Comparative Study of the Reactions of Two Alkynes and an Alkene with Chiral Cyclopalladated Complexes Derived from *N*,*N*-Dimethyl-α-(2-naphthyl)ethylamine and *N*,*N*-Dimethyl-α-methylbenzylamine: Insertion or Cycloaddition

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The chiral cyclopalladated complexes containing coordinated 3,4-dimethyl-1-phenylphosphole, DMPP, and an N-donor ligand, (S_C)-**1** or (S_C)-**3**, reacted with dimethylacetylene dicarboxylate, DMAD, and diphenylacetylene to produce exclusively the insertion products (S_C)-**2**, (S_C)-**4**, (S_C)-**5**, and (S_C)-**6**, respectively, although [4+2] Diels−Alder cycloaddition reactions between DMAD or diphenylacetylene and coordinated DMPP were possible. *N*-Phenylmaleimide underwent [4+2] Diels−Alder cycloaddition to the coordinated DMPP in the insertion product (S_C)-**2** to form two stereoisomers of (S_C)-**7** in a 1.55:1 ratio. However, under similar conditions the insertion product (S_C)-**4** did not react with *N*-phenylmaleimide. Complexes (S_C)-**1** and (S_C)-**3** reacted with *N*-phenylmaleimide to give only one enantiomer of the [4+2] Diels−Alder cycloaddition product, although two diastereomeric products were possible in each reaction. The cycloaddition product (S_C)-**8** reacted with DMAD to give only one stereoisomer of the insertion product (S_C)-**7**, but under similar conditions the cycloaddition product (S_C)-**9** did not react with DMAD. New complexes were characterized by elemental analyses, physical properties, polarimetry, ^{1}H, ^{1}H{^{31}P}, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy, and in several cases X-ray crystallography.

Introduction

Cyclopalladated complexes exhibit high reactivity toward a wide variety of substrates, with reagents such as CO, isocyanides, alkenes, and alkynes inserting into the Pd−C bond.[1] These reaction types make cyclopalladated compounds attractive starting materials for organic syntheses.[2] In addition to insertion into palladium carbon bonds,[3] electron-deficient alkenes and alkynes also undergo [4+2] Diels−Alder cycloaddition to 3,4-dimethyl-1-phenylphosphole, DMPP.[4] Coordination of DMPP to a transition metal significantly enhances its reactivity as a diene because of a reduction in the small amount of cyclic conjugation that exists in the free ligand.[5] Coordinated DMPP often undergoes highly diastereoselective intramolecular or intermolecular [4+2] cycloadditions in the environment of a chiral ligand.[4m,6]

The (DMPP)M(CO)$_5$ (M = Mo, W) complexes undergo [4+2] Diels−Alder cycloadditions with dimethylacetylene dicarboxylate, DMAD, and the products eliminate arene forming a phosphinidene intermediate that adds to alkenes and alkynes to form complexes of phosphiranes and phosphirenes (Scheme 1).[7] If the DMPP coordinated to a chiral palladacycle were to undergo similar diastereoselective [4+2] cycloaddition of DMAD followed by elimination of arene, then addition of a

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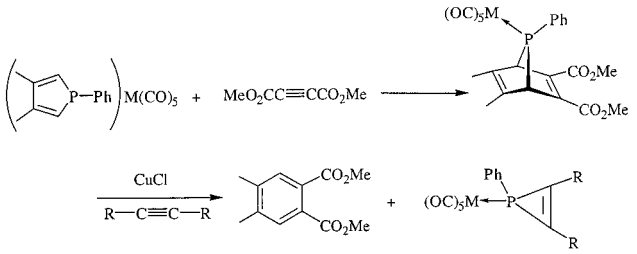
Scheme 1



prochiral alkene or alkyne to the coordinated phosphinidene intermediate could form the basis of asymmetric syntheses of phosphiranes and phosphirenes.

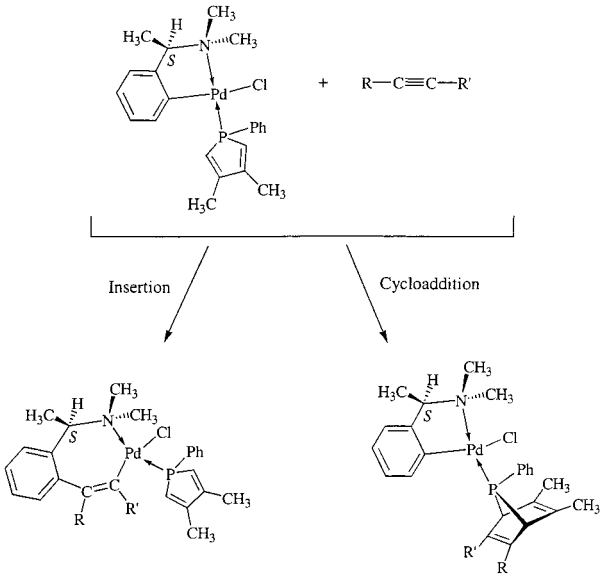
The Pd−C(aryl) bond in cyclopalladated complexes containing N-donor ligands shows variable reactivity toward alkyne insertion.[3] This may be related to several factors including (1) the lability of the Pd−N bond, (2) the electron donor/acceptor nature of the alkyne substituents, (3) the structure of the palladacycle, and (4) the nature of the other ligands coordinated to palladium. The relative importance of these factors has not been clearly established, and no study has been reported on the reactions of alkynes with chiral cyclopalladated complexes containing an N-donor ligand and coordinated DMPP. Here, we compare the reactivities of the Pd−C(aryl) bond and the coordinated DMPP in chiral cyclopalladated complexes derived from *N*,*N*-dimethyl-α-(2-naphthyl)ethylamine and *N*,*N*-dimethyl-α-methylbenzylamine with the two alkynes $MeCO_2C{\equiv}CCO_2Me$ and PhC≡CPh and the alkene *N*-phenylmaleimide. We seek to establish the relative proclivities of insertion and cycloaddition of electron-deficient alkynes and alkenes to cyclopalladated complexes containing coordinated DMPP (Scheme 2).

Results and Discussion

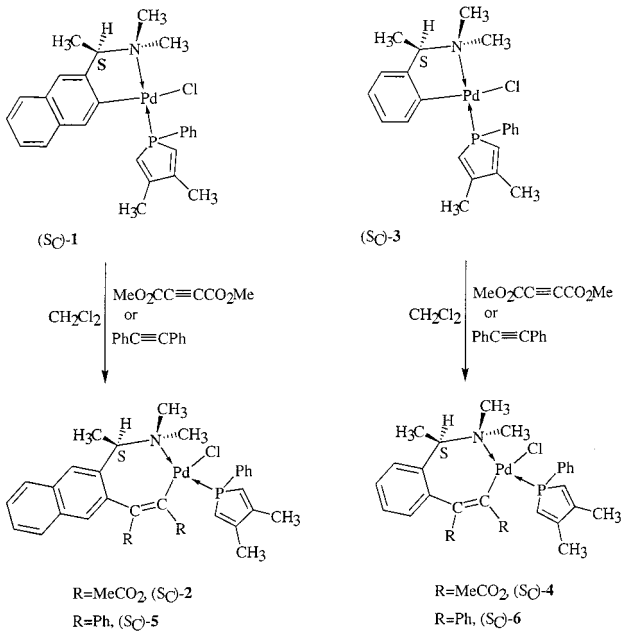
As illustrated in Scheme 3, the two electron-deficient alkynes, $MeCO_2C{\equiv}CCO_2Me$ (DMAD) and PhC≡CPh (tolan), insert into the Pd−C bonds of the palladacycles (S_C)-**1** and (S_C)-**3** under mild conditions. Differentiation of the two possible product types, insertion or cycloaddition (Scheme 2), is readily achieved by NMR spectroscopy. Complete assignments of all proton and carbon chemical shifts were made with the aid of $^1H\{^{31}P\}$, APT, COSY, and HETCOR spectra. Little difference is anticipated in the ^{31}P chemical shifts of the starting palladacycle and the alkyne insertion product. In contrast, the ^{31}P chemical shift of the [4+2] Diels−Alder cycloaddition product should be considerably downfield of that of the starting palladacycle.[4i,8] The ^{31}P chemical shifts of the products, 29.2 (**2**), 29.5 (**4**), and 25.4 ppm (**5** or **6**), are all slightly upfield of those of the starting materials, 37.3 (**1**) and 37.8 (**3**).

The ^1H NMR spectra are also diagnostic. For the insertion products, two characteristic doublets with

Scheme 2



Scheme 3



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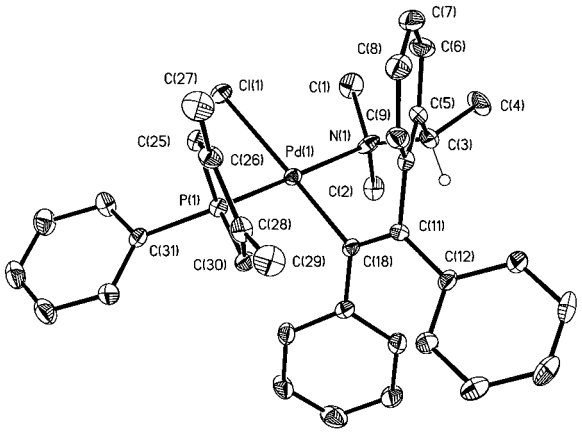

Figure 1. Structural drawing of (S_C)-**6** showing the atom-numbering scheme (20% probability ellipsoids). The hydrogen atom on C(3) has an arbitrary radius. Selected bond lengths (Å): Pd(1)−P(1), 2.248(3); Pd(1)−N(1), 2.219(10); Pd(1)−C(18), 2.016(9); Pd(1)−Cl(1), 2.419(2); C(11)−C(18), 1.362(13); C(25)−C(26), 1.342(14); C(28)−C(30), 1.332(12). Selected angles (deg): P(1)−Pd(1)−C(18), 88.1(3); C(18)−Pd(1)−N(1), 88.8(3); N(1)−Pd(1)−Cl(1), 95.3(2); Cl(1)−Pd(1)−P(1), 87.52(10).

^2J(PH) of about 30 Hz, assignable to the α-CH phosphole ring protons, are observed in the 6−7 ppm range. These resonances would be replaced by two new resonances in the 4−5 ppm region for the bridgehead protons of the cycloaddition product.[4,6] The ^{1}H and ^{13}C{^{1}H} NCH_3 resonances all exhibit ^4J(PH) and ^3J(PC) couplings of 1−4 Hz. The CH nuclei of the stereogenic carbon moiety are similarly coupled to phosphorus. These NMR data indicate that the phosphole remains *trans* to nitrogen in these alkyne insertion products.

As further confirmation of the structures of these compounds, the crystal structure of (S_C)-**6** (Figure 1) was determined. Crystallographic data are given in Table 1, and selected bond distances and angles are listed in the figure caption. The structure consists of a palladium atom in a planar coordination environment with phosphorus *trans* to nitrogen, as concluded from the NMR data. The coordination geometry is not quite square, as the bond angles range from the Cl(1)−Pd(1)−P(1) angle of 87.521(10)° to the N(1)−Pd(1)−Cl(1) angle of 95.3(2)°. The bond distances involving palladium [Pd(1)−C(18), 2.016(9) Å; Pd(1)−Cl(1), 2.419(2) Å; Pd(1)−P(1), 2.248(3) Å; Pd(1)−N(1), 2.219(10) Å] are very similar to those observed for (S_C)-**1**[6k] [Pd(1)−C(1), 2.08(2) Å; Pd(1)−P(1), 2.219(6) Å; Pd(1)−N(1), 2.20(2) Å; Pd(1)−Cl(1), 2.372(7) Å]. The C(11)−C(18), C(28)−C(30), and C(25)−C(26) bond lengths are all typical of carbon−carbon double bonds. The seven-membered palladacyclic chelate ring has a boat conformation with the palladium atom at the bow and the fused phenyl ring at the stern. The C(11)−C(18) and C(3)−N(1) vectors are nearly parallel.

Complexes (S_C)-**2** and (S_C)-**4** did not react further with excess alkyne, even after a week at 50 °C, though double alkyne insertions have been reported.[1a] However, (S_C)-**2**, but not (S_C)-**4**, did undergo [4+2] Diels−Alder cycloaddition with *N*-phenylmaleimide (Scheme 4) to produce a 1.55:1 mixture of diastereomers. There are four possible diastereomeric Diels−Alder products in this reaction, viz., *syn-exo*, *syn-endo*, *anti-exo*, and *anti-endo* (Scheme 5). Free DMPP undergoes diastereoselective [4+2] Diels−Alder cycloaddition of *N*-phenylmaleimide to form only the *anti-endo* diastereomer.[9] The *endo* and *exo* diastereomers may be distinguished on the basis of the magnitude of ^3J(PH), which for the latter is 30−40 Hz and for the former is much smaller (0−5 Hz).[10] Although a complete assignment of the ^{1}H NMR spectrum of the mixture of diastereomers was not possible, selective ^{1}H{^{31}P} experiments showed that there are no resonances in the 3−5 ppm region with large-magnitude P−H couplings. Thus, the two diastereomers that formed are the *syn-endo* and *anti-endo* diastereomers.

Both (S_C)-**1** and (S_C)-**3** react with *N*-phenylmaleimide to undergo diastereoselective [4+2] Diels−Alder cycloaddition (Scheme 6). The ^{31}P{^{1}H} NMR spectra of the crude reaction mixtures showed only one singlet at 137.2 (S_C)-**8** or 137.6 ppm (S_C)-**9**. The near identity of the ^{31}P chemical shifts suggests that these two products have the same overall stereochemistry. The ^{1}H NMR resonances of the H_b and H_c protons are singlets, ^3J(PH) = 0, for both compounds. Thus, (S_C)-**8** and (S_C)-**9** are both *anti-endo* diastereomers. The average ^{31}P coordination chemical shifts, $\Delta\delta$ ^{31}P, for this 7-phosphanorbornene ligand, defined as $\Delta\delta\ ^{31}P = \delta\ ^{31}P_{complex} - \delta\ ^{31}P_{ligand}$, is large, 91.9 ppm ($\delta^{31}P_{ligand}$ = 45.5 ppm).[9] To the same metal centers the coordination chemical shift for DMPP is much smaller, 35 ppm. On the basis of the ^{31}P coordination chemical shift, this 7-phosphanorbornene is a better donor than DMPP.

The structures of (S_C)-**8** and (S_C)-**9** were confirmed by X-ray crystallography (Figures 2 and 3, respectively). Crystallographic data are given in Table 1, and selected bond distances and angles are listed in the figure captions. For both complexes the palladium coordination geometry is essentially planar but not square. As expected, there are only very small differences between the analogous metrical parameters involving palladium for the two structures. Both complexes are the *anti-endo* diastereomers, as was concluded from the NMR data.

(S_C)-**8** reacts with DMAD (Scheme 7) to afford the alkyne insertion product (S_C)-**7** in high yield. Under similar conditions (S_C)-**9** did not react with DMAD. The ^{31}P chemical shift of (S_C)-**7** (128.4 ppm) formed by this route is the same as that of the minor diastereomer formed by cycloaddition of *N*-phenylmaleimide to (S_C)-**2**. The ^{1}H NMR spectrum of this compound shows singlet resonances for H_b and H_c, suggesting that it is an *endo* diastereomer. The crystal structure (Figure 4) confirms that it is the *anti-endo* diastereomer. Crystallographic data are given in Table 1, and selected bond distances and angles are listed in the figure caption. The palladium coordination geometry is essentially planar but not square. The seven-membered palladacyclic chelate ring has a boat conformation with the palladium atom the bow and the fused phenyl ring the stern. The C(18)−C(15) and C(3)−N(1) vectors are nearly parallel. The C(21)−P(1)−C(26) angle is acute (81.5(4)°), as is also the case for the 7-phosphanorbornene moieties of

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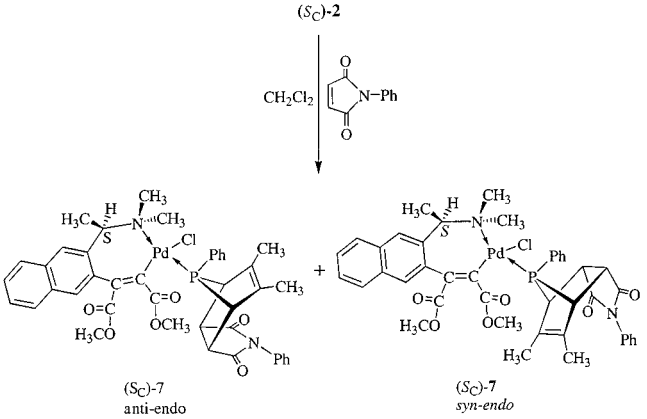
Table 1. Crystallographic Data for (S_C)-6, (S_C)-7, (S_C)-8, and (S_C)-9

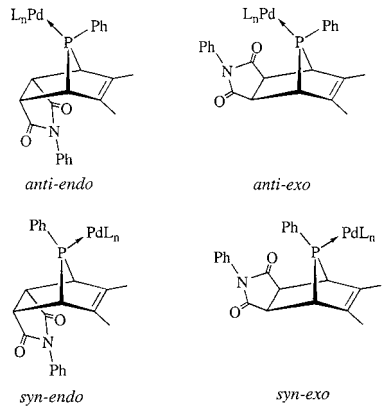
	(S_C)-**6**	(S_C)-**7**	(S_C)-**8**	(S_C)-**9**
emp formula	$C_{36}H_{39}ClNPPd\cdot CH_2Cl_2$	$C_{42}H_{42}ClN_2O_6PPd$	$C_{36}H_{36}ClN_2O_2PPd$	$C_{32.25}H_{34.5}Cl_{1.5}N_2O_{2.25}PPd$
fw	741.41	843.62	701.49	676.66
cryst syst	triclinic	triclinic	orthorhombic	triclinic
a (Å)	9.0907(18)	9.655(3)	10.646(2)	11.0213(11)
b (Å)	9.6894(14)	11.756(2)	12.821(6)	13.1228(12)
c (Å)	10.8057(15)	18.500(3)	24.329(5)	13.3025(15)
α (deg)	90.159(10)	82.593(15)	90	87.025(11)
β (deg)	101.016(18)	81.425(17)	90	66.498(8)
γ (deg)	112.241(13)	73.426(16)	90	79.711(10)
V (Å^3)	861.8(2)	1981.7(8)	3320.5(17)	1735.6(3)
Z	1	2	4	2
space group	*P*1	*P*1	$P2_12_12_1$	*P*1
ρ_{calcd} (Mg/m^3)	1.429	1.412	1.403	1.295
μ (mm^{-1})	0.844	0.625	0.721	0.725
$R_1(F)$,[a] $[I>2\sigma(I)]$	0.0450	0.0680	0.0633	0.0623
$wR_2(F^2)$[b]	0.0933	0.1080	0.1281	0.1755
GOF	1.059	1.370	1.025	1.084
Flack param	−0.01(4)		−0.04(7)	0.03(4)

[a] $R_1(F) = \sum(||F_o| - |F_c||)/\sum(|F_o|)$. [b] $wR_2(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Scheme 4



Scheme 5



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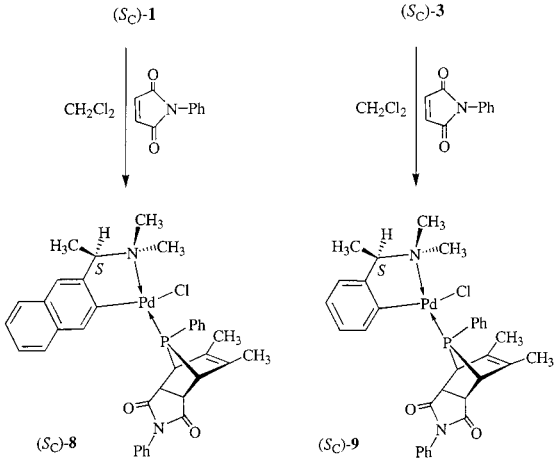


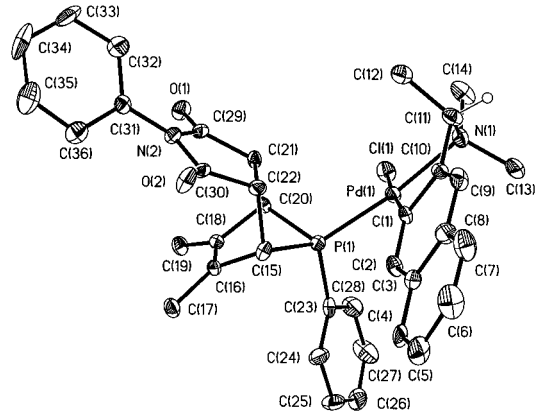


Figure 2. Structural drawing of (S_C)-**8** showing the atom-numbering scheme (20% probability ellipsoids). The hydrogen atom on C(11) has an arbitrary radius. Selected bond lengths (Å): Pd(1)−P(1), 2.224(3); Pd(1)−N(1), 2.156(9); Pd(1)−C(1), 1.990(10); Pd(1)−Cl(1), 2.387(3); C(16)−C(18), 1.325(15); C(25)−C(26), 1.342(14); C(28)−C(30), 1.332(12). Selected angles (deg): P(1)−Pd(1)−C(1), 94.2(3); C(1)−Pd(1)−N(1), 81.9(4); N(1)−Pd(1)−Cl(1), 94.7(3); Cl(1)−Pd(1)−P(1), 89.47(10); C(15)−P(1)−C(20), 81.1(4).

(S_C)-**8**, (S_C)-**9**, and others reported in the literature.[4,6] The metrical parameters of the two alkyne insertion products (S_C)-**6** and (S_C)-**7** are not very different.

Conclusions

Electron-deficient alkynes insert into the Pd−C bond of chiral palladacycles containing coordinated DMPP, while an electron-deficient alkene undergoes diastereoselective [4+2] Diels−Alder cycloaddition to the coordinated DMPP. These reactions occur under mild conditions and with high yields. The presence of the coordinated phosphole does not inhibit the insertion reaction, whereas for closely related compounds coordinated pyridine reduced the rate of insertion by a factor of 500.[1a] However, the presence of the coordinated phosphole completely inhibited the insertion of a second

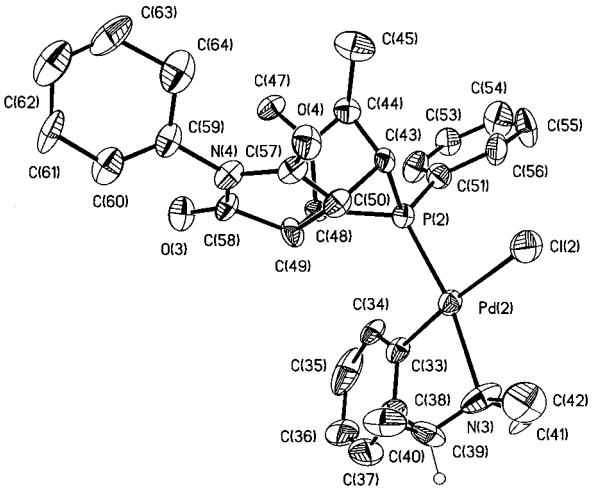
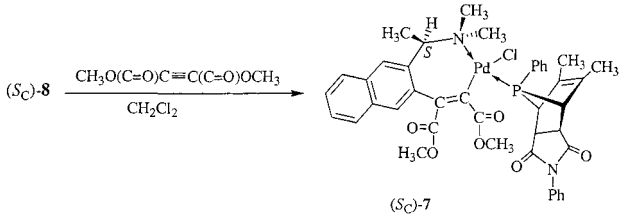


Figure 3. Structural drawing of one of the two inequivalent molecules of (S_C)-**9** present in the asymmetric unit showing the atom-numbering scheme (30% probability ellipsoids). The hydrogen atom on C(40) has an arbitrary radius. Selected bond lengths (Å): Pd(2)−C(33), 1.971(13); Pd(2)−N(3), 2.176(15); Pd(2)−P(2), 2.211(4); Pd(2)−Cl(2), 2.385(5); C(44)−C(46), 1.37(2). Selected angles (deg): P(2)−Pd(2)−C(33), 94.5(4); C(33)−Pd(2)−N(3), 78.9(6); N(3)−Pd(2)−Cl(2), 97.8(5); Cl(2)−Pd(2)−P(2), 89.27(16); C(43)−P(2)−C(48), 81.4(5).

Scheme 7



alkyne. In similar systems[1a] double insertion of diphenylacetylene usually occurred.

Experimental Section

A. Reagents and Physical Measurements. All reagents were reagent grade and were used as received from commercial sources (Aldrich, Fischer Scientific). (S_C)-TMBA was a gift of HEXEL Corporation. (S_C)-TMNA[11] and the chiral complexes (S_C)-**1** and (S_C)-**3**[6k,n,12] were obtained as previously described. Silica gel for column chromatography (grade 200−300 mesh) was obtained from Natland International Corporation. DMPP[13] was prepared by the literature method. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Melting points were determined on a Mel-Temp apparatus and are uncorrected. Optical rotations were measured on a Perkin-Elmer model 141 polarimeter. ^{1}H, ^{1}H{^{31}P}, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded at 499.8, 499.8, 125.7, and 202.3 MHz, respectively, on a Varian Unity-plus 500 FT-NMR spectrometer. Proton and carbon chemical shifts are relative to internal Me_4Si or solvent resonances, and phosphorus chemical shifts are relative to external 85% H_3PO_4(aq), with positive values being downfield of the respective reference.

B. Syntheses. (S_C)-2. A mixture of complex (S_C)-**1** (0.600 g, 1.14 mmol) and dimethylacetylene dicarboxylate, DMAD (0.17 mL, 1.36 mmol), in dichloromethane (30 mL) was stirred

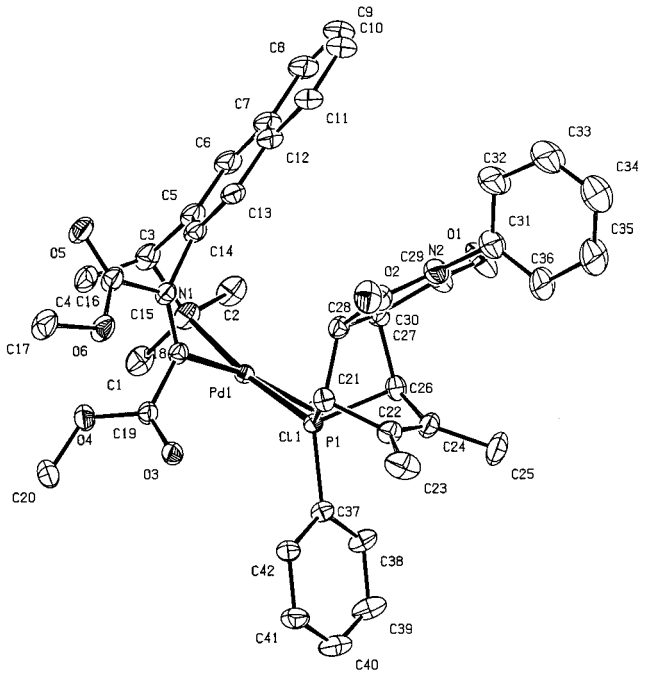
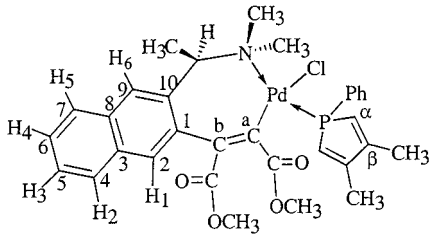


Figure 4. Structural drawing of one of the two inequivalent molecules of (S_C)-**7** present in the asymmetric unit showing the atom-numbering scheme (30% probability ellipsoids). Selected bond lengths (Å): Pd(1)−Cl(1), 2.379(2); Pd(1)−P(1), 2.232(2); Pd(1)−N(1), 2.219(6); Pd(1)−C(18), 2.007(5); C(15)−C(18), 1.335(6); C(22)−C(24), 1.333(13). Selected angles (deg): P(1)−Pd(1)−C(18), 94.7(1); P(1)−Pd(1)−Cl(1), 83.0(1); Cl(1)−Pd(1)−N(1), 93.2(2); N(1)−Pd(1)−C(18), 89.9(2); C(21)−P(1)−C(26), 81.5(4).

for 10 h at room temperature. The pale yellow solution was taken to dryness on a rotary evaporator to give (S_C)-**2** as a deep yellow solid. Complex (S_C)-**2** could not be crystallized from any of the solvents tried. Yield: 0.73 g (96%). Mp: 188−190 °C (blackens at 184 °C). $[\alpha]_D$ +53.6° (*c* 0.2, CH_2Cl_2). Anal. Calcd for $C_{32}H_{35}ClNO_4PPd$: C, 57.35; H, 5.22; Cl, 5.29. Found: C, 57.18; H, 5.26; Cl, 5.03. ^{31}P{^{1}H} NMR (202.3 MHz, $CDCl_3$,



25 °C): δ 29.2 (s, 1P, DMPP). ^{1}H NMR (499.8 MHz, $CDCl_3$, 25 °C): δ 7.86 (s, 1H, H_1), 7.84 (d, $^3J(H_2H_3)$ = 6.0 Hz, 1H, H_2), 7.73 (m, 1H, H_5), 7.69 (m, 2H, H_o), 7.52 (s, 1H, H_6), 7.48 (m, 2H, $H_{3,4}$), 7.34 (m, 1H, H_p), 7.27 (m, 2H, H_m), 6.67 (dq, ^2J(PH) = 31.0 Hz, ^4J(HH) = 1.0 Hz, 1H, H_α), 6.23 (dq, ^2J(PH) = 31.5 Hz, ^4J(HH) = 1.0 Hz, 1H, H_α), 4.58 (q, ^3J(HH) = 7.0 Hz, 1H, CH), 3.68 (s, 3H, OCH_3), 3.40 (s, 3H, OCH_3), 2.95 (d, ^4J(PH) = 1.5 Hz, 3H, NCH_3), 2.77 (d, ^4J(PH) = 3.0 Hz, 3H, NCH_3), 2.19 (d, ^4J(HH) = 1.0 Hz, 3H, DMPP−CH_3), 1.70 (d, ^4J(HH) = 1.0 Hz, 3H, DMPP−CH_3), 1.48 (d, ^3J(HH) = 7.0 Hz, 3H, CCH_3). ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$, 25 °C): δ 171.88 (d, ^3J(PC) = 7.4 Hz, CO), 168.80 (d, ^4J(PC) = 4.5 Hz, CO), 162.96 (d, ^4J(PC) = 1.5 Hz, C_1), 151.74 (d, ^2J(PC) = 12.4 Hz, C_β), 149.74 (d, ^2J(PC) = 12.4 Hz, C_β), 137.45 (d, ^4J(PC) = 2.0 Hz, C_{10}), 136.69 (s, C_a), 133.24 (d, ^2J(PC) = 11.7 Hz, C_o), 132.20 (s, C_3), 132.03 (s, C_8), 130.84 (d,

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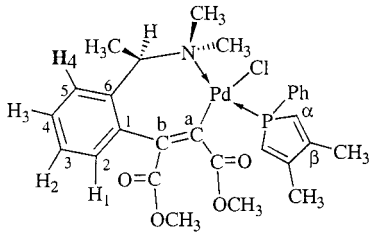
(12) (a) Tani, K.; Brown, L. D.; Ahmed, J.; Ibers, J. A.; Yokota, M.; Nakamura, A.; Otsuka, S.*J. Am. Chem. Soc.* **1977**, *99*, 7876. (b) Gül, N.; Nelson, J. H. *Organometallics* **2000**, *19*, 91.
(13) Breque, A.; Mathey, F.; Savignac, P. *Synthesis* **1981**, 983.

^3J(PC) = 2.8 Hz, C_b), 130.64 (d, ^4J(PC) = 2.8 Hz, C_p), 128.28 (s, C_2), 128.23 (d, ^2J(PC) = 11.4 Hz, C_m), 127.81 (s, C_4), 126.87 (s, C_5), 126.83 (s, C_6), 126.49 (s, C_7), 126.08 (d, ^1J(PC) = 56.3 Hz, C_α), 126.03 (d, ^1J(PC) = 56.7 Hz, C_α), 126.00 (s, C_9), 125.67 (d, ^1J(PC) = 53.2 Hz, C_i), 60.92 (d, ^3J(PC) = 2.6 Hz, CH), 51.91-(s, OCH_3), 50.95 (s, OCH_3), 47.66 (d, ^3J(PC) = 3.3 Hz, NCH_3), 40.04 (d, ^3J(PC) = 2.5 Hz, NCH_3), 17.72 (d, ^3J(PC) = 14.0 Hz, DMPP−CH_3), 17.09 (d, ^3J(PC) = 14.0 Hz, DMPP−CH_3), 9.33 (d, ^4J(PC) = 1.3 Hz, CCH_3).

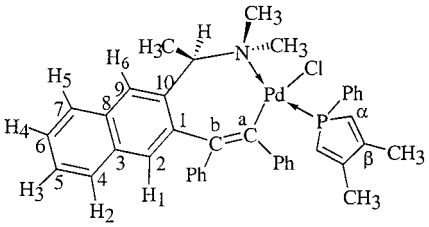
(*S*$_C$)-4. Complex (*S*$_C$)-**4** was prepared similarly from a mixture of complex (*S*$_C$)-**3** (0.600 g, 1.26 mmol) and dimethylacetylene dicarboxylate, DMAD (0.19 mL, 1.51 mmol), as a deep yellow solid. Yield: 0.72 g (93%). Mp: 185−187 °C (blackens at 180 °C). $[\alpha]_D$ +83.6° (*c* 0.2, CH_2Cl_2). Anal. Calcd for $C_{28}H_{33}ClNO_4PPd$: C, 54.23; H, 5.32; Cl, 5.72. Found: C, 54.16; H, 5.20; Cl, 5.63. $^{31}P\{^1H\}$ NMR (202.3 MHz, $CDCl_3$, 25



(S$_C$)-*4*

°C): δ 29.5 (s, 1P, DMPP). ^1H NMR (499.8 MHz, $CDCl_3$, 25 °C): δ 7.72 (m, 2H, H_o), 7.40 (d, $^3J(H_3H_4)$ = 7.5 Hz, 1H, H_4), 7.35 (m, 1H, H_p), 7.30 (apparent t, $^3J(H_3H_4) = {}^3J(H_2H_3)$ = 7.5 Hz, 1H, H_3), 7.30 (m, 2H, H_m), 7.22 (apparent t, $^3J(H_2H_3) = {}^3J(H_1H_2)$ = 7.5 Hz, 1H, H_2), 7.09 (d, $^3J(H_1H_2)$ = 7.5 Hz, 1H, H_1), 6.61 (d, ^2J(PH) = 31.0 Hz, 1H, H_α), 6.36 (d, ^2J(PH) = 31.5 Hz, 1H, H_α), 4.38 (q, ^3J(HH) = 7.0 Hz, 1H, CH), 3.64 (s, 3H, OCH_3), 3.34 (s, 3H, OCH_3), 2.89 (s, 3H, NCH_3), 2.68 (d, ^4J(PH) = 3.0 Hz, 3H, NCH_3), 2.10 (s, 3H, DMPP−CH_3), 1.89 (s, 3H, DMPP−CH_3), 1.36 (d, ^3J(HH) = 7.0 Hz, 3H, CCH_3). $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 25 °C): δ 171.96 (d, ^3J(PC) = 6.2 Hz, CO), 168.89 (d, ^4J(PC) = 4.5 Hz, CO), 162.77 (d, ^4J(PC) = 1.4 Hz, C_6), 151.81 (d, ^2J(PC) = 12.4 Hz, C_β), 149.67 (d, ^2J(PC) = 12.4 Hz, C_β), 140.32 (d, ^4J(PC) = 1.8 Hz, C_1), 139.18 (s, C_a), 133.26 (d, ^2J(PC) = 11.6 Hz, C_o), 130.65 (d, ^4J(PC) = 2.4 Hz, C_p), 130.35 (d, ^2J(PC) = 2.6 Hz, C_6), 129.03 (s, C_2), 128.27 (d, ^3J(PC) = 11.6 Hz, C_m), 127.28 (s, C_5), 126.97 (s, C_4), 126.59 (s, C_3), 126.27 (d, ^1J(PC) = 56.2 Hz, C_α), 126.15 (d, ^1J(PC) = 55.4 Hz, C_α), 125.75 (d, ^1J(PC) = 52.7 Hz, C_i), 60.96 (d, ^3J(PC) = 2.3 Hz, CH), 51.82(s, OCH_3), 50.86 (d, ^5J(PC) = 3.0 Hz, OCH_3), 47.46 (d, ^3J(PC) = 3.1 Hz, NCH_3), 40.03 (d, ^3J(PC) = 2.3 Hz, NCH_3), 17.56 (d, ^3J(PC) = 13.8 Hz, DMPP−CH_3), 17.30 (d, ^3J(PC) = 14.0 Hz, DMPP−CH_3), 8.81 (s, CCH_3).

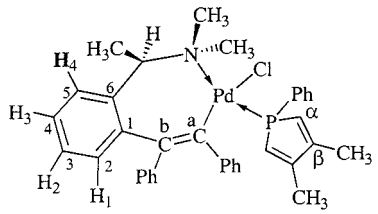
(*S*$_C$)-5. A mixture of (*S*$_C$)-**1** (0.600 g, 1.14 mmol) and diphenylacetylene (0.220 g, 1.23 mmol) in 1,2-dichloroethane (40 mL) was stirred for 1 day at 75 °C. The solvent was removed under reduced pressure to give a brownish (foamy) solid residue. This solid was purified by column chromatography on silica gel with dichloromethane−*n*-hexane (1:10) as eluant. This resulted in a very dark brown band (containing elemental Pd and organic impurities) at the top of the column and a yellow band, which moved with the solvent front. The yellow eluate was collected, and the solvent was removed in vacuo. The resulting deep yellow solid was washed with several small portions of *n*-hexane−diethyl ether (10:1) and air-dried. Complex (*S*$_C$)-**5** could not be crystallized from any of the solvents tried. Yield: 0.59 g (73.8%). Mp: 183−185 °C (blackens at 175 °C). $[\alpha]_D$ +78.3° (*c* 0.2, CH_2Cl_2). Anal. Calcd for $C_{40}H_{39}ClNPPd$: C, 66.90; H, 5.72; Cl, 5.20. Found: C, 66.73; H, 5.58; Cl, 5.04. $^{31}P\{^1H\}$ NMR (202.3 MHz, $CDCl_3$, 25 °C): δ



(S$_C$)-*5*

25.4 (s, 1P, DMPP). ^1H NMR (499.8 MHz, $CDCl_3$, 25 °C): δ 8.03 (s, 1H, H_1), 7.94 (dd, $^3J(H_2H_3)$ = 8.0 Hz, $^4J(H_2H_4)$ = 0.5 Hz, 1H, H_2), 7.51 (ddd, $^3J(H_2H_3)$ = 8.0 Hz, $^3J(H_3H_4)$ = 6.0 Hz, $^4J(H_3H_5)$ = 2.0 Hz, 1H, H_3), 7.40 (m, 2H, $H_{4,5}$), 7.29 (s, 1H, H_6), 7.11 (m, 5H, $H_{o,m,p}$CPh), 6.98 (m, 8H, $H_{o,m,p}$CPh, $H_{o,p}$PPh), 6.79 (d quin, ^2J(PH) = 32.0 Hz, ^4J(HH) = ^4J(HH) = 1.0 Hz, 1H, H_α), 6.60 (m, 2H, H_mPPh), 6.54 (d quin, ^2J(PH) = 31.5 Hz, ^4J(HH) = ^4J(HH) = 1.0 Hz, 1H, H_α), 4.85 (q, ^3J(HH) = 7.0 Hz, 1H, CH), 2.93 (d, ^4J(PH) = 2.5 Hz, 3H, NCH_3), 2.48 (s, 3H, NCH_3), 2.19 (d, ^4J(HH) = 1.0 Hz, 3H, DMPP−CH_3), 1.98 (d, ^4J(HH) = 1.0 Hz, 3H, DMPP−CH_3), 1.59 (d, ^3J(HH) = 7.0 Hz, 3H, $CHCH_3$). $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 25 °C): δ 156.10 (d, ^4J(PC) = 2.3 Hz, C_{10}), 151.48 (d, ^2J(PC) = 10.3 Hz, C_β), 150.98 (^2J(PC) = 10.2 Hz, C_β), 145.41 (d, ^4J(PC) = 3.2 Hz, C_1), 143.65 (d, ^3J(PC) = 5.4 Hz, C_6), 142.52 (d, ^6J(PC) = 1.8 Hz, C_8), 139.18 (s, C_3), 137.25 (d, ^2J(PC) = 6.3 Hz, C_a), 133.16 (d, ^2J(PC) = 12.3 Hz, C_oPPh), 133.02 (s, C_iCPh), 131.76 (s, C_iCPh), 130.19 (d, ^4J(PC) = 3.5 Hz, C_pPPh), 129.93 (s, C_pCPh), 129.90 (s, C_oCPh), 128.41 (d, ^1J(PC) = 51.4 Hz, C_α), 128.23 (s, C_9), 127.95 (s, C_4), 127.79 (s, C_7), 127.64 (s, C_mCPh), 127.48 (d, ^3J(PC) = 11.7 Hz, C_mPPh), 126.27 (d, ^1J(PC) = 52.4 Hz, C_α), 126.25 (d, ^1J(PC) = 52.3 Hz, C_iPPh), 125.83 (s, C_6), 125.74 (s, C_2), 125.72 (s, C_5), 125.60 (s, C_pCPh), 61.45 (d, ^3J(PC) = 2.3 Hz, $CHCH_3$), 48.47 (d, ^3J(PC) = 2.8 Hz, NCH_3), 41.28 (d, ^3J(PC) = 1.9 Hz, NCH_3), 17.60 (d, ^3J(PC) = 12.7 Hz, DMPP−CH_3), 17.49 (d, ^3J(PC) = 12.2 Hz, DMPP−CH_3), 9.77 (s, $CHCH_3$).

(*S*$_C$)-6. Complex (*S*$_C$)-**6** was prepared similarly from a mixture of (*S*$_C$)-**3** (0.600 g, 1.26 mmol) and diphenylacetylene (0.240 g, 1.38 mmol) as a deep yellow solid. Complex (*S*$_C$)-**6** was crystallized from CH_2Cl_2−*n*-hexane, forming yellow prisms. Yield: 0.62 g (75.4%). Mp: 185−187 °C (blackens at 180 °C). $[\alpha]_D$ +110.5° (*c* 0.2, CH_2Cl_2). Anal. Calcd for $C_{36}H_{37}ClNPPd$: C, 65.89; H, 5.64; Cl, 5.40. Found: C, 65.78; H, 5.81; Cl, 5.43.



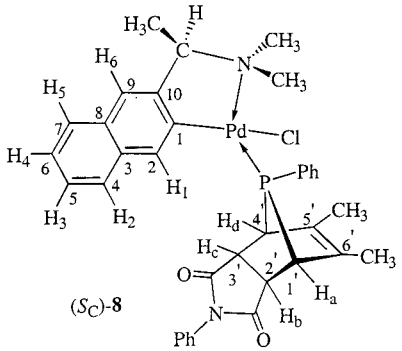
(S$_C$)-*6*

$^{31}P\{^1H\}$ NMR (202.3 MHz, $CDCl_3$, 25 °C): δ 25.4 (s, 1P, DMPP). ^1H NMR (499.8 MHz, $CDCl_3$, 25 °C): δ 7.59 (dd, $^3J(H_3H_4)$ = 8.5 Hz, $^4J(H_2H_4)$ = 1.0 Hz, 1H, H_4), 7.35 (ddd, $^3J(H_3H_4)$ = 8.5 Hz, $^3J(H_2H_3)$ = 7.5 Hz, $^4J(H_1H_3)$ = 1.0 Hz, 1H, H_3), 7.31 (m, 3H, $H_{o,p}$PPh), 7.14 (m, 8H, $H_{o,m,p}$CPh, $H_{m,p}$PPh), 7.11 (ddd, $^3J(H_1H_2) = {}^3J(H_2H_3)$ = 7.5 Hz, $^4J(H_2H_4)$ = 1.0 Hz, 1H, H_2), 7.03 (m, 3H, $H_{m,p}$CPh), 6.90 (m, 2H, H_oCPh), 6.83 (dd, $^3J(H_1H_2)$ = 7.5 Hz, $^4J(H_1H_3)$ = 1.0 Hz, 1H, H_1), 6.80 (d quin, ^2J(PH) = 32.0 Hz, ^4J(HH) = ^4J(HH) = 1.0 Hz, 1H, H_α), 6.51 (d quin, ^2J(PH) = 31.5 Hz, ^4J(HH) = ^4J(HH) = 1.0 Hz, 1H, H_α), 4.66 (q, ^3J(HH) = 7.0 Hz, 1H, CH), 2.86 (d, ^4J(PH) = 2.5 Hz, 3H, NCH_3), 2.47 (d, ^4J(PH) = 1.5 Hz, 3H, NCH_3), 2.17 (d, ^4J(HH) = 1.0 Hz, 3H, DMPP−CH_3), 2.03 (d, ^4J(HH) = 1.0 Hz, 3H, DMPP−CH_3), 1.50 (d, ^3J(HH) = 7.0 Hz, 3H, $CHCH_3$). $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 25 °C): δ 155.37 (d, ^4J(PC) = 2.4 Hz, C_6), 151.30 (d, ^2J(PC) = 10.3 Hz, C_β), 150.61 (d,

^2J(PC) = 10.2 Hz, C_β), 147.22 (d, ^4J(PC) = 3.4 Hz, C_1), 143.54 (d, ^2J(PC) = 5.8 Hz, C_a), 137.17 (d, ^3J(PC) = 6.2 Hz, C_b), 133.73 (s, C_iCPh), 133.59 (d, ^2J(PC) = 12.3 Hz, C_oPPh), 130.21 (s, C_pCPh), 130.18 (s, C_mCPh), 130.02 (d, ^4J(PC) = 2.8 Hz, C_pPPh), 129.71 (s, C_oCPh), 129.37 (s, C_2), 128.06 (d, ^1J(PC) = 51.5 Hz, C_α), 127.79 (d, ^3J(PC) = 10.9 Hz, C_mPPh), 127.69 (s, C_oCPh), 127.55 (s, C_mCPh), 127.36(s, C_pCPh), 126.76 (d, ^1J(PC) = 51.5 Hz, C_α), 126.67 (d, ^1J(PC) = 51.9 Hz, C_iPPh), 126.32 (s, C_5), 125.93 (s, C_4), 125.67 (s, C_3), 125.50 (s, C_pCPh), 74.46 (d, ^3J(PC) = 3.1 Hz, *C*HCH$_3$), 48.30 (d, ^3J(PC) = 2.8 Hz, NCH$_3$), 41.28 (d, ^3J(PC) = 2.0 Hz, NCH$_3$), 17.54 (d, ^3J(PC) = 10.3 Hz, DMPP−CH$_3$), 17.44 (d, ^3J(PC) = 10.1 Hz, DMPP−CH$_3$), 9.14 (s, CH*C*H$_3$).

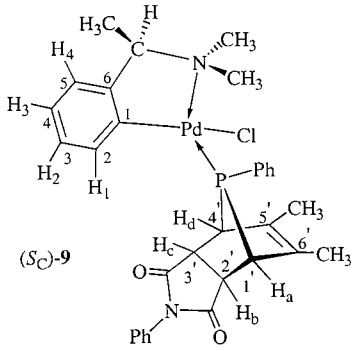
(*S*$_C$)-7. A mixture of complex (*S*$_C$)-**2** (0.600 g, 0.895 mmol) and *N*-phenylmaleimide (0.155 g, 0.896 mmol) in dichloromethane (35 mL) was stirred for 5 days at room temperature. The solvent was removed under reduced pressure to give a pale yellow solid. The product (0.62 g) was shown by ^{31}P{^{1}H} NMR spectroscopy to be a 1.55:1 mixture of *anti-endo* (*S*$_C$)-**7** and *syn-endo* (*S*$_C$)-**7**. Increasing the reaction time to 10 days produced the mixture in the same chemical yield and ratio as described above. The two stereoisomers could not be separated by fractional crystallization or column chromatography. Interestingly, under the same conditions (*S*$_C$)-**4** did not react with *N*-phenylmaleimide. ^{31}P{^{1}H} NMR (202.3 MHz, CDCl$_3$, 25 °C): δ 139.0 and 128.4 with the ratio of 1.55:1, respectively.

(*S*$_C$)-8. A mixture of complex (*S*$_C$)-**1** (0.600 g, 1.14 mmol) and *N*-phenylmaleimide (0.197 g, 1.14 mmol) in dichloromethane (30 mL) was stirred for 1 day at room temperature. The pale yellow solution was taken to dryness on a rotary evaporator to give complex (*S*$_C$)-**8** as a pale yellow solid. Recrystallization from CH_2Cl_2−hexane−ether afforded pale yellow prisms. Yield: 0.77 g (96.5%). Mp: 190−192 °C (blackens at 187 °C). $[\alpha]_D$ +95.6° (*c* 0.2, CH_2Cl_2). Anal. Calcd for $C_{36}H_{36}ClN_2O_2PPd$: C, 61.66; H, 5.13; Cl, 5.06. Found: C, 61.44; H, 5.02; Cl, 4.93. ^{31}P{^{1}H} NMR (202.3 MHz, CDCl$_3$, 25



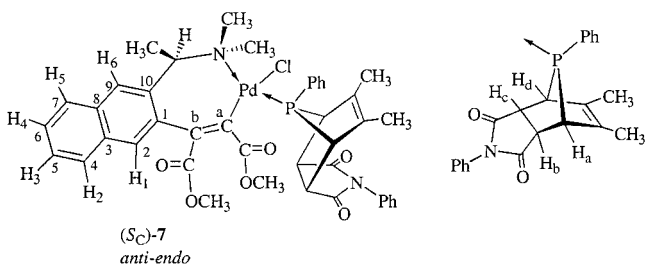
°C): δ 137.2 (s, 1P). ^{1}H NMR (499.8 MHz, CDCl$_3$, 25 °C): δ 7.95 (m, 2H, H$_o$PPh), 7.70 (dd, ^3J(H$_2$H$_3$) = 7.5 Hz, ^4J(H$_2$H$_4$) = 1.5 Hz, 1H, H$_2$), 7.63 (dd, ^3J(H$_4$H$_5$) = 7.5 Hz, ^4J(H$_3$H$_5$) = 1.5 Hz, 1H, H$_5$), 7.52 (m, 3H, H$_1$, H$_p$PPh, H$_p$NPh), 7.47 (s, 1H, H$_6$), 7.38 (m, 6H, H$_{3,4}$, H$_m$PPh, H$_m$NPh), 7.05 (m, 2H, H$_o$NPh), 4.58 (s, 1H, H$_d$), 4.23 (s, 1H, H$_a$), 4.07 (s, 1H, H$_c$), 3.89 (s, 1H, H$_b$), 3.88 (q, ^3J(HH) = 6.5 Hz, 1H, CH), 2.69 (s, 6H, 2NCH$_3$), 1.79 (d, ^3J(HH) = 6.5 Hz, 3H, CCH$_3$), 1.76 (s, 3H, C=C−CH$_3$), 1.63 (s, 3H, C=C−CH$_3$). ^{13}C{^{1}H} NMR (125.7 MHz, CDCl$_3$, 25 °C): δ 175.07 (d, ^3J(PC) = 16.7 Hz, CO), 174.93 (d, ^3J(PC) = 16.7 Hz, CO), 152.33 (s, C$_1$), 147.41 (s, C$_{10}$), 133.66 (s, C$_i$NPh), 133.56 (d, ^3J(PC) = 13.2 Hz, C$_2$), 133.06 (s, C$_3$), 132.76 (d, ^3J(PC) = 10.1 Hz, C$_o$PPh), 132.42 (d, ^2J(PC) = 5.7 Hz, C$_{6'}$), 131.66 (d, ^2J(PC) = 1.1 Hz, C$_{5'}$), 131.44 (s, C$_8$), 131.03 (d, ^4J(PC) = 2.4 Hz, C$_p$PPh), 129.18 (s, C$_o$NPh), 128.73 (s, C$_p$NPh), 128.67 (d, ^3J(PC) = 9.4 Hz, C$_m$PPh), 127.84 (d, ^1J(PC) = 34.8 Hz, C$_i$PPh), 127.20 (s, C$_4$), 126.58 (s, C$_7$), 126.36 (s, C$_m$NPh), 125.37 (s, C$_6$), 124.93 (s C$_5$), 121.13 (s, C$_9$), 74.09 (s, *C*HCH$_3$), 50.90 (d, ^2J(PC) = 40.0 Hz, C$_{3'}$), 49.97 (s, 2NCH$_3$), 49.62 (d, ^2J(PC) = 35.9 Hz, C$_{2'}$), 45.61 (d, ^1J(PC) = 24.3 Hz, C$_{1'}$), 45.37 (d, ^1J(PC) = 26.4 Hz, C$_{4'}$), 22.0 (bs, CH*C*H$_3$), 15.43 (d, ^3J(PC) = 1.9 Hz, C=C*C*H$_3$), 15.25 (d, ^3J(PC) = 2.1 Hz, C=*C*CH$_3$).

(*S*$_C$)-9. Complex (*S*$_C$)-**9** was prepared similarly from a mixture of (*S*$_C$)-**3** (0.600 g, 1.26 mmol) and *N*-phenylmaleimide (0.220 g, 1.26 mmol) as a yellow solid. Complex (*S*$_C$)-**9** was crystallized from CH_2Cl_2−hexane−ether, forming pale yellow prisms. Yield: 0.80 g (94.5%). Mp: 186−188 °C (blackens at 185 °C). $[\alpha]_D$ +105.3° (*c* 0.2, CH_2Cl_2). Anal. Calcd for $C_{32}H_{34}ClN_2O_2PPd$: C, 59.02; H, 5.22; Cl, 5.44. Found: C, 58.89; H, 5.11; Cl, 5.28. ^{31}P{^{1}H} NMR (202.3 MHz, CDCl$_3$, 25 °C): δ



137.6 (s, 1P). ^{1}H NMR (499.8 MHz, CDCl$_3$, 25 °C): δ 7.85 (m, 2H, H$_o$PPh), 7.44 (m, 3H, H$_{m,p}$PPh), 7.40 (m, 2H, H$_m$NPh), 7.34 (m, 1H, H$_p$NPh), 6.78−7.06 (m, 4H, H$_1$−H$_4$), 6.94 (m, 2H, H$_o$NPh), 4.55 (s, 1H, H$_d$), 4.16 (s, 1H, H$_a$), 4.04 (s, 1H, H$_c$), 3.82 (s, 1H, H$_b$), 3.69 (unresolved multiplet, 1H, CH), 2.65 (s, 3H, NCH$_3$), 2.64 (s, 3H, NCH$_3$), 1.72 (s, 3H, C=C−CH$_3$), 1.66 (d, ^3J(HH) = 6.0 Hz, 3H, CCH$_3$), 1.57 (s, 3H, C=C−CH$_3$). ^{13}C-{^{1}H} NMR (125.7 MHz, CDCl$_3$, 25 °C): δ 175.12 (d, ^3J(PC) = 16.8 Hz, CO), 174.89 (d, ^3J(PC) = 16.5 Hz, CO), 154.44 (s, C$_1$), 148.77 (s, C$_6$), 134.94 (d, ^3J(PC) = 12.9 Hz, C$_2$), 133.56 (s, C$_i$NPh), 132.88 (s, C$_{5'}$), 132.53 (d, ^2J(PC) = 10.1 Hz, C$_o$PPh), 131.59 (d, ^2J(PC) = 1.3 Hz, C$_{6'}$), 130.82 (d, ^4J(PC) = 2.0 Hz, C$_p$PPh), 129.10 (s, C$_o$NPh), 128.65 (s, C$_p$NPh), 128.50 (d, ^3J(PC) = 9.3 Hz, C$_m$PPh), 127.84 (d, ^1J(PC) = 34.8 Hz, C$_i$PPh), 126.34 (s, C$_3$), 126.30 (s, C$_m$NPh), 124.77 (s, C$_4$), 123.17 (s, C$_5$), 74.41 (s, *C*HCH$_3$), 50.90 (d, ^2J(PC) = 31.4 Hz, C$_{2'}$), 49.98 (s, NCH$_3$), 49.36 (d, ^2J(PC) = 29.7 Hz, C$_{3'}$), 45.49 (d, ^1J(PC) = 23.9 Hz, C$_{4'}$), 45.24 (d, ^1J(PC) = 26.5 Hz, C$_{1'}$), 22.00 (bs, CCH$_3$), 15.29 (d, ^3J(PC) = 1.9 Hz, C=C-*C*H$_3$), 15.11 (d, ^3J(PC) = 2.3 Hz, C=C−*C*H$_3$).

Diastereomerically Pure (*S*$_C$)-7. A mixture of complex (*S*$_C$)-**8** (0.600 g, 0.855 mmol) and dimethylacetylene dicarboxylate (0.12 mL, 0.94 mmol) in dichloromethane (35 mL) was stirred for 5 days at room temperature. The pale yellow solution was taken to dryness on a rotary evaporator to give diastereomerically pure (*S*$_C$)-**7** as a pale yellow solid. The product was crystallized from CH_2Cl_2−hexane, forming pale yellow prisms. Yield: 0.58 g (83.5%). Mp: 195−197 °C (blackens at 189 °C). $[\alpha]_D$ +98.7° (*c* 0.2, CH_2Cl_2). Anal. Calcd for $C_{42}H_{42}ClN_2O_6PPd$: C, 59.82; H, 4.98; Cl, 4.20. Found: C, 59.66; H, 4.80; Cl, 4.13. ^{31}P{^{1}H} NMR (202.3 MHz, CDCl$_3$, 25



°C): δ 128.4 (s, 1P). ^{1}H NMR (499.8 MHz, CDCl$_3$, 25 °C): δ 7.86 (m, 2H, H$_o$PPh), 7.47 (m, 2H, H$_{2,5}$), 7.44 (m, 1H, H$_p$NPh), 7.43 (s, 1H, H$_1$), 7.41 (s, 1H, H$_6$), 7.37 (m, 7H, H$_{3,4}$, H$_p$PPh,

H_mPPh, H_mNPh), 7.05 (m, 2H, H_oNPh), 4.31 (q, ^3J(HH) = 7.0 Hz, 1H, CH), 4.03 (d, $^4J(H_aH_d)$ = 3.5 Hz, 1H, H_d) 3.93 (d, $^4J(H_dH_a)$ = 3.5 Hz, 1H, H_a), 3.83 (s, 1H, H_c), 3.69 (s, 1H, H_b), 3.68 (s, 3H, OCH_3), 3.46 (s, 3H, OCH_3), 2.78 (s, 3H, NCH_3), 2.70 (d, ^4J(PH) = 2.5 Hz, 3H, NCH_3), 1.66 (s, 3H, C═C−CH_3), 1.39 (s, 3H, C═C−CH_3), 1.36 (d, ^3J(HH) = 7.0 Hz, 3H, CCH_3). Under the same conditions (S_C)-**9** did not react with dimethylacetylene dicarboxylate.

C. X-ray Data Collection and Processing. Crystals of the complexes were obtained from CH_2Cl_2−hexane (**6**, **7**), acetone−hexane−ether (**8**), or CH_2Cl_2−hexane−ether (**9**). They were mounted on glass fibers, coated with epoxy, and placed on a Simens P4 diffractometer. Intensity data were taken in the ω-mode at 298 K with Mo Kα graphite-monochromated radiation (λ = 0.71073 Å). Three check reflections monitored every 100 reflections showed random (<2%) variation during the data collections. The data were corrected for Lorentz, polarization effects and except for **7** for absorption using an empirical model derived from azimuthal data collections. Scattering factors and corrections for anomalous dispension were taken from a standard source.[14] Calculations were performed with the Siemens SHELXTL plus version 5.10 software package on a personal computer. The structures were solved by the Patterson method. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. Hydrogen atoms were refined at calculated positions with a riding model in which the C−H vector was fixed at 0.96 Å. Compound **6** crystallized as a CH_2Cl_2 solvate, and for **9** 0.5 CH_2Cl_2 and 0.5 H_2O molecules are present in the asymmetric unit. For **7** the structure contains two molecules per asymmetric unit that are pseudo inversion related. Each corresponding atom in the second molecule has a prime added to its label. Chiral centers are C(3) and C(3)′, and synthesis imposed the same chirality to these two stereo centers. The pseudo inversion in the crystal implies that only the interchange of a H and a methyl group stops whole molecules being inversion related. Initially, the structure was determined and refined in $P\bar{1}$. This produced a structure in which C(4) lies in the plane of C(3), C(5), and N(1) with C(4) having a large anisotropic displacement perpendicular to this plane. This is consistent with the apparent electron density imposed by the real component of the structure factors $F(\mathbf{h}) = A(\mathbf{h}) + iB(\mathbf{h})$ for the true structure. $A(\mathbf{h})$ is the Fourier transform of $[p(\mathbf{r}) + p(-\mathbf{r})^*]/2$, and $iB(\mathbf{h})$ is the Fourier transform of $[p(\mathbf{r}) - p(-\mathbf{r})^*]/2$. A refinement problem results when the structure is refined in $P1$ since $iB(\mathbf{h})$ is poorly determined, being initially phased by correctly locating C(4) and C(4)′. As a consequence, differences across the inversion center are poorly determined.

The program RAELSOO[15] was used for constrained refinement, as it allows a progressive relaxation of the pseudo inversion symmetry. The origin of the structure was chosen so that Pd(1) is inversion related through the origin to Pd(1)′. It was impossible to tell the difference between inversion-related crystal structures. Consequently, the chirality at C(3) was chosen to be *S*, in agreement with the synthesis. Rigid body *TLX* thermal parametrizations[16] were used to describe the thermal motion. A 15 parameter *TLX* model was used for a whole molecule with additional librations for the fragment [C(21) to C(36), O(1), O(2), and N(2)] and the phenyl ring [C(37) to C(42)], both centered on the P atom. It was found that a single reorientable libration was a meaningful model with an additional reorientable libration centered on N(2) for the phenyl ring [C(31) to C(36)]. A single libration about the C−C bond was used for the carboxy methyl groups attached to C(5) and C(8). Parameters for inversion-related fragments were constrained to be equivalent. Additional anisotropic parameters were given to Pd, Cl, and P atoms with equal parameters for Pd′, Cl′, and P′, respectively. Pseudo equivalent fragments were refined using refinable local coordinates defined relative to refinable local axes.[16,17] The use of the same local coordinates imposed inversion-related local geometries for pseudo inversion-related fragments. The phenyl and naphthyl rings were constrained to have local *mm2* symmetry, while the fragments [C(21) to C(26)] and [N(1), C(27) to C(31), O(1), and O(2)] and the geometry of the central atom (e.g., C(16), C(19)) of the carboxy methyl groups were constrained to be planar. It was not possible to progress past a model where only C(4), C(16), C(17), O(5), O(6), C(19), C(20), O(3), O(4), and their pseudo equivalents departed from an exact inversion relationship imposed by the coupling of parameter changes.[18] Atoms C(4) and C(4)′ were restrained to obtain the correct local geometry with equivalent bond lengths and angles to the adjacent atoms. If an exact inversion symmetry is imposed on the pseudo equivalent carboxy methyl groups, then two short contacts C(4)−C(17)′ and C(20)′^{a} result ($a = 1 + x,y,z$). It is possible to maintain the average structure while increasing these contacts if the carboxy methyl groups are refined independently. Those containing C(17) and C(20) are free to shift so as to maintain the average structure. They were refined using condition constraints that maintained the above contacts at 3.5 Å or greater. Hydrogen atoms were relocated in geometrically sensible positions after each refinement cycle. Standard deviations are calculated using the inverse of the matrix used for the least squares and assume the correctness of the various constraints and restraints described above.

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Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates, isotropic and anisotropic displacement parameters, bond lengths and angles, and hydrogen coordinates for **6**−**9**. This material is available free of charge at http://pubs.acs.org.

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