Asymmetric Synthesis of P-Chiral Diphosphines. Steric Effects on the Palladium-Complex-Promoted Asymmetric Diels−Alder Reaction between a Dimethylphenylphosphole and (*E/Z*)-Methyl-Substituted Diphenylvinylphosphines

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The organopalladium complex containing ortho-metalated (*S*)-(1-(dimethylamino)ethyl)naphthalene as the chiral auxiliary has been used successfully to promote the asymmetric [4+2] Diels−Alder reactions between 1-phenyl-3,4-dimethylphosphole and the following coordinated dienophiles: (a) diphenylvinylphosphine; (b) (*E*)-diphenyl-1-propenylphosphine; (c) (*Z*)-diphenyl-1-propenylphosphine. Reaction a generates three carbon and one phosphorus stereogenic centers while reactions b and c each produce four carbon and one phosphorus chiral centers. In dichloromethane, all three reactions proceeded smoothly at room temperature giving the corresponding rigid diphosphines in high yields. Under similar reaction conditions, the reaction times observed for reactions a−c are 2, 3, and 50 h, respectively. Two-dimensional ROESY NMR studies confirmed that the prolonged reaction time required for reaction c is due to several major repulsive interactions between the chiral naphthylamine auxiliary and the (*Z*)-methyl-substituted vinylphosphine in the transition state. Nevertheless, all three reactions gave the corresponding rigid diphosphine in high yields. The absolute stereochemistries of the three bidentate phosphine ligands that were produced from the cycloaddition reactions have been assigned by 2D ROESY NMR spectroscopy. These diphosphines are powerful sequesterers of group 8 metals although they are highly air-sensitive in the free ligand form. The coordination chemistry and the absolute stereochemistry of the optically active complex [1α,4α,5α(*S*),6α(*S*),7*R*]-dichloro[5-(diphenylphosphino)-2,3,6-trimethy-7-phenyl-7-phosphabicyclo[2.2.1]-hept-2-ene-*P*[5],*P*[7]]palladium-(II) has been studied by single-crystal X-ray analysis. Crystal structure data: $C_{27}H_{28}Cl_2P_2Pd$, $M_r = 591.7$; triclinic; space group *P*1; $a = 8.643(3)$, $b = 9.044(6)$, $c = 9.058(4)$ Å; $\alpha = 102.75(4)°$, $\beta = 108.59(2)°$, $\gamma = 97.82(3)°$; $V = 638.0(5)$ Å^3; $Z = 1$; $R_1 = 0.036$.

Introduction

The asymmetric Diels−Alder reaction is one of the most efficient and elegant methods for the construction of chiral six-membered rings.[1] The formation of two carbon−carbon bonds leading to the creation of up to four concatenated stereogenic centers in a single step, from achiral dienes and dienophiles, is an attractive feature that renders the Diels−Alder reaction to be one of the most fascinating methodologies for asymmetric organic synthesis. Its usefulness has been illustrated numerously by strategic application to the syntheses of important chiral natural products such as antibiotics and prostaglandins. Recently, we have successfully utilized this powerful synthetic tool for the enantiospecific synthesis of a series of bidentate phosphines[2−4] as well as functionalized phosphines[5−8] that contain resolved phosphorus stereogenic centers by using a chiral organopalladium complex as the reaction promoter. In some instances, we were able to generate up to five stereogenic centers in a single concerted [4+2] cycloaddition reaction.[7,8] The Diels−Alder reaction therefore offers a simple and efficient approach for these critically important functionalized P-chiral phosphines without classic resolution or separation of diastereomers.[9] In order to investigate systematically the mechanistic details in this palladium-complex-promoted asymmetric Diels−Alder synthesis, we report here the steric factors that affect the rate of the cycloaddition process during the preparation of the chiral diphosphine ligands (S_p)-**1a**−**c**.[10,11] It is noteworthy that there are five stereogenic centers being generated in the new ligands (S_p)-**1b,c**.

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(10) For clarity, simplified descriptors have been used in the text for stereoisomers. Full stereochemical descriptors, consistent with those employed by the Chemical Abstracts Service, are given in the Experimental Section.

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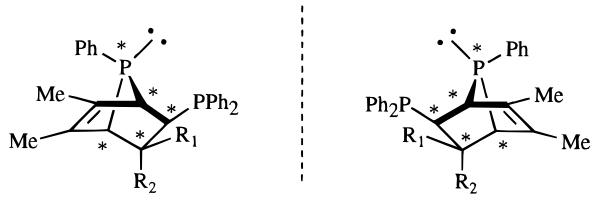

(R_p)-**1a-c** (S_p)-**1a-c**

a: $R_1 = R_2 = H$; **b**: $R_1 = H$, R_2 =Me; **c**: R_1 = Me, $R_2 = H$

Results and Discussion

Asymmetric Diels−Alder Synthesis. The chiral diphosphines (S_p)-**1a−c** were obtained enantioselectively in high yields from the asymmetric Diels−Alder reaction between 1-phenyl-3,4-dimethylphosphole (DMPP) and the corresponding diphenylvinylphosphines using the organopalladium complex **2** as the reaction promoter (Scheme 1). Using this synthetic approach, diphenylvinylphosphines were initially activated by coordinating to palladium(II).[12] Due to the unique electronic directing effects originating from the strong π-accepting aromatic carbon and the σ-donating nitrogen donor of the organopalladium unit,[13] the monodentate phosphine ligands split the chlorine bridges in (S_c)-**2** regiospecifically to give (S_c)-(+)-**3a−c**. All three monomeric complexes were isolated as stable pale yellow crystals. The unsubstituted complex (S_c)-**3a** was obtained in 91% isolated yield while the substituted analogues, (S_c)-**3b** and (S_c)-**3c**, are somewhat more soluble and could only be crystallized in 79 and 67% yields, respectively. All three neutral complexes are soluble in most noncoordinating solvents. In $CDCl_3$, the 202 MHz ^{31}P NMR spectra of (S_c)-(+)-**3a−c** each exhibited a sharp singlet at δ 32.9, 31.4, and 16.3 with respective coordination shifts of 44.3, 45.7, and 49.0 ppm.

To activate the subsequent asymmetric [4+2] cycloaddition reactions with DMPP, it is necessary to allow the incoming cyclic diene and the dienophiles to be coordinated simultaneously on the chiral metal template.[12] Thus, as illustrated in Scheme 1, addition of stoichiometric quantities of aqueous silver perchlorate to the stirring dichloromethane solutions containing the chloro complexes (S_c)-**3a−c** yielded the intermediate nonconducting perchlorato complex (S_c)-**4a−c** in essentially quantitative yields. We have recently reported on the isolation and X-ray structural analysis of an analogous palladium(II) complex containing DMPP and a coordinating perchlorato ligand.[14] In routine synthesis, however, these highly reactive species were not isolated and, upon removal of the silver chloride and drying with magnesium sulfate, the dichloromethane solutions of the perchlorato complexes were treated directly with stoichiometric amounts of DMPP at room temperature. The cycloaddition reaction was monitored by ^{31}P NMR spectroscopy. Interestingly, it was observed that the reaction involving (S_c)-**4a** as the starting material required only 2 h to complete while reactions involving the (*E*)-methyl substituted analogue (S_c)-**4b** required about 3 h. A further dramatic observation was the prolonged cycloaddition process (ca. 50 h) between the (*Z*)-methyl-substituted complex (S_c)-**4c** and DMPP under very similar reaction conditions. Nevertheless, NMR studies indicated that all three reactions proceeded to completion and gave the corresponding Diels−Alder products (S_c,R_p)-**5a−c** as opaque white crystals in 61−76% isolated yields. In $CDCl_3$, the ^{31}P NMR spectrum of each Diels−Alder complex exhibited a pair of doublets for the two nonequivalent phosphorus nuclei (Table 1). The same NMR signals were recorded from the crude products before crystallization. The low-field resonances (112−125 ppm) are typical for the bridgehead phosphorus adopting the *exo-syn* relative stereochemistry.[12,15] It is noteworthy that all known Diels−Alder reactions involving vinylphosphines and DMPP require the presence of a transition metal ion and invariably display this *exo-syn* stereochemistry in their cycloaddition products.[2−8,12] Selected ^1H and ^{31}P NMR data of these complexes are given in Table 1. The ^1H and ^{31}P spectral assignments are based on a combination

Scheme 1

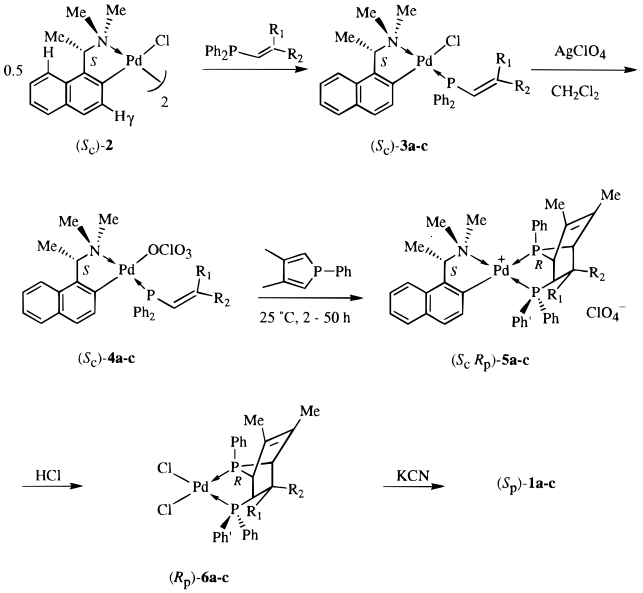

Table 1. Selected ^1H and ^{31}P Chemical Shifts in ppm of (R_c,R_p)-**5a−c** in $CDCl_3$ Solution

	(R_c,R_p)-**5a**	(R_c,R_p)-**5b**	(R_c,R_p)-**5c**
H1	3.65	3.74	3.32
Me2	1.73	1.78	1.78
Me3	1.39	1.45	1.37
H4	2.81	2.73	2.66
H5	3.05	2.54	3.40
H6/Me6(endo)	1.85(H)	0.80(Me)	2.47(H)
H6/Me6(exo)	2.35(H)	2.95(H)	1.38(Me)
Ph7	7.51	7.51	7.52
o-Ph8	7.84	7.92	7.98
o-Ph8′	8.23	8.26	8.34
Me9(ax)	2.56	2.58	2.49
Me9(eq)	2.63	2.69	2.76
H10	4.44	4.46	4.46
Me10	1.96	2.00	1.99
H13	6.83	6.83	7.02
H17	7.74	7.73	7.74
P7	116.9	124.9	112.3
P8	52.7	50.7	43.7

(11) See ref 2 for a preliminary account of the synthetic work involving (S_p)-**1a**. In this preliminary report, we used acetonitrile as the solvent in the chloro displacement procedure. We have subsequently observed that the Diels−Alder reaction can be completed much faster if coordinating solvents are not involved.

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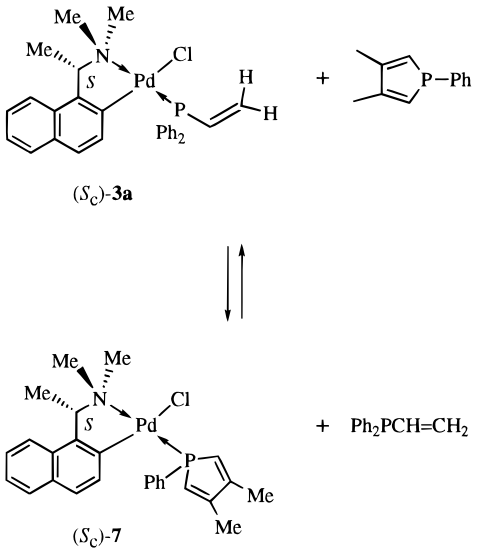
Scheme 2



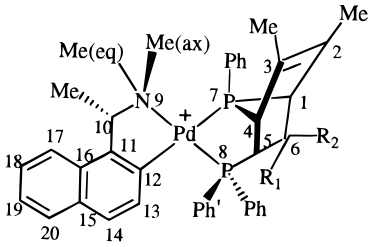


Figure 1. Numbering scheme used for complexes (S_c,R_p)-**5a**−**c** in the ROESY NMR studies.

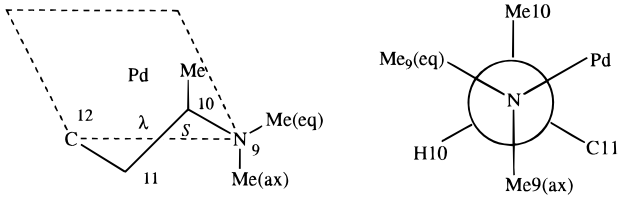


Figure 2. Absolute conformation of the PdCN ring and the staggered orientation of its N9 and C10 substituents.

of selectively ^{31}P-decoupled proton spectra and proton COSY, HMQC, and ROESY experiments.

Interestingly, the cycloadditions proceeded smoothly in noncoordinating solvents such as dichloromethane and chloroform. However, when a trace amount of acetonitrile or other coordinating solvent was added, these palladium promoted reactions were slowed down significantly.[2] Similarily, the abstraction of the chloro ligands from (S_c)-**3** prior to the addition of DMPP is an important prerequisite for the Diels−Alder coupling reaction. For example, in a separate experiment, the chloro complex (S_c)-**3a** was treated directly with the cyclic diene in dichloromethane at room temperature. After 12 h, the corresponding ^{31}P NMR spectrum exhibited four sharp singlet resonances of ca. equal intensities corresponding to the starting materials (S_c)-**3a** (δ 32.9) and free DMPP (δ −2.1), together with two newly generated species being identified as the DMPP complex (S_c)-**7** (δ 36.2)[7] and the uncoordinated diphenylvinylphosphine ligand (δ −11.4). No other phosphorus resonances could be detected. Thus, under these experimental conditions, the treatment of (S_c)-**3a** with DMPP did not produce the desired cycloaddition product but rather formed an equilibrium mixture in solution as a consequence of the ligand redistribution process as illustrated in Scheme 2. A similar regiospecific ligand redistribution process involving monodentate phosphines and this particular organopalladium unit has been utilized recently by Dunina and co-workers for the kinetic resolution of chiral tertiary phosphines.[16]

Absolute Stereochemistry Assignment. ROESY NMR Studies of (R_p)-5a−c. Although complexes (S_c,R_p)-**5a**−**c** are chemically stable and are readily dissolved and recrystallized from most organic solvent systems, these crystals generally suffer from problems of rapid desolvation and numerous capillaries are found within the lattices. Consequently, these opaque crystals are not suitable for single-crystal X-ray structural investigations.

Recently, we have established that the 2-D rotating frame nuclear Overhauser enhancement (ROESY) NMR spectra of **5a** can be used for the unambiguous absolute stereochemistry assignment of coordinated **1a**.[3] Figure 1 shows the numbering scheme used in this series of spectroscopic studies for the Diels−Alder complexes. In this documented approach, the unique and predictable absolute chirality of the chiral organopalladium−naphthylamine unit is used as the internal stereochemical reference.[3,17] Due to an extremely unfavorable intra-chelate interaction between Me10 of the organopalladium ring and the naphthylene proton H17, this carbon−methyl group of the (*S*)-naphthylamine auxiliary invariably adopts an axial disposition in the rigid five-membered chelate ring of λ absolute conformation (Figure 2). Consequently, the prochiral N−Me groups are locked into noninterconvertable axial and equatorial positions. In addition, the aromatic proton H13 protrudes invariably toward the space somewhat below P8. On the basis of the inter-chelate NOE contacts between these stereochemically well-defined NMR probes in the naphthylamine auxiliary and the diphosphine in **5a**, it was deduced that when (*S*)-naphthylamine was used as the chiral auxiliary, the absolute chirality of the coordinated bridge-head phosphorus stereogenic center produced in **5a** is *R*, and, in separate experiments, its enantiomeric form was produced in a similar manner when (*R*)-naphthylamine was employed.[2,3]

Figures 3 and 4 show the ROESY NMR spectra of the new methyl-substituted analogues (S_c,R_p)-**5b** and (S_c,R_p)-**5c**. In both spectra, the characteristic NOE patterns within the five-membered (*S*)-metalated naphthylamine ring are clearly recorded. For example, strong NOE signals (A−C) for the expected interactions between H10 and all the three methyl groups on N9 and C10 are observed. The driving forces for Me10 to assume the axial position, i.e. H10−H17 (D) and Me10−H17 (E) repulsive interactions, are prominently reflected in the spectra. In agreement with the exclusive adoption of the λ conformation by the (*S*)-naphthylamine ring, Me10 interacts strongly (F) with NMe(eq) but not with NMe(ax). The regio-stereochemistries in both complexes are established by the NOE contacts between H13 with Ph8 and Ph8′ (signals G and H).[4] It is important to note that these prochiral phenyl rings at P8 are locked into stereochemically distinct axial and equatorial positions by the rigid five membered P7-C4-C5-P8 chelate ring.

The inter-chelate NOE signals allow the assignment of the absolute stereochemistry in both (S_c,R_p)-**5b** and (S_c,R_p)-**5c**. Figure 5 illustrates the expected intra- as well as inter-chelate NOE interactions between the (*S*)-naphthylamine auxiliary and the two possible enantiomeric forms of the chelating diphosphine.[3] An analysis of the ROESY spectrum for (S_c,R_p)-**5b** (Figure 3) revealed that H5 only interacts strongly with Me6

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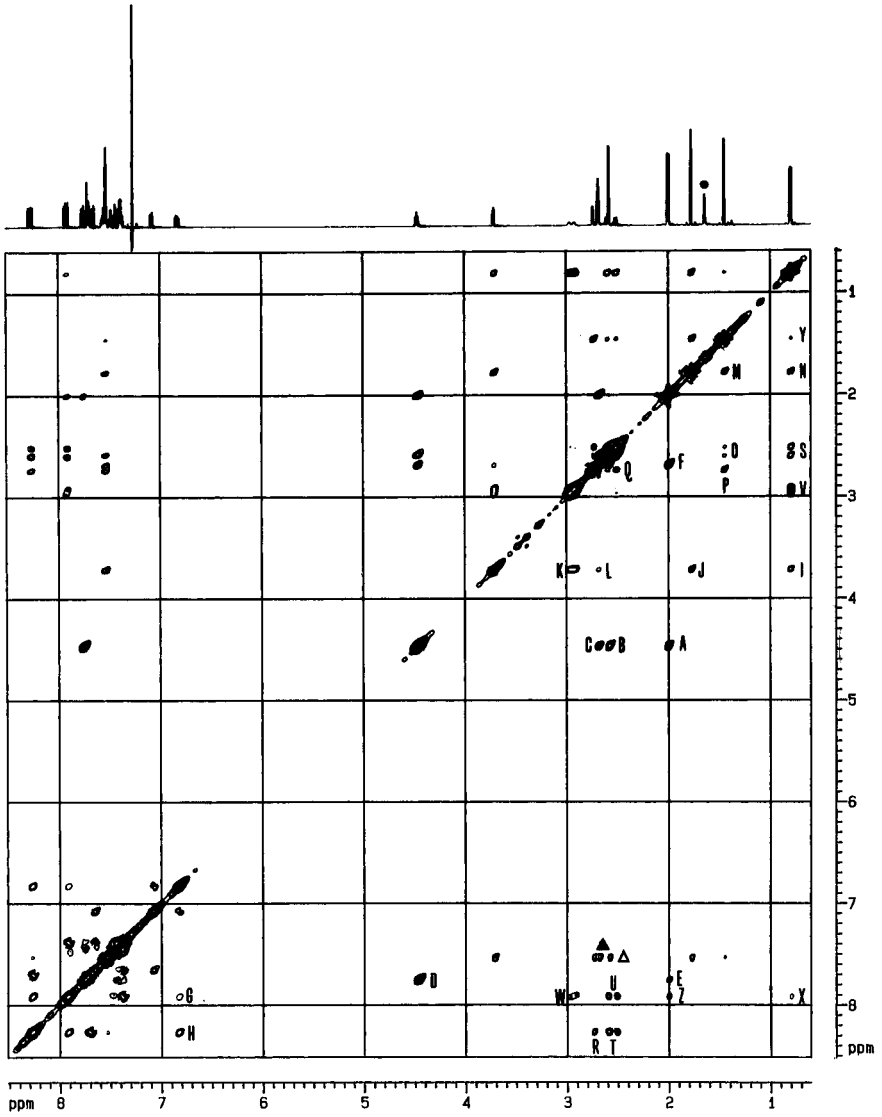

Figure 3. 2D ^{1}H ROESY NMR spectrum of (S_c,R_p)-**5b** in $CDCl_3$. All off-diagonal peaks are of negative intensity. Selected NOE contacts: A, H10−Me10; B, H10−NMe(ax); C, H10−NMe(eq); D, H10−H17; E, Me10−H17; F, Me10−NMe(eq); G, *o*-Ph8−H13; H, *o*-Ph8′−H13; I, H1−Me6; J, H1−Me2; K, H1−H6(exo); L, H1−NMe(eq); M, Me2−Me3; N, Me2−Me6; O, Me3−H5, P, Me3−H4; Q, H4−H5; R, H4−*o*-Ph8′; S, H5−Me6; T, H5−*o*-Ph8′; U, H5−*o*-Ph8; V, H6(exo)−Me6; W, H6(exo)−*o*-Ph8; X, Me6−*o*-Ph8; Y, Me3−Me6; Z, Me10−*o*-Ph8; Δ, Ph7−NMe-(ax); ▲, Ph7−NMe(eq); ●, H_2O signal.

(signal S) but not with H6. This observation is consistent with the *endo*-occupancy of Me6 and its *E*-geometrical relationship with the PPh_2 group. On the other hand, the NOE signals recorded in the same spectrum for the H1−NMe(eq) (L) and Me10−*o*-Ph8 (Z) suggested that these protons are on the same side above the square-plane. These NOE patterns, together with the closeness observed between Ph7 and NMe(ax) (signal Δ), are consistent with the structure illustrated in Figure 5a. Hence, the absolute configuration at P7 in (S_c,R_p)-**5b** is *R*.

Similar to the *E*-methyl substituted analogue, the ROESY spectrum of (S_c,R_p)-**5c** (Figure 4) showed all the expected NOE signals for the intrachelate within the organometallic and the diphosphine ring. For instance, while the strong contact between H5 and H6 is clearly recorded (S), no interaction is detected between H5 and Me6. Hence, the *exo*-occupancy of Me6 can be established. In contrast to Me6(endo) in (S_c,R_p)-**5b**, Me6-(exo) in (S_c,R_p)-**5c** is projecting somewhat toward the (*S*)-naphthylamine auxiliary and therefore gives rise to several significant long-range NOE patterns such as Me6−Me10 (W), Me6−NMe(eq) (X), and Me6−*o*-Ph8 (Y). These signals, together with the Me10−*o*-Ph8 (Z) contact, are in agreement with the structure illustrated in Figure 5a. This stereochemical assignment is further supported by the H4−*o*-Ph8′ (T), Ph7−NMe(ax) (Δ), and long-range *o*-Ph8′−NMe(ax) (n) contact patterns which indicate that all these groups are on the same side below the square-plane. This ROESY spectrum therefore confirms that the absolute configuration at the coordinated P7 stereogenic center is *R*.

The *endo* and *exo* dispositions observed in complexes (S_c,R_p)-**5b** and (S_c,R_p)-**5c**, respectively, are consistent with the facial mode of addition that takes place in the majority of Diels−Alder reactions.[18] In addition, the ROESY spectrum of (S_c,R_p)-**5c** clearly indicated that the *exo*-Me6 group of the diphosphine is projecting significantly toward the (*S*)-naphthylamine auxiliary. However, no comparable proximity can be detected between the relatively small *exo*-H6 proton and the organometallic ring in (S_c,R_p)-**5b**. The *endo*-Me6 group in the latter complex is indeed projecting away from the palladium coordination atmosphere. This difference in the steric properties between the two Diels−Alder complexes, in conjunction with the dramatic slow rate detected for the formation of (S_c,R_p)-**5c**,

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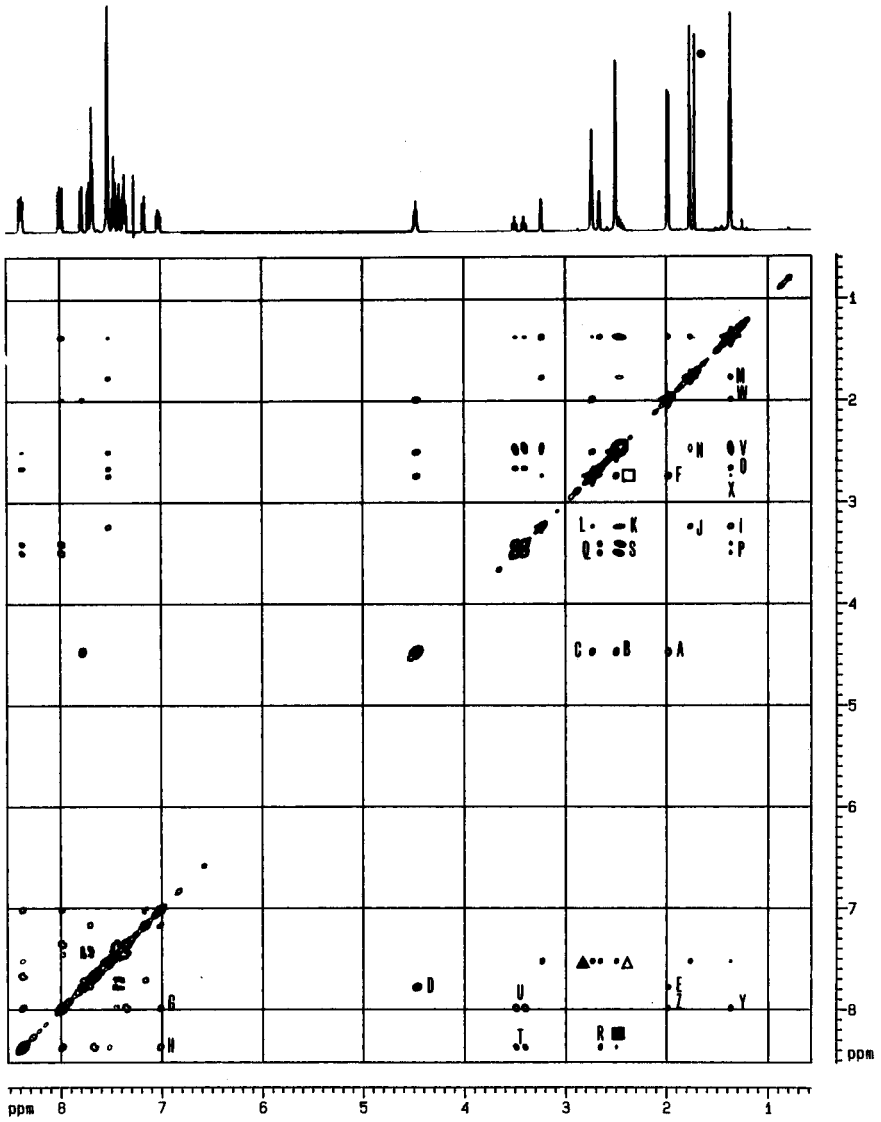

Figure 4. 2D ^{1}H ROESY NMR spectrum of (S_c,R_p)-**5c** in $CDCl_3$. All off-diagonal peaks are of negative intensity. Selected NOE contacts: A, H10−Me10; B, H10−NMe(ax); C, H10−NMe(eq); D, H10−H17; E, Me10−H17; F, Me10−NMe(eq); G, *o*-Ph8−H13; H, *o*-Ph8′−H13; I, H1−Me6; J, H1−Me2; K, H1−H6(endo); L, H1−NMe(eq); M, Me2−Me3; N, Me2−H6(endo); O, Me3−H4; P, Me3−H5; Q, H4−H5; R, H4−*o*-Ph8′; S, H5−H6(endo); T, H5−*o*-Ph8′; U, H5−*o*-Ph8; V, H6(endo)−Me6; W, Me6−Me10; X, Me6−NMe(eq); Y, Me6−*o*-Ph8; Z, Me10−*o*-Ph8; △, Ph7−NMe(ax); ▲, Ph7−NMe(eq); □, NMe(ax)−NMe(eq); ■, NMe(ax)−*o*-Ph8′; ●, H_2O signal.

is in agreement with the observation by Nelson and co-workers[12] that this type of palladium-promoted Diels−Alder reaction requires both the labile[16] monodentate cyclic diene and the monodentate dienophile to be coordinated to the metal simultaneously in the proper orientation during the course of cycloaddition reaction. Due to the steric repulsion between the chiral auxiliary and the *Z*-substituted methyl group in the vinyl phosphine precursor and, perhaps, the positioning of Me6(exo) proximal to the filled palladium nonbonding d-orbitals, the adoption of such transition state geometry would certainly be more difficult in the case of (S_c,R_p)-**5c**.

Removal of Chiral Auxiliary and Structure Analysis of (R_p)-6c. The chiral naphthylamine auxiliary in (S_c,R_p)-**5a**−**c** can be removed from the palladium templates chemoselectively by treatment with hydrochloric acid in acetone. The chiral auxiliary was recovered quantitatively from the mother liquor after treatment with base. On the other hand, the neutral dichloro complexes (S_p)-**6a**−**c** were obtained efficiently as stable pale yellow crystals in 89−92% isolated yields. Similar to (S_c,R_p)-**5a**−**c**, the ^{31}P NMR spectrum of each dichloro complex exhibited a pair of doublets for the two nonequivalent phosphorus nuclei with the resonances for the bridge-head phosphorus nuclei recorded at δ 124.9, 132.7, and 119.9, respectively, for complexes (R_p)-**6a**−**c**. The corresponding PPh_2 signals were observed at δ 35.2, 33.1, and 23.6, respectively. It is significant to note that the phosphorus−phosphorus coupling constants (4.3−7.5 Hz) recorded for all three dichloro complexes are markedly smaller than that observed for their naphthylamine analogues which uncannily show identical couplings at 41.5 Hz. It is well established that within a P−M−P′ chelate ring, the P−P coupling is divided into "through-the-backbone" and "through-the-metal" contributions.[19] In a five-membered system, these contributions are nearly equal but of opposite sign. In agreement, it has been recorded by Nelson co-workers that when the racemic form of **1a** was coordinated to palladium(II), the J_{PP} values are invariably small (0−7.3 Hz).[12,20] Thus, the relatively large P−P couplings observed in the Diels−Alder products (S_c,R_p)-**5a**−**c** must be the result of an unusually strong P−Pd−P′ electronic interaction within these complexes. Such

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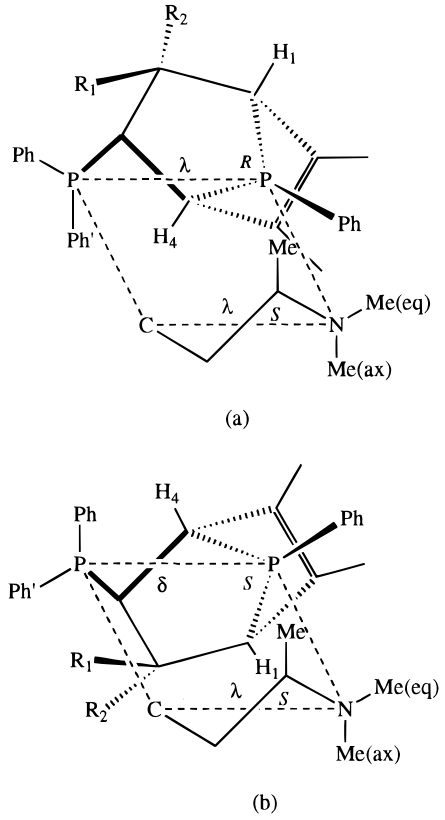


Figure 5. The two possible diastereomers of **5** containing the (*S*)-naphthylamine auxiliary.

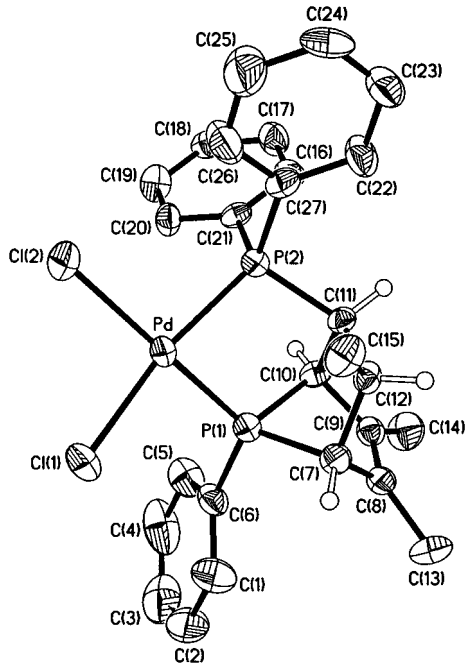


Figure 6. Molecular structure and absolute configuration of (R_p)-**6c**.

strong electronic interactions are clearly triggered by the organopalladium unit and, indeed, are probably the major electronic factors for the activation of these asymmetric [4+2] cycloaddition reactions.

The X-ray analysis of (R_p)-**6c** reafirms that, as desired, an enantiomerically pure complex has been formed (Figure 6). The analysis shows that the template-directed synthesis of the palladium diphosphine adduct has proceeded with the desired retention of chirality at the P(1), C(7), C(10), and C(11) centers (*R*, *R*, *R*, and *S*, respectively) and has also maintained a *syn*

Table 2. Selected Bond Lengths (Å) and Angles (deg) for (R_p)-**6c**

Pd−P(1)	2.223(4)	Pd−P(2)	2.264(3)
Pd−Cl(1)	2.360(4)	Pd−Cl(2)	2.364(4)
P(1)−C(6)	1.795(6)	P(1)−C(10)	1.845(10)
P(1)−C(7)	1.852(11)	P(2)−C(21)	1.812(5)
P(2)−C(27)	1.819(6)	P(2)−C(11)	1.852(9)
C(7)−C(8)	1.491(14)	C(7)−C(12)	1.575(13)
C(8)−C(9)	1.330(13)	C(8)−C(13)	1.508(14)
C(9)−C(10)	1.489(13)	C(9)−C(14)	1.500(14)
C(10)−C(11)	1.588(12)	C(11)−C(12)	1.590(13)
C(12)−C(15)	1.514(13)		
P(1)−Pd−P(2)	81.88(13)	P(1)−Pd−Cl(1)	90.09(14)
P(2)−Pd−Cl(1)	169.19(12)	P(1)−Pd−Cl(2)	172.1(2)
P(2)−Pd−Cl(2)	96.56(13)	Cl(1)−Pd−Cl(2)	92.37(14)
C(6)−P(1)−C(10)	108.9(4)	C(6)−P(1)−C(7)	111.1(4)
C(10)−P(1)−C(7)	80.7(4)	C(6)−P(1)−Pd	118.5(3)
C(10)−P(1)−Pd	112.4(3)	C(7)−P(1)−Pd	118.8(3)
C(21)−P(2)−C(27)	103.4(3)	C(21)−P(2)−C(11)	106.0(4)
C(27)−P(2)−C(11)	107.0(4)	C(21)−P(2)−Pd	112.5(2)
C(27)−P(2)−Pd	122.1(3)	C(11)−P(2)−Pd	104.8(3)
C(5)−C(6)−P(1)	117.4(4)	C(1)−C(6)−P(1)	122.6(4)
C(8)−C(7)−C(12)	108.3(7)	C(8)−C(7)−P(1)	100.6(7)
C(12)−C(7)−P(1)	100.3(6)	C(9)−C(8)−C(7)	110.3(9)
C(9)−C(8)−C(13)	130.1(10)	C(7)−C(8)−C(13)	119.5(9)
C(8)−C(9)−C(10)	111.4(8)	C(8)−C(9)−C(14)	127.0(10)
C(10)−C(9)−C(14)	121.6(9)	C(9)−C(10)−C(11)	112.9(8)
C(9)−C(10)−P(1)	101.5(6)	C(11)−C(10)−P(1)	94.8(6)
C(10)−C(11)−C(12)	104.1(7)	C(10)−C(11)−P(2)	104.3(6)
C(12)−C(11)−P(2)	113.0(6)	C(15)−C(12)−C(7)	114.2(8)
C(15)−C(12)−C(11)	117.4(8)	C(7)−C(12)−C(11)	104.5(7)
C(20)−C(21)−P(2)	120.1(3)	C(16)−C(21)−P(2)	119.9(3)
C(26)−C(27)−P(2)	119.9(4)	C(22)−C(27)−P(2)	120.0(4)

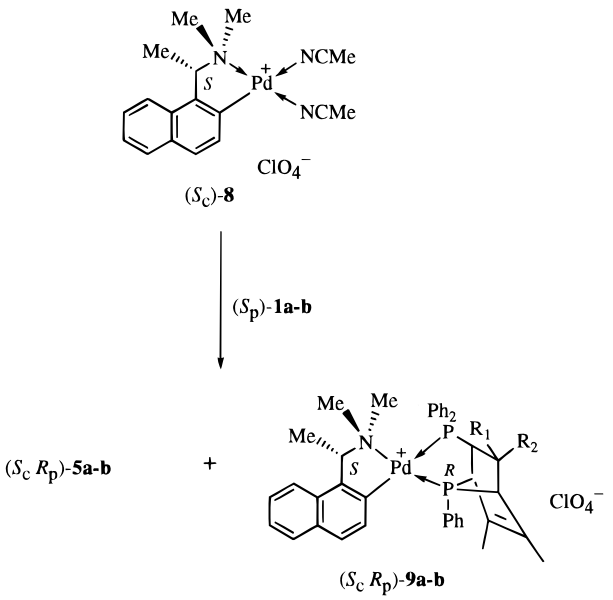
relationship between P(2) and the C(12) methyl substituent C(15), creating a new chiral center (*S*) at C(12). The geometry at palladium is distorted square planar (tetrahedral distortion with a twist angle of 10°) with angles at palladium in the ranges 81.9(1)−96.6(1) and 169.2(1)−172.1(2)°. The two Pd−Cl bonds are, within statistical significance, the same [2.360(4) and 2.364(4) Å], but the Pd−P bond lengths differ by 0.04 Å (Table 2), the longer being the Pd−P(2) bond, implying a possible steric effect due to the two phenyl rings. The C−P−C angle within the phosphorus−norbornene skeleton [80.7(4)°] is acute, the two associated P−C bonds being the same [1.85(1) Å for both C(7) and C(10)] and also the same as that observed for P(2)−C(11). The five-membered chelate ring has a typical folded geometry and has a λ conformation, with C(11) and C(10) lying 0.55 and 0.50 Å above and below the P−Pd−P plane, respectively.

The generation of the *S* stereochemistry at C(12), with retention of a *syn* geometry for C(12) and P(2), results in an axial positioning of the C(15) methyl group relative to the six-membered chelate ring. Hence, the slow rate of reaction for the Diels−Alder [4+2] cycloaddition for this isomer (*vide supra*) is possibly due to a combination of the sterically hindered relationship between this axial methyl group and the methyl group on the chiral center of the (*S*)-naphthylamine auxiliary (which lies on the same side of the palladium coordination plane) and the positioning of C(15) proximal to the filled palladium nonbonding d-orbitals (the closest Me−H···Pd approach being 2.76 Å).

There are no significant intermolecular interactions other than van der Waals.

Liberation and Optical Purities of (S_p)-1b,c. The liberation of (S_p)-**1a** has been reported in our first communication.[2] The optically active diphosphines (S_p)-**1b,c** could be liberated similarly from the corresponding dichloro species (S_c,R_p)-**5a−c** by the treatment of the complexes with aqueous potassium cyanide.[21] Thus, the diphosphines were obtained as highly air-sensitive colorless viscous oils in 90−95% yields with $[\alpha]_D$ of −62.5° (CH_2Cl_2), −14.4° (CH_2Cl_2), and −56.0° (CH_2Cl_2),

Scheme 3



respectively, for (S_p)-**1b,c**. Stereospecific displacement of the chiral diphosphines from palladium was confirmed by the quantitative repreparation of (S_c,R_p)-**5a**−**c** from the corresponding liberated diphosphine with (S_c)-**2**: The 202 MHz ^{31}P NMR spectra of the crude products indicated diastereomers (S_c,R_p)-**5a**−**c** only. In a further test of optical purity, the diastereomeric complexes (R_c,R_p)-**5a**−**c** were prepared from (S_p)-**1b,c** and the equally accessible (R_c)-**2**; only the signals due to the (R_c,R_p) diastereomers were observed. It should be reiterated that the (R_c,R_p)-**5a**−**c** diastereomers could not be produced directly from the respective asymmetric Diels−Alder reactions when (*R*)-naphthylamine was used as the chiral auxiliary and, instead, only (R_c,S_p)-**5a**−**c** were obtained in these enantiomeric reactions.

It is interesting to note that all the three optically pure diphosphines (S_p)-**1a**−**c** are capable of splitting the chlorine bridges in (S_c)-**2** in a regioselective manner to give only (S_c,R_p)-**5a**−**c**. However, while the coordination of (S_p)-**1c** to the analogous bis(acetonitrile) complex **8**[23] retains its regiospecificity, the complexation of the less sterically demanding diphosphines (S_p)-**1a** and (S_p)-**1b** to this cationic complex is nonselective. Hence, when these optically pure diphosphines were treated with (S_c)-**8**, mixtures containing *ca.* 1:1 of the two possible regio-isomers, i.e. (S_c,R_p)-**5** and (S_c,R_p)-**9**, were formed (Scheme 3). In $CDCl_3$, the ^{31}P NMR spectrum of each new regio-isomer exhibited a pair of doublets for the two nonequivalent phosphorus nuclei at δ 29.9 and 118.3 (J_{PP} = 41.5 Hz) for (S_c,R_p)-**9a** and δ 26.8 and 126.6 (J_{PP} = 41.5 Hz) for (S_c,R_p)-**9b**. The upfield shifts of the PPh_2 resonances (ca. 23−24 ppm) from (S_c,R_p)-**5** to (S_c,R_p)-**9** are in close agreement with the disposition of this moiety *cis* to the NMe_2 group in this particular family of organometallic units.[24] Similarly, the diastereomeric complexes (R_c,R_p)-**9a,b** were observed when the corresponding diphosphines were treated with (R_c)-**8**. (R_c,R_p)-**9a** exhibited the pair of ^{31}P NMR doublets at δ 34.8 and 119.8 (J_{PP} = 41.5 Hz), and (R_c,R_p)-**9b** exhibited these signals at δ 31.1 and 129.1 (J_{PP} = 41.5 Hz). Interestingly, NMR studies confirmed that complexes **5** are stable and do not rearrange into their regio counterparts **9** in solution over a peroid of 4 months. It should be noted, however, that when higher temperatures or coordinating solvents are used during the asymmetric cycloaddition process for the direct synthesis of (S_c,R_p)-**5a,b**, small quantities (3−10%) of the corresponding regio-isomers (S_c,R_p)-**9a,b** are observed in the crude products. Since the absolute stereochemistry of coordinated diphosphine ligands in these regio-isomers are identical, such conditions did not affect the optical purities of the resulting ligands. However, as all diastereomeric forms of **9** are highly soluble and could not be crystallized from any of the solvents tried, the formation of these materials under the stronger reaction conditions would practically lower the isolated yield of the desired Diels−Alder complexes.

Experimental Section

Reactions involving air-sensitive compounds were performed under a positive pressure of purified nitrogen. For NMR all samples were dissolved in *ca.* 0.6 mL of $CDCl_3$ in 5 mm o.d. NMR tubes and examined at 23 °C. Proton spectra were recorded at 500.14 MHz and ^{31}P spectra at 202.46 MHz on a Brucker AMX500 NMR spectrometer. The phase-sensitive ROESY experiments were acquired into a 1024 × 512 matrix with a 250 ms spin locking time and a spin lock field strength such that $\gamma B_1/2\pi$ = 5000 Hz and then transformed into 1024 × 1024 points using a sine bell weighting function in both dimensions. Optical rotations were measured on the specified solutions in a 1-dm cell at 25 °C with a Perkin-Elmer Model 341 polarimeter. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry at the National University of Singapore.

Both of the enantiomerically pure forms of bis(μ-chloro)bis[(*R*/*S*)-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C,N*]dipalladium(II) dichloromethane solvate,[25] **2**, the *E* and *Z* forms of diphenyl-1-propenylphosphine,[26] and the optically pure forms of complexes **3a**−**6a** were prepared as previously described.

[*SP*-4-4-(*S*)-Chloro[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C,N*][diphenyl-1-propenyl-(*E*)-phosphine-*P*]palladium(II) [(S_c)-3b]. A mixture of diphenyl-1-propenyl-(*E*)-phosphine (3.0 g) and (*S*)-**2** (5.0 g) in dichloromethane (300 mL) was stirred at room temperature until all the dimeric complex had dissolved (ca. 1 h). The solvent was removed from the reaction mixture, and the residue was recrystallized from dichloromethane−ethanol mixture, forming yellow prisms: Mp 196−198 °C; $[\alpha]_D$ +79.4° (*c* 1.0, $CHCl_3$); 6.0 g (79% yield). Anal. Calcd for $C_{29}H_{31}ClNPPd$: C, 61.5; H, 5.5; N, 2.5; Cl, 6.3; P, 5.5. Found: C, 61.5; H, 5.6; N, 2.5; Cl, 6.4; P, 5.7. ^{31}P NMR ($CDCl_3$): δ 31.5(s). ^{1}H NMR ($CDCl_3$): δ 1.89 (ddd, 3H, $^3J_{HH}$ = 6.5, $^4J_{HH}$ = $^4J_{PH}$ = 1.6 Hz, PC=C*Me*), 2.02 (d, 3H, $^3J_{HH}$ = 6.3 Hz, CH*Me*), 2.74 (d, 3H, $^4J_{PH}$ = 1.3 Hz, NMe), 2.96 (d, 3H, $^4J_{PH}$ = 3.4 Hz, NMe), 4.35 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.3 Hz, C*H*Me), 6.00 (ddq, 1H, $^3J_{PH}$ = 17.3, $^3J_{HH}$ = 16.4, $^3J_{HH}$ = 6.5 Hz, PC=C*H*), 6.60 (ddd, 1H, $^2J_{PH}$ = $^3J_{HH}$ = 16.4, $^4J_{HH}$ = 1.6 Hz, PC*H*), 6.62−8.00 (m, 16H, aromatics).

[*SP*-4-4-(*S*)-Chloro[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C,N*][diphenyl-1-propenyl-(*Z*)-phosphine-*P*]palladium(II) [(S_c)-3c]. The complex was prepared similarly from diphenyl-1-propenyl-(*Z*)-phosphine (0.9 g) and (*S*)-**2** (1.5 g). The crude product was recrystallized from dichloromethane−diethyl ether, forming yellow prisms: Mp 193−195 °C; $[\alpha]_D$ +66.5° (*c* 0.8, $CHCl_3$); 1.5 g (67% yield). Anal. Calcd for $C_{29}H_{31}ClNPPd$: C, 61.5; H, 5.5; N, 2.5; Cl, 6.3; P, 5.5. Found: C, 61.5; H, 5.6; N, 2.6; Cl, 6.5; P, 5.6. ^{31}P NMR ($CDCl_3$): δ 16.3(s). ^{1}H NMR ($CDCl_3$): δ 2.00 (d, 3H, $^3J_{HH}$ = 6.4 Hz, CH*Me*), 2.28 (ddd, 3H, $^3J_{HH}$ = 7.1, $^4J_{PH}$ = 2.5, $^4J_{HH}$ = 1.6 Hz, PC=C*Me*), 2.75 (d, 3H, $^4J_{PH}$ = 1.4 Hz, NMe), 2.95 (d, 3H, $^4J_{PH}$ = 3.2 Hz, NMe), 4.35 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.4 Hz, C*H*Me), 6.42 (ddq, 1H, $^3J_{HH}$ = 12.2, $^2J_{PH}$ = 9.2, $^4J_{HH}$ = 1.6 Hz, PC*H*), 6.74 (ddq, 1H, $^3J_{PH}$ = 35.8, $^3J_{HH}$ = 12.2, $^3J_{HH}$ = 7.1 Hz PC=C*H*), 6.80−7.80 (m, 16H, aromatics).

(21) The apparent inversion of configuration of the bridge-head phosphorus that takes place when the diphosphine is liberated from the metal is consistent with the specification of Cahn−Ingold−Prelog (CIP) sequence rules.[22]

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{(*S*)-1-[1-(Dimethylamino)ethyl]naphthyl-*C*^{2},*N*}{(1α,4α,5α(*S*),6*β*-(*R*),7*R*)-[5-(diphenylphosphino)-2,3,6-trimethy-7-phenyl-7-phosphabicyclo[2.2.1]hept-2-ene-*P*^{5},*P*^{7}}palladium(II) Perchlorate, [(*S*$_c$,*R*$_p$)-5b]. A solution of (*S*$_c$)-**3b** (4.0 g) in dichloromethane (150 mL) was subjected to chloride abstraction using silver perchlorate (1.46 g) in water (5 mL). The colorless organic layer, after the removal of AgCl and dried ($MgSO_4$), was treated with DMPP (1.33 g) at room temperature. The reaction was monitored by ^{31}P NMR spectroscopy and was found to be complete in 3 h. Removal of the solvent gave (*S*$_c$,*R*$_p$)-**5b** as a white residue which was then crystallized from chloroform−diethyl ether to give the complex as white needles: Mp 188−189 °C; $[\alpha]_D$ +40.0° (*c* 1.0, $CHCl_3$); 3.5 g (61% yield). Anal. Calcd for $C_{41}H_{44}ClNO_4P_2Pd\cdot0.5H_2O$: C, 59.5; H, 5.5; N, 1.7; Cl, 4.3; P, 7.5. Found: C, 59.6; H, 5.3; N, 1.6; Cl, 4.6; P, 7.6. ^{31}P NMR ($CDCl_3$): δ 50.7 (d, J_{PP} = 41.5 Hz, P_5), 124.9 (d, J_{PP} = 41.5 Hz, P_7). ^{1}H NMR ($CDCl_3$): δ 0.80 (d, 3H, $^3J_{HH}$ = 6.8 Hz, PCC*Me*), 1.45 (s, 3H, C=C*Me*), 1.78 (s, 3H, C=C*Me*), 2.00 (d, 3H, $^3J_{HH}$ = 6.2 Hz, CH*Me*), 2.54 (dddd, 1H, $^3J_{PH}$ = 42.5, $^2J_{PH}$ = 8.3, $^3J_{HH}$ = $^3J_{HH'}$ = 1.8 Hz, H_5), 2.58 (d, 3H, $^4J_{PH}$ = 1.3 Hz, NMe), 2.69 (dd, 3H, $^4J_{PH}$ = $^4J_{P'H}$ = 3.4 Hz, NMe), 2.73 (d, 1H, $^3J_{HH}$ = 1.8 Hz, H_4), 2.95 (dqdd, 1H, $^3J_{PH}$ = 24.7, $^3J_{HH}$ = 6.8, $^3J_{H'H}$ = $^3J_{HH''}$ = 1.8 Hz, H_6), 3.74 (d, 1H, $^3J_{HH}$ = 1.8 Hz, H_1), 4.46 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.2 Hz, C*H*Me), 6.80−8.33 (m, 21H, aromatics).

{(*S*)-1-[1-(Dimethylamino)ethyl]naphthyl-*C*^{2},*N*}{(1α,4α,5α(*S*),6α-(*S*),7*R*)-[5-(diphenylphosphino)-2,3,6-trimethy-7-phenyl-7-phosphabicyclo[2.2.1]hept-2-ene-*P*^{5},*P*^{7}}palladium(II) Perchlorate, [(*S*$_c$,*R*$_p$)-5c]. The cycloaddition reaction was performed similarly from (*S*$_c$)-**3c** (1.0 g) and DMPP (0.33 g). The crude product was recrystallized from dichloromethane−diethyl ether, forming white needles: Mp 213−214 °C; $[\alpha]_D$ +60.7° (*c* 1.0, $CHCl_3$); 1.1 g (76% yield). Anal. Calcd for $C_{41}H_{44}ClNO_4P_2Pd$: C, 60.1; H, 5.4; N, 1.7; Cl, 4.3; P, 7.6. Found: C, 59.8; H, 5.4; N, 1.7; Cl, 4.4; P, 7.3. ^{31}P NMR ($CDCl_3$): δ 43.7 (d, J_{PP} = 41.5 Hz, P_5), 112.3 (d, J_{PP} = 41.5 Hz, P_7). ^{1}H NMR ($CDCl_3$): δ 1.37 (s, 3H, C=C*Me*), 1.38 (d, 3H, $^3J_{HH}$ = 6.3 Hz, PCC*Me*), 1.78 (s, 3H, C=C*Me*), 1.99 (d, 3H, $^3J_{HH}$ = 6.3 Hz, CH*Me*), 2.47 (m, 1H, H_6), 2.49 (d, 3H, $^4J_{PH}$ = 1.7 Hz, NMe), 2.66 (s, 1H, H_4), 2.76 (dd, 3H, $^4J_{PH}$ = $^4J_{P'H}$ = 3.6 Hz, NMe), 3.32 (d, 1H, $^3J_{HH}$ = 2.1 Hz, H_1), 3.40 (dddd, 1H, $^3J_{PH}$ = 45.4, $^2J_{PH}$ = $^3J_{HH}$ = 8.4, $^3J_{HH'}$ = 2.1 Hz, H_5), 4.46 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.3 Hz, C*H*Me), 7.00−8.40 (m, 21H, aromatics).

[*SP*-4−2-[(1α,4α,5α(*S*),6*β*(*R*),7*R*]]-Dichloro[5-(diphenylphosphino)-2,3,6-trimethy-7-phenyl-7-phosphabicyclo[2.2.1]hept-2-ene-*P*^{5},*P*^{7}]-palladium(II) [(*R*$_p$)-6b]. The Diels−Alder template complex (*S*$_c$,*R*$_p$)-**5b** (2.0 g) was dissolved in acetone (100 mL), and the elution was treated with hydrochloric acid (10 M, 3 mL). The reaction mixture was then refluxed for 15 min. Bright yellow microcrystals of (*R*$_p$)-**6b** precipitated out during this period. The product was then filtered and recrystallized from dichloromethane−diethyl ether: Mp > 280 °C; $[\alpha]_D$ +40.4° (*c* 1.0, CH_2Cl_2); 1.3 g (89% yield). Anal. Calcd for $C_{27}H_{28}Cl_2P_2Pd\cdot0.5H_2O$: C, 53.9; H, 4.8; Cl, 11.8; P, 10.3. Found: C, 53.9; H, 4.8; Cl, 11.8; P, 10.4. ^{31}P NMR ($CDCl_3$): δ 33.1 (d, J_{PP} = 4.3 Hz, P_5), 132.7 (d, J_{PP} = 4.3 Hz, P_7). ^{1}H NMR ($CDCl_3$): δ 0.75 (d, 3H, $^3J_{HH}$ = 6.8 Hz, PCC*Me*), 1.56 (s, 3H, C=C*Me*), 1.63 (s, 3H, C=C*Me*), 2.44 (dddd, 1H, $^3J_{PH}$ = 49.7, $^2J_{PH}$ = 7.0, $^3J_{HH}$ = $^3J_{HH'}$ = 1.8 Hz, H_5), 2.97 (dqdd, 1H, $^3J_{PH}$ = 23.9, $^3J_{HH}$ = 6.8, $^3J_{H'H}$ = $^3J_{HH''}$ = 1.8 Hz, H_6), 3.11 (dd, 1H, $^2J_{PH}$ = $^3J_{HH}$ = 1.8 Hz, H_1), 3.32 (dd, 1H, $^2J_{PH}$ = $^3J_{HH}$ = 1.8 Hz, H_4), 7.40−8.20 (m, 15H, aromatics).

[*SP*-4−2-[(1α,4α,5α(*S*),6α(*S*),7*R*]]-Dichloro[5-(diphenylphosphino)-2,3,6-trimethy-7-phenyl-7-phosphabicyclo[2.2.1]hept-2-ene-*P*^{5},*P*^{7}]-palladium(II) [(*R*$_p$)-6c]. The chiral auxiliary was removed similarly from (*S*$_c$,*R*$_p$)-**5c** (0.5 g) using HCl. The crude product was recrystallized from dichloromethane−diethyl ether: Mp > 280 °C; $[\alpha]_D$ −43.6° (*c* 0.5, CH_2Cl_2); 0.33 g (91% yield). Anal. Calcd for $C_{27}H_{28}Cl_2P_2Pd\cdot0.5H_2O$: C, 53.9; H, 4.8; Cl, 11.8; P, 10.3. Found: C, 53.7; H, 4.5; Cl, 11.8; P, 9.8. ^{31}P NMR (CD_2Cl_2): δ 23.6 (d, J_{PP} = 7.5 Hz, P_5), 119.9 (d, J_{PP} = 7.5 Hz, P_7). ^{1}H NMR (CD_2Cl_2): δ 1.46 (s, 3H, C=C*Me*), 1.56 (d, 3H, $^3J_{HH}$ = 7.5 Hz, PCC*Me*), 1.69 (s, 3H, C=C*Me*), 2.49 (dqdd, 1H, $^3J_{PH}$ = $^3J_{P'H}$ = 17.2, $^3J_{HH}$ = 8.6, $^3J_{H'H}$ = 7.5 Hz, H_6), 2.90 (s, 1H, H_1), 3.00 (s, 1H, H_4), 3.28 (ddd, 1H, $^3J_{PH}$ = 51.7, $^2J_{PH}$ = $^3J_{HH}$ = 8.6 Hz, H_5), 7.40−8.50 (m, 15H, aromatics).

(1α,4α,5α(*S*),6*β*(*R*),7*S*)-[5-(Diphenylphosphino)-2,3,6-trimethy-7-phenyl-7-phosphabicyclo[2.2.1]hept-2-ene] [(*S*$_p$)-1b]. A solution of (*R*$_p$)-**6b** (0.18 g) in dichloromethane was stirred vigorously with a saturated aqueous solution of potassium cyanide (1 g) for 30 min. The resulting colorless organic layer was separated, washed with water, and then dried ($MgSO_4$). Upon the removal of solvent, a highly air-sensitive low-melting solid was obtained: $[\alpha]_D$ −14.4° (*c* 0.5, CH_2Cl_2); 0.12 g (95% yield). ^{31}P NMR ($CDCl_3$): δ 24.2 (d, J_{PP} = 21.3 Hz, P_5), 130.0 (d, J_{PP} = 21.3 Hz, P_7). Due to its stereodynamic instability, the free ligand was not isolated and was immediately used for recomplexation reactions.[15]

(1α,4α,5α(*S*),6α(*S*),7*S*)-[5-(diphenylphosphino)-2,3,6-trimethy-7-phenyl-7-phosphabicyclo[2.2.1]hept-2-ene] [(*S*$_p$)-1c]. The free diphosphine ligand was liberated similarily from (*R*$_p$)-**6c** (0.20 g) by treatment with aqueous potassium cyanide: $[\alpha]_D$ −56.0° (*c* 0.5, CH_2Cl_2); 0.12 g (95% yield). ^{31}P NMR ($CDCl_3$): δ 23.3 (d, J_{PP} = 26.8 Hz, P_5), 110.8 (d, J_{PP} = 26.8 Hz, P_7). As in the case of (*S*$_p$)-**1b**, the free ligand was not purified further and was immediately used for recomplexation reactions.

{(*R*)-1-[1-(dimethylamino)ethyl]naphthyl-*C*^{2},*N*}{(1α,4α,5α(*S*),6*β*-(*R*),7*R*)-[5-(diphenylphosphino)-2,3,6-trimethy-7-phenyl-7-phosphabicyclo[2.2.1]hept-2-ene-*P*^{5},*P*^{7}}palladium(II) Chloride/Perchlorate [(*R*$_c$,*R*$_p$)-5b]. A fresh sample of (*S*$_p$)-**1b** (0.1 g) in dichloromethane (20 mL) was stirred with a solution of (*R*$_c$)-**2** (0.12 g) in dichloromethane (20 mL). After 15 min the solvent was removed to give the corresponding chloride salt as a white solid. The ^{31}P NMR spectrum of this material in $CDCl_3$ exhibited a pair of doublets at δ 48.1 (d, J_{PP} = 41.5 Hz, P_5), 127.9 (d, J_{PP} = 41.5 Hz, P_7). The crude product was crystallized from chloroform−diethyl ether to give the chloride salt as pale yellow prisms: Mp 172−175 °C; $[\alpha]_D$ +11.4° (*c* 0.2, $CHCl_3$); 0.15 g (75% yield). Anal. Calcd for $C_{41}H_{44}ClNP_2Pd$: C, 65.2; H, 5.9; N, 1.9; Cl, 4.7; P, 8.2. Found: C, 65.6; H, 5.5; N, 1.6; Cl, 4.6; P, 8.6. ^{31}P NMR ($CDCl_3$): δ 48.1 (d, J_{PP} = 41.5 Hz, P_5), 127.9 (d, J_{PP} = 41.5 Hz, P_7). ^{1}H NMR ($CDCl_3$): δ 0.70 (d, 3H, $^3J_{HH}$ = 6.8 Hz, PCC*Me*), 1.44 (s, 3H, C=C*Me*), 1.68 (d, 3H, $^3J_{HH}$ = 6.2 Hz, CH*Me*), 1.72 (s, 3H, C=C*Me*), 2.41 (dd, 1H, $^3J_{PH}$ = 41.2, $^2J_{PH}$ = 8.3, H_5), 2.57 (dd, 3H, $^4J_{PH}$ = $^4J_{P'H}$ = 3.7 Hz, NMe), 2.66 (s, 1H, H_4), 3.25 (s, 3H, NMe), 3.27 (m, 1, H_6), 4.38 (d, 1H, $^3J_{HH}$ = 1.8 Hz, H_1), 4.40 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.2 Hz, C*H*Me), 6.80−8.25 (m, 21H, aromatics). The chloride salt was subsequently treated with silver perchlorate to give the corresponding perchlorate salt. The ^{31}P NMR spectrum of this material in $CDCl_3$ was identical to that recorded for the chloride.

{(*R*)-1-[1-(Dimethylamino)ethyl]naphthyl-*C*^{2},*N*}{(1α,4α,5α(*S*),6α-(*S*),7*R*)-[5-(diphenylphosphino)-2,3,6-trimethy-7-phenyl-7-phosphabicyclo[2.2.1]hept-2-ene-*P*^{5},*P*^{7}}palladium(II) Chloride/Perchlorate [(*R*$_c$,*R*$_p$)-5c]. The diastereomeric complex was initially prepared as its chloride salt from (*S*$_p$)-**1c** (0.5 g) and (*R*$_c$)-**2** (0.5 g). The ^{31}P NMR spectrum of the crude product in $CDCl_3$ exhibited a pair of doublets at δ 45.2 (d, J_{PP} = 41.5 Hz, P_5) and 113.5 (d, J_{PP} = 41.5 Hz, P_7). The chloride salt of (*R*$_c$,*R*$_p$)-**5c** was crystallized from chloroform−diethyl ether as pale yellow needles: Mp 168−169 °C; $[\alpha]_D$ +12.8° (*c* 0.5, $CHCl_3$); 0.8 g (84% yield). Anal. Calcd for $C_{41}H_{44}ClNP_2Pd$: C, 65.2; H, 5.9; N, 1.9; Cl, 4.7; P, 8.2. Found: C, 65.1; H, 5.7; N, 2.0; Cl, 4.6; P, 8.7. ^{31}P NMR ($CDCl_3$): δ 45.2 (d, J_{PP} = 41.5 Hz, P_5), 113.5 (d, J_{PP} = 41.5 Hz, P_7). ^{1}H NMR ($CDCl_3$): δ 1.38 (s, 3H, C=C*Me*), 1.48 (d, 3H, $^3J_{HH}$ = 7.3 Hz, PCC*Me*), 1.61 (d, 3H, $^3J_{HH}$ = 6.2 Hz, CH*Me*), 1.76 (s, 3H, C=C*Me*), 2.49 (dqdd, 1H, $^3J_{PH}$ = $^3J_{P'H}$ = 17.2, $^3J_{HH}$ = 8.6, $^3J_{H'H}$ = 7.3 Hz, H_6), 2.58 (dd, 3H, $^4J_{PH}$ = $^4J_{P'H}$ = 3.8 Hz, NMe), 2.65 (s, 1H, H_4), 3.32 (s, 3H, NMe), 3.91 (s, 1H, H_1), 3.47 (ddd, 1H, $^3J_{PH}$ = 44.8, $^2J_{PH}$ = $^3J_{HH}$ = 8.6 Hz, H_5), 4.50 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.2 Hz, C*H*Me), 7.00−8.30 (m, 21H, aromatics). The corresponding perchlorate salt obtained subsequently by the treatment with silver perchlorate gave NMR signals identical to those of the chloride salt.

Crystal Structure Determination of (*R*$_p$)-6c. Crystal data for (*R*$_p$)-**6c** and a summary of the crystallographic analysis are given in Table 3. A total of 1794 unique reflections were measured ($2\theta \leq 45°$) on a Siemens P4 diffractometer using ω-scans, of which 1697 had $|F_o| > 4\sigma(|F_o|)$ and were considered to be observed. The data were corrected for Lorentz and polarization factors but not for absorption. The structure was solved by direct methods, and all the non-hydrogen atoms were refined anisotropically with the phenyl rings being treated as idealized rigid bodies. The hydrogen atoms of the methyl groups attached to sp^2 centers were located from a ΔF map and subsequently optimized. The remaining hydrogen atoms were placed in calculated positions. All of the H-atoms were assigned isotropic thermal

Table 3. Crystallographic Data for Complex (R_p)-**6c**

formula	$C_{27}H_{28}Cl_2P_2Pd$
fw	591.7
space group	*P*1
a/Å	8.643(3)
b/Å	9.044(6)
c/Å	9.058(4)
α/deg	102.75(4)
β/deg	108.59(2)
γ/deg	97.82(3)
V/Å^3	638.0(5)
Z	1
T/K	293
ρ_{calcd}/g cm^{-3}	1.540
λ/Å	0.71073 (Mo)
μ/cm^{-1}	10.8
R_1 (obsd data)[a]	0.0355
wR_2 (obsd data)[b]	0.0830

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

parameters, $U(H) = 1.2U_{eq}(C)$ [$U(H) = 1.5U_{eq}(C-Me)$], and allowed to ride on their parent carbon atoms. Refinements were by full-matrix least squares based on F^2. The absolute stereochemistry was determined by both an *R*-factor test [$R^+ = 0.0364$, $R^- = 0.0378$] and by use of the Flack parameter [$x^+ = -0.07(11)$, $x^- = +1.07(11)$].

Computations were carried out on a Pentium PC computer using the SHELXTL PC program system.[27] Additional material available from the Cambridge Crystallographic Data Centre comprises H atom coordinates, thermal parameters, and remaining bond lengths and angles.

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Supporting Information Available: For (R_p)-**6c** tables of crystal data and data collection, solution, and refinement parameters, final positional parameters, bond distances and angles, thermal parameters of non-hydrogen atoms, and calculated hydrogen parameters (5 pages). Ordering information is given on any current masthead page.

IC961479S

(27) SHELXTL PC version 5.03, Siemens Analytical X-Ray Instruments, Inc., Madison, WI, 1994.