or moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or with glovebox techniques under prepurified argon. ¹H NMR (at 400 MHz) and ¹³C NMR (at 101 MHz) chemical shifts are reported in ppm downfield of internal tetramethylsilane. ³¹P NMR (at 162 MHz) chemical shifts are externally referenced to 85% H₃PO₄. Tetrahydrofuran was distilled from benzophenone-ketyl under nitrogen prior to use. Dichloromethane was distilled from CaH₂ under nitrogen prior to use. [PdCl(π -allyl)]₂,¹³ NaBAR^F₄,⁸ 2-bromo-1,3-dienes (**2a**,^{2a} **2b**,^{1c} **2c**,^{1a} **2d**,⁷ and **2e**^{2c}), and 1,3-dien-2-yl triflate **2f**^d were prepared according to the reported methods. All other chemicals were obtained from commercial sources.

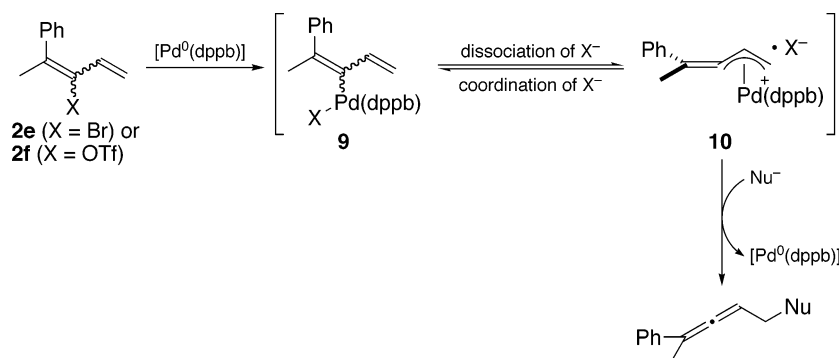
Preparation of [Pd(η^3 -CH₂CHC=CM₂Ph)(dppb)]·B[C₆H₃-3,5-(CF₃)₂]₄ (1**).** A mixture of [PdCl(η^3 -C₃H₅)₂] (84.5 mg, 462 μ mol/Pd), dppb (200 mg, 469 μ mol), and Na[CMe(CO₂Me)₂] (82.0 mg, 488 μ mol) was placed in a Schlenk flask, and to this was added dry THF (5 mL) under nitrogen. The mixture was stirred at room temperature for 20 min, then Me₂C=CB₂=CMe=CH₂ (**2d**, 98.0 mg, 560 μ mol) was added to the flask by means of a syringe. After stirring the reddish-orange solution for 5 h at room temperature, all the volatiles were removed under reduced pressure. To the residue were added NaBAR^F₄ (470 mg, 530 μ mol) and CH₂Cl₂ (5 mL), and the mixture was stirred over night at room temperature. The precipitates were removed by filtration, and the filtrate was evaporated to dryness under reduced pressure. The yellow residue was chromatographed on silica gel with CHCl₃ as an eluent to give the complex (655 mg, 95% yield) as a pale yellow, viscous oil. Recrystallization from Et₂O/pentane gave colorless, prismatic crystals. ¹H NMR (CDCl₃): δ 0.95 (s, 3H), 1.55–1.89 (m, 4H), 1.83 (s, 3H), 1.96 (s, 3H), 2.33–2.51 (m, 4H), 3.05 (d, *J*_{HP} = 8.6 Hz, 1H), 4.03 (d, *J*_{HP} = 5.1 Hz, 1H), 7.23–7.28 (m, 2H), 7.34–7.56 (m, 19H), 7.59–7.63 (m, 1H), 7.71–7.77 (m, 10H). ³¹P{¹H} NMR (CDCl₃): δ 15.3 (d, *J*_{PP} = 46.3 Hz), 30.7 (d, *J*_{PP} = 46.3

(11) dppb = 2,2'-bis(diphenylphosphino)-1,1'-biphenyl. See: Ogasawara, M.; Yoshida, K.; Hayashi, T. *Organometallics* **2000**, *19*, 1567, and references therein.

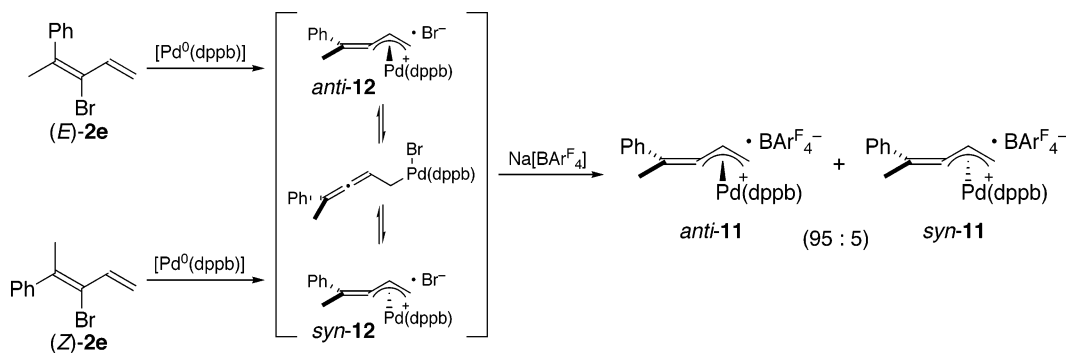
(12) The specific rotation value for **4en** of 58% ee is [α]_D^{26.0} –38.7 (c 1.26, CHCl₃). The absolute configuration of **4en** was deduced by the Lowe-Brewster rule; see: (a) Lowe, G. *Chem. Commun.* **1965**, 411. (b) Brewster, J. H. *Top. Stereochem.* **1967**, *2*, 1.

(13) Tatsuno, A.; Yoshida, T.; Otsuka, S. *Inorg. Synth.* **1979**, *19*, 220.

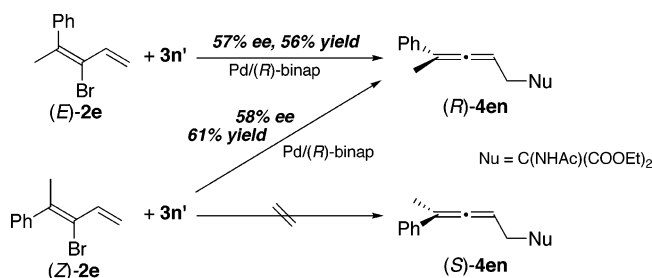
Scheme 5



Scheme 6



Scheme 7



Hz). Anal. Calcd for C₆₇H₅₁P₂BF₂₄Pd: C, 53.96; H, 3.45. Found: C, 53.95; H, 3.41.

Stoichiometric Reaction of 1 with Na[CMe(CO₂Me)₂]: Preparation of 4dm. A mixture of 1 (502 mg, 337 mmol) and Na[CMe(CO₂Me)₂] (3m, 59.1 mg, 352 mmol) was placed in a Schlenk flask and dissolved in dry THF (5 mL). After stirring for 3 h at room temperature, the solution was filtered through a short pad of SiO₂. The silica gel pad was washed with a small amount of Et₂O three times, and the combined solution was evaporated to dryness under reduced pressure. The yellow residue was chromatographed on silica gel (hexane/Et₂O = 1:1) to give the allene 4dm (63.2 mg, 78%) as a colorless oil. All the spectroscopic data are consistent with those reported previously.^{2c}

Stoichiometric Reaction of 1 with PhCH₂MgCl: Preparation of 3-Benzyl-2,4-dimethyl-1,3-pentadiene (7). To a THF (2 mL) solution of 1 (149 mg, 0.10 mmol) was added PhCH₂MgCl (0.97 M in THF, 0.21 mL, 0.20 mmol) at room temperature. The colorless solution turned dark brown in color immediately. After stirring the mixture for 1 h, the mixture was partitioned between ether and water. The organic layer was washed with water and brine successively and then dried over MgSO₄. The crude product was

purified by silica gel chromatography (with hexane) to give 7 (12.6 mg, 68%) in pure form. ¹H NMR (CDCl₃): δ 1.67 (br, 3H), 1.76 (s, 3H), 1.79 (s, 3H), 3.48 (s, 2H) 4.46 (dd, *J* = 1.8 and 0.8 Hz, 1H), 4.85 (br, 1H), 7.13–7.16 (m, 3H), 7.22–7.26 (m, 2H). ¹³C-{¹H} NMR (CDCl₃): δ 20.3, 21.9, 22.9, 37.6, 113.7, 125.6, 127.0, 128.1, 128.6, 135.1, 140.8, 146.4. EI-HRMS: calcd for C₁₄H₁₈ 186.1409, found 186.1413.

Preparation of Allenes 4 Catalyzed by Pd Complex 1: General Procedure. A mixture of the palladium complex 1 (6.0 mg, 4.0 mmol) and the nucleophile 3 (0.22 mmol) was dissolved in THF (3 mL), and to this was added the diene substrate 2 (0.20 mmol) via a syringe. The mixture was stirred at appropriate temperature until total consumption of the substrate, then filtered through a short pad of silica gel to remove precipitated inorganic salts. The silica gel pad was washed with a small amount of Et₂O, and the combined solution was evaporated to dryness under reduced pressure. The residue was chromatographed on silica gel to give allene 4 in pure form. All the allenenes obtained here are known compounds and were characterized by comparison of their spectroscopic data with those reported previously (4am,^{2a} 4an,^{1a} 4ao,^{2a} 4bo,^{4b} 4co,^{4b} 4dm,^{2c} 4em,^{2c} 4en^{2c}).

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Supporting Information Available: ¹H, ¹³C, and ³¹P NMR spectra for all the new compounds and the allenic compounds, and crystallographic data for 1 (in CIF format). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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