Metal Template Effects on the Asymmetric Cycloaddition Reaction between Diphenylvinylphosphine and 2-Diphenylphosphinofuran

Wee-Chuan Yeo,[1a] Jagadese J. Vittal,[1a] Andrew J. P. White,[1b] David J. Williams,[1b] and Pak-Hing Leung*,[1a]

Department of Chemistry, National University of Singapore, Kent Ridge, Singapore 119260 and Department of Chemistry, Imperial College, London, UK SW7 2AY

Received December 13, 2000

The organoplatinum complex containing ortho-metalated (*S*)-(1-(dimethylamino)ethyl)-naphthalene as the chiral auxiliary has been used efficiently to promote the asymmetric [4 + 2] Diels−Alder reaction between diphenylvinylphosphine and 2-diphenylphosphinofuran to generate the chelating diphosphine *exo*-cycloadduct, 4(*R*),5(*R*)-bis(diphenylphosphino)-7-oxabicyclo[2.2.1]hept-2-ene in 70% isolated yield. At room temperature, the reaction was complete in 5 d. However, the cycloaddition reaction proceeded at a significantly slower rate and exhibited a markedly lower stereoselectivity when the chiral platinum template was replaced by its organopalladium counterpart. The diphosphino-substituted oxanorbornene metal complexes are stable and the oxygen−carbon bonds are inert toward treatments with strong acids. Upon liberation from the metal ions, however, the chiral cycloadduct becomes unstable and undergoes the retro Diels−Alder reaction slowly to regenerate diphenylvinylphosphine and 2-diphenylphosphinofuran.

Introduction

Over the past decade, chiral cyclopalladated-amine complexes have contributed significantly to many aspects of synthetic chemistry.[2] These organometallic compounds have been routinely used as resolving agents for chiral ligands,[3] clear and reliable references for the NMR assignment of unknown absolute configurations,[4] diamagnetic chiral shift reagents for the determination of optical purity of organic compounds,[5] efficient chiral catalysts for asymmetric Claisen rearrangements,[6] and reaction promoters for the oxidative coupling between vinylphosphines and imines.[7] Recently, we discovered that these palladium complexes can also be used as excellent chiral templates for the asymmetric Diels−Alder reaction between 3,4-dimethyl-1-phenylphosphole (DMPP) and a range of dienophiles, including styrene.[8] Thus a series of functionalized optically active 7-phospha-substituted norbornenes have been synthesized. Upon metal complexation, these new chiral phosphanorbornene ligands are not sensitive to air and are stereochemically stable. Upon liberation from metal ions, however, the stereogenic bridgehead-phosphorus centers are highly air-sensitive and undergo rapid inversion.

During our earlier studies in the asymmetric synthesis of phosphanorbornenes, we observed several dramatic changes in these cycloaddition reactions when different metal ions were used. For example, although DMPP can be activated efficiently as a cyclic diene in a series of asymmetric Diels−Alder reactions by coordinating the phosphole ligand onto the well-known orga-

(1) (a) National University of Singapore. (b) Imperial College.

(2) Hockless, D. C. R.; Gugger, P. A.; Leung, P. H.; Mayadunne, R. C.; Pabel, M.; Wild, S. B. *Tetrahedron* **1997**, *53*, 4083.

(3) For recent examples, see: Wild, S. B. *Coord. Chem. Rev.* **1997**, *166*, 291. Doucet, H.; Brown, J. M. *Tetrahedron: Asymmetry* **1997**, *8*, 3775. Albert, J.; Cadena, J. M.; Granell, J.; Muller, G.; Ordinas, J. I.; Panyella, D.; Puerta, C.; Sanudo, C,; Valerga, P. *Organometallics* **1999**, *18*, 3623. Pattinari, C.; Pellei, M.; Cavicchio, G.; Crucianelli, M.; Panzeri, W.; Colapietro, M.; Cassetta, A.; *Organometallics* **1999**, *18*, 555. Wu, Y. J.; Cui, X. L.; Du, C. X.; Wang, W. L.; Guo, R. Y.; Chen, R. F. *J. Chem. Soc., Dalton Trans.* **1998**, 3727. Bienewald, F.; Ricard, L.; Mercier, F.; Mathey, F. *Tetrahedron: Asymmetry* **1999**, *10*, 4701. He, G. S.; Mok, K. F.; Leung, P. H. *Organometallics* **1999**, *18*, 4027.

(4) Bookham, J. L.; McFarlane, W. *J. Chem. Soc., Chem. Commun.* **1993**, 1352. Aw, B. W.; Selvaratnam, S.; Leung, P. H.; Rees, N. H.; McFarlane, W. *Tetrahedron: Asymmetry* **1996**, *7*, 1753. Leung, P. H.; Selvaratnam, S.; Cheng, C. R.; Mok, K. F.; Rees, N. H.; McFarlane, W. *J. Chem. Soc., Chem. Commun.* **1997**, 751. W. Dunina, V. V.; Kuzmina, L. G.; Rubina, M. Y.; Grishin, Y. K.; Veits, Y. A.; Kazakova, E. I. *Tetrahedron: Asymmetry* **1999**, *10*, 1483.

(5) Chooi, S. Y. M.; Leung. P. H.; Lim, C. C.; Mok, K. F.; Quek, G. H.; Sim, K. Y.; Tan, M. K. *Tetrahedron: Asymmetry* **1992**, *3*, 529. Lopez, C.; Bosque, R.; Sainz, D.; Solans, X.; FontBardia, M. *Organometallics* **1997**, *16*, 3261. Uccello-Barretta, G.; Bernardini, R.; Lazzaroni, R.; Salvadori, P. *Org. Lett.* **2000**, *2*, 1795. Dunina, V. V.; Gorunova, O. N.; Livantsov, M. V.; Grishiu, Y. K. *Tetrahedron: Asymmetry* **2000**, *11*, 2907.

(6) Hollis, T. K.; Overman, L. E. *Tetrahedron Lett.* **1997**, *38*, 8837. Leung, P. H.; Ng, K. H.; Li, Y.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1999**, 2435.

(7) Liu, X.; Mok, K. F.; Vittal, J. J.; Leung, P. H. *Organometallics* **2000**, *19*, 3722.

(8) Aw, B. H.; Leung, P. H. *Tetrahedron: Asymmetry* **1994**, *5*, 1167. Aw, B. H.; Leung, P. H.; White, A. J. P.; Williams, D. J. *Organometallics* **1996**, *15*, 3640. Selvaratnam, S.; Mok, K. F.; Leung, P. H.; White, A. J. P.; Williams, D. J. *Inorg. Chem.* **1996**, *35*, 4798. Liu, A. M.; Mok, K. F.; Leung, P. H. *J. Chem. Soc., Chem. Commun.* **1997**, 2397. Leung, P. H.; Loh, S. K.; Vittal, J. J.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1997**, 1987. Leung, P. H.; Siah, S. Y.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1998**, 893. He, G. S.; Loh, S. K.; Vittal, J. J.; Mok, K. F.; Leung, P. H. *Organometallics* **1998**, *17*, 3931. Song, Y. C.; Vittal, J. J.; Chan, S. H.; Leung, P. H. *Organometallics* **1999**, *18*, 650. Leung, P. H.; Liu, A. M.; Mok, K. F. *Tetrahedron: Asymmetry* **1999**, *10*, 1309. Leung, P. H.; He, G.; Lang, H.; Liu, A.; Loh, S. K.; Selvaratnam, S.; Mok, K. F.; White, A. J. P.; Williams, D. J. *Tetrahedron* **2000**, *56*, 7. Leung, P. H.; Lang, H.; Zhang, X.; Selvaratnam, S.; Vittal, J. J. *Tetrahedron: Asymmetry* **2000**, *11*, 2661.

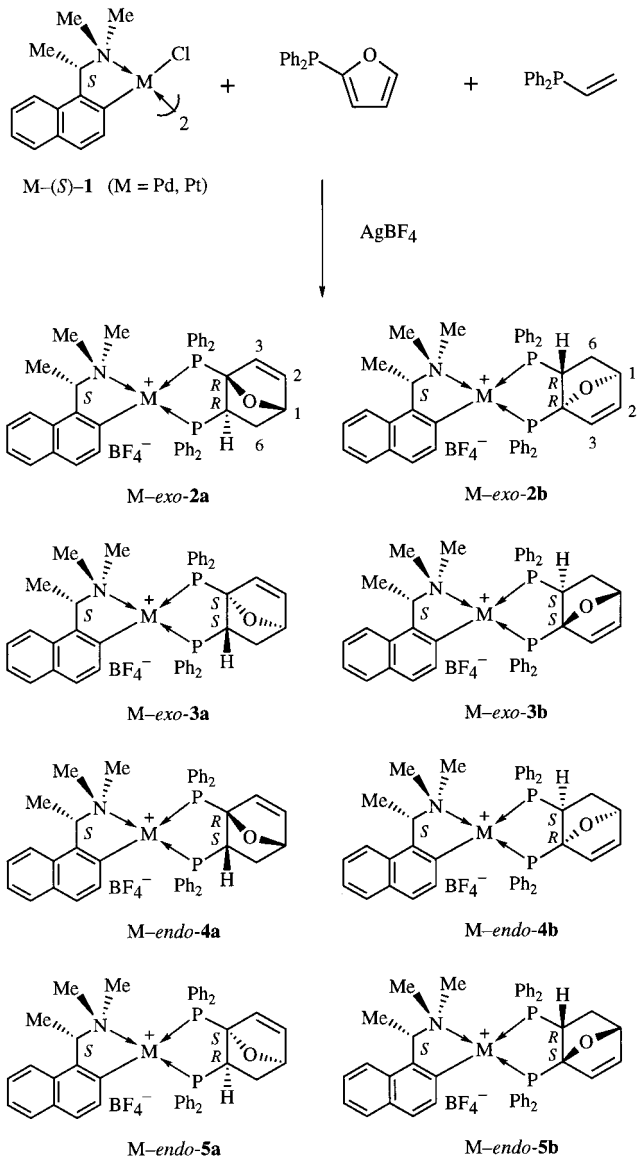
10.1021/om001063t CCC: $20.00
Publication on Web 04/26/2001

nopalladium(II) complex derived from *ortho*-metalated *N*,*N*-dimethyl-1-(1-naphthyl)ethylamine), the palladium template failed to promote the asymmetric [4 + 2] dimerization of DMPP.[9] On the other hand, when the analogous cycloplatinum complex was used, optically pure DMPP dimer was obtained efficiently.[9] In pursuing our interest in this class of metal template promoted reactions and to prepare a range of functionalized chiral diphosphines, we hereby report the chiral metal template promoted asymmetric Diels−Alder reaction between diphenylvinylphosphine and 2-diphenylphosphinofuran. Both the organopalladium and platinum complexes derived from (*S*)-*N*,*N*-dimethyl-1-(1-naphthyl)-ethylamine) were used in dint to further investigate the stereoelectronic effects of these two important chiral templates.

Results and Discussion

Stereochemical Considerations. In the absence of a metal template, no reaction was observed between 2-diphenylphosphinofuran and diphenylvinylphosphine, even under prolonged heating. The corresponding Diels−Alder reaction, however, could be induced efficiently in the presence of either Pd−(*S*)-**1** or Pt−(*S*)-**1** to produce the diphenylphosphino-substituted cycloadducts which coordinated as bidentate chelates onto the chiral template (Scheme 1). In principle, these square-planar diphosphine template complexes may exhibit diastereomerism from three different sources: (a) The relative regioarrangement of the four nonequivalent donor atoms on the plane. Due to the distinct electronic features of the ortho-metalated naphthylamine rings, monodentate phosphines perferentially coordinate to the position trans to the σ-donating nitrogen atom.[10] While the organometallic rings are kinetically stable, the monodentate P → M bonds are generally labile and facile ligand redistribution processes have been frequently observed, particularly when a mixture of nonequivalent phosphine ligands were involved.[11] The ligand redistribution processes usually occur much faster (within seconds) than the Diels−Alder reaction involving vinylphosphines as the dienophiles (ranged from several hours to several weeks).[8] Thus, regardless of the sequences of introducing the diphenylphosphino-substituted diene and the dienophile to the chiral template, regioisomers are still possible due to the faster precursor exchange process. (b) The adoption of both the *endo*- and the *exo*-cycloaddition reaction pathways will lead to the formation of the nonequivalent *endo*- and *exo* -cycloadducts. A simple steric consideration using Dreiding models suggested that both types of cycloadducts, once formed, are able to bind as bidentate diphosphine chelates on the chiral template. (c) The adoption of different absolute configurations of the three newly generated stereogenic centers within the rigid oxanorbornene skeleton. Thus up to eight stereochemically distinct template complexes may be generated in these chiral template promoted asymmetric cycloaddition reactions.

Scheme 1



Scheme 1 shows the molecular connectivities and the absolute stereochemistries of the eight possible isomers. The four pairs of isomers labeled **a** and **b**, are regioisomers in which the absolute stereochemistry of the coordinated diphosphine ligands are identical. In all the **a** isomers, the PPh_2 moieties attached to C-5 of the oxanorbornene skeletons occupy the positions trans to the NMe_2 groups. On the other hand, in the **b** isomers, the PPh_2 moieties on C-5 occupy the positions trans to the aromatic carbon atoms. Isomers **2** and **3** contain the *exo*-cycloadducts, but their diphosphine ligands are of opposite absolute configurations. For instances, in both isomers **2a** and **2b**, the absolute configurations at C1, C4 and C5 are *S*, *R*, and *R*, respectively. In isomers **3a** and **3b**, however, the absolute configurations at these three stereogenic centers are *R*, *S*, and *S*, respectively. Similarly, isomers **4** and **5** contain a pair of enantiomeric *endo*-substituted diphosphine cycloadducts. It is worth noting that, in this series of graphical illustrations, it is more convenient to view the *endo*-*exo* orientations by referring to the position of oxygen atom in the

(9) He, G.; Qin, Y.; Mok, K. F.; Leung, P. H. *J. Chem. Soc., Chem. Commun*. **2000**, 167.
(10) Chooi, S. Y. M.; Hor, T. S. A.; Leung. P. H.; Mok, K. F. *Inorg. Chem*. **1992**, *31*, 1494. Chooi, S. Y. M.; Tan, M. K.; Leung. P. H.; Mok, K. F. *Inorg. Chem*. **1994**, *33*, 3096.
(11) Dunina, V. V.; Golovan, E. B.; Gulyukina, N. S.; Buyevich, A. V. *Tetrahedron: Asymmetry* **1995**, *6*, 2731. Aw, B. H.; Hor, T. S. A.; Selvaratnam, S.; Mok, K. F.; White, A. J. P.; Williams, D. J.; Rees, N. H.; McFarlane, W.; Leung, P. H. *Inorg. Chem*. **1997**, *36*, 2138.

oxanorbornenes. In all *exo*-cycloadducts, the oxygen and the PPh_2 moiety on C-5 are located on the same side of the six-membered rings. In the *endo*-isomers, however, these two hetero-substituents are located on opposite sides of the rigid rings. These eight diastereomers are nonequivalent and, if isolated, each may show different physical properties such as chemical shifts and different polarization capacities. Hence these isomers should be readily identifiable by NMR spectroscopy.

Asymmetric Diels−Alder Synthesis. Recently, it has been highlighted several times in the literature that the dimeric complexes Pd−(*S*)-**1** and Pt−(*S*)-**1** themselves are not efficient chiral templates as the M−Cl bonds that are trans to the coordinated aromatic carbons are thermodynamically and kinetically stable.[11] These chloro ligands thus occupied one of the two essential coordination sites on the templates and hindered all coupling reactions. Upon removal of all chloro ligands with stoichoimetric quantities of silver salts, however, both Pd−(*S*)-**1** and Pt−(*S*)-**1** are excellent activators for the cycloaddition reaction between 2-diphenylphosphinofuran and diphenylvinylphosphine. Of the two chiral metal templates, Pt−(*S*)-**1** was found to produce significantly better product stereoselectivity. Stoichiometric amounts of Pt−(*S*)-**1**, diphenylvinylphosphine, and diphenylphosphinofuran in dichloromethane were treated with aqueous silver tetrafluoroborate at room temperature. The cycloaddition reaction was monitored by ^{31}P NMR spectroscopy and was found to be complete in 5 d. Before purification, the ^{31}P NMR spectrum of the reaction mixture in CD_2Cl_2 exhibited three pairs of doublets in the ratio of 1:2:10, thus indicating that three diastereomeric complexes had been formed. Of the three diastereomers produced, however, only the major diastereomer could be isolated by fractional crystallization. The stereoisomeric platinum complex was obtained as pale yellow prisms from dichloromethane-diethyl ether in 70% yield, $[\alpha]_{365}$ −380° (CH_2Cl_2). The ^{31}P NMR spectrum of this crystallized product in CD_2Cl_2 showed the two expected doublets at δ 42.8 ($J_{P-P'} = 7.6$ Hz, $J_{P-Pt} = 1846$ Hz) and 47.8 ($J_{P-P'} = 7.6$ Hz, $J_{P-Pt} = 3624$ Hz). It is important to note that the phosphorus−platinum coupling constants recorded for the two doublet resonance signals within the same complex are markedly different from each other. The relatively small phosphorus−platinum coupling constant observed for the doublet signal at δ 42.8 is diagnostic of the PPh_2 group coordinated trans to the strong π-accepting aromatic carbon atom. On the other hand, the doublet at δ 47.8 which showed the larger phosphorus−platinum coupling constant is unambiguously assigned to the PPh_2 group which is coordinated trans to the σ-donating nitrogen atom. This crystallized major diastereomer was subsequently confirmed by X-ray crystallography to be isomer Pt-*exo*-**2a**, as depicted in Scheme 1. The structural analysis affirmed that a bis-diphenylphosphino-substituted *exo*-cycloadduct has been produced in the cycloaddition reaction (Figure 1). Selected bond distances and angles of Pt-*exo*-**2a** are given in Table 1. The PPh_2 originating from the dienophile is coordinated in the position trans to the NMe_2 group and the two carbon atoms carrying the PPh_2 groups are both of the *R* absolute configurations. In concert with the marked differences in the two Pt−P coupling constants observed in the ^{31}P NMR spectra, the Pt−P(1) distance [2.327(2) Å] is clearly longer than the Pt−P(2) bond [2.238(2) Å)]. These spectroscopic and structural data thus confirm that the unique *trans*-electronic influences which originate from the organoplatinum unit operate strongly both in the solid state and in solution. Another interesting structural feature observed in Pt-*exo*-**2a** is that within the diphosphine chelate, the P(1)−C(16) distance [1.850(7) Å] is significantly shorter than the P(2)−C(17) bond [1.883(7) Å]. As for the oxygen−carbon bonds within the oxanorbornene skeleton, the O(22)−C(16) [1.422(8) Å] bond length is markedly shorter than the O(22)−C(19) bond [1.476(10) Å]. The relatively short P(1)−C(16) and O(22)−C(16) bonding patterns apparently indicate that

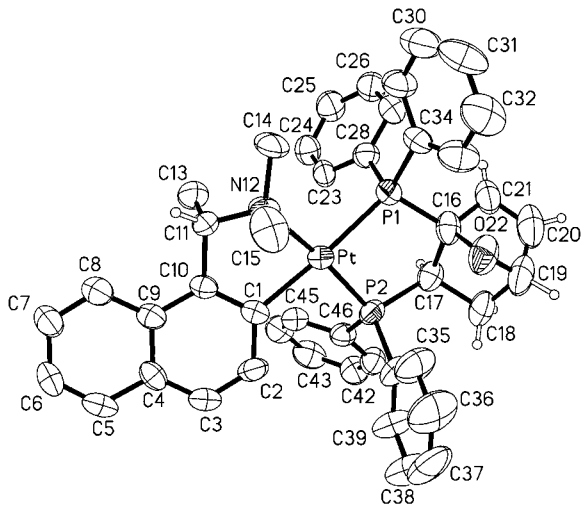
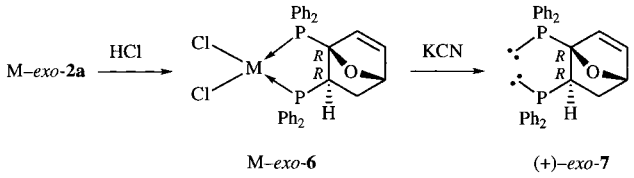


Figure 1. Molecular structure and absolute stereochemistry of the cationic complex Pt-*exo*-**2a**.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Pt-*exo*-2a and Pd-*exo*-2a

	Pt-*exo*-**2a**	Pd-*exo*-**2a**
M−C(1)	2.060(6)	2.075(8)
M−N(12)	2.131(5)	2.140(7)
M−P(1)	2.327(2)	2.374(2)
M−P(2)	2.238(2)	2.264(2)
P(1)−C(16)	1.850(7)	1.855(9)
P(2)−C(17)	1.883(7)	1.887(9)
O(22)−C(16)	1.422(8)	1.441(10)
O(22)−C(19)	1.476(10)	1.461(13)
C(16)−C(17)	1.554(10)	1.552(12)
C(16)−C(21)	1.505(10)	1.537(13)
C(17)−C(18)	1.541(9)	1.543(12)
C(18)−C(19)	1.553(11)	1.550(14)
C(19)−C(20)	1.458(12)	1.530(20)
C(20)−C(21)	1.303(10)	1.290(20)
C(1)−M−P(1)	174.3(2)	174.4(2)
C(1)−M−P(2)	95.3(2)	94.8(2)
C(1)−M−N(12)	79.4(2)	79.4(3)
N(12)−M−P(1)	99.7(2)	100.6(2)
N(12)−M−P(2)	174.3(2)	173.8(2)
P(1)−M−P(2)	85.8(1)	85.4(1)
P(1)−C(16)−O(22)	115.1(5)	114.8(6)
P(1)−C(16)−C(17)	111.2(4)	112.2(5)
P(2)−C(17)−C(16)	110.7(4)	111.0(6)
P(2)−C(17)−C(18)	115.0(5)	114.6(7)
C(16)−O(22)−C(19)	95.9(6)	95.8(8)
C(16)−C(17)−C(18)	102.2(6)	102.1(7)
C(17)−C(18)−C(19)	100.4(6)	100.5(7)
C(18)−C(19)−C(20)	107.0(8)	107.1(10)
C(19)−C(20)−C(21)	109.1(8)	106.5(11)
C(20)−C(21)−C(16)	104.3(8)	106.2(11)
C(21)−C(16)−C(17)	108.1(6)	107.8(8)

Scheme 2



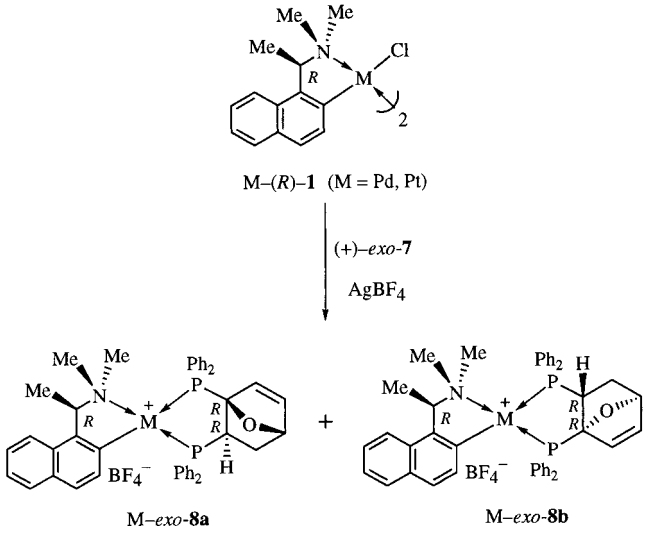
there may be an electronic interaction between the oxanorbornene-oxygen atom and the P(1) → Pt bond.

In contrast to many organic oxanorbornenes,[12] the bridgehead C−O bonds in the chelating diphosphine cycloadduct in Pt-*exo*-**2a** are stable toward acid treatments. Thus the naphthylamine auxiliary could be removed chemoselectively from Pt-*exo*-**2a** by treatment with concentrated hydrochloric acid to generate Pt-*exo*-**6** (Scheme 2). The dichloro complex was subsequently crystallized from dichloromethane-diethyl ether as white prisms, 95% yield, $[\alpha]_{365}$ −180° (CH_2Cl_2). The ^{31}P NMR spectrum of this neutral dichloro complex in CD_2Cl_2 exhibited two doublets at δ 37.9 ($J_{P-P'}$ = 9.5 Hz, J_{P-Pt} = 3677 Hz) and 49.1 ($J_{P-P'}$ = 9.5 Hz, J_{P-Pt} = 3570 Hz). In the absence of the asymmetric naphthylamine auxiliary, the two Pt−P coupling constants are similar in magnitude. Further treatment of Pt-*exo*-**6** with aqueous cyanide liberated the optically pure bisdiphenylphosphino-substituted exo-cycloadduct (+)-*exo*-**7** as an air-stable white solid in quantitative yields, $[\alpha]_{365}$ +46° (CH_2ClCH_2Cl). The ^{31}P NMR spectrum of this asymmetric diphosphine ligand in $CDCl_3$ exhibited two doublets at δ −11.2 ($J_{P-P'}$ = 80.1 Hz) and −15.2 ($J_{P-P'}$ = 80.1 Hz).

To establish the identity of the two minor diastereomers generated in the cycloaddition reaction, the liberated (+)-*exo*-**7** was recoordinated to Pt−(*S*)-**1**. The resulting chloride anion was replaced by a tetrafluoroborate with the standard silver salt treatment. In contrast to the original cycloaddition reaction, both the metal template complex and the reacting diphosphine used in this recoordination process are optically pure. Hence only one or both of the two possible regioisomers Pt-*exo*-**2a** and Pt-*exo*-**2b** could be produced in this reaction. The ^{31}P NMR spectrum of the crude reaction mixture in CD_2Cl_2 indicated that, interestingly, both regioisomers were generated as a 1:1 stereoisomeric mixture. The spectrum showed four doublets of ca. equal intensities with two of them being identical to those recorded previously for Pt-*exo*-**2a**. The two additional doublets were observed at δ 37.7 ($J_{P-P'}$ = 7.6 Hz, J_{P-Pt} = 3746 Hz) and 54.2 ($J_{P-P'}$ = 7.6 Hz, J_{P-Pt} = 1785 Hz). Therefore these doublet signals can be unambigiously assigned to the only other possible regioisomer, Pt-*exo*-**2b**. These additional NMR doublet patterns, importantly, are identical to those recorded for the lesser of the two minor isomers in the original 1:2:10 diastereomeric mixture obtained directly from the asymmetric Diels−Alder reaction. It is interesting to note that via

(12) Wong, H. N. C.; Ng, T. K.; Wong, T. Y.; Xing, Y. D. *Heterocycles* **1984**, *22*, 875. Hanessian, S.; Beaulieu, P.; Dube, D. *Tetrahedron Lett.* **1986**, *27*, 5071. Takayama, H.; Hayashi, K.; Koizumi, T. *Tetrahedron Lett.* **1986**, *27*, 5509. Harwood, L. M.; JAckson, B.; Prout, K.; Witt, F. J.*Tetrahedron Lett.* **1990**, *31*, 1885. Koreeda, M.; Jung, K. Y.; Hirota, M. *J. Am. Chem. Soc.* **1990**, *112*, 7413. Ogawa, S.; Yoshikawa, M.; Taki. T. *J. Chem. Soc., Chem. Commun.* **1992**, 406. Shiu, L. H.; Shu, H. K.; Cheng, D. H.; Hwang, H. L.; Wang, S. L.; Liao, F. L.; Liu, R. S. *Organometallics* **1998**, *17*, 4206.

Scheme 3



the direct metal template promoted cycloaddition reaction, Pt-*exo*-**2a** and Pt-*exo*-**2b** were generated in unequal amounts in the ratio of 10:1. However these two regioisomers were generated in about equal quantities by the recoordination pathway described above. Attempts to isolate the regioisomer Pt-*exo*-**2b** by fractional crystallization proved to be futile, despite the diverse solvent systems that were employed. Indeed, it was found that it was rather difficult to induce the diastereomeric complexes, including Pt-*exo*-**2a**, to crystallize from the recoordination product mixture.

The identity of the third isomer produced in the platinum complex promoted cycloaddition reaction was uncovered by recoordinating the liberated (+)-*exo*-**7** to the enantiomeric complex Pt−(*R*)-**1**. The chloride anion was subsequently replaced by a tetrafluoroborate with the standard silver salt treatment. As illustrated in Scheme 3, a maximun of two regioisomers Pt-*exo*-**8a** and Pt-*exo*-**8b** can be generated from this simple metal complexation reaction. It is important to note that complexes Pt-*exo*-**8a** and Pt-*exo*-**8b** are the enantiomeric forms of Pt-*exo*-**3a** and Pt-*exo*-**3b**, respectively. In the absence of any chiral NMR solvent, the NMR spectra of Pt-*exo*-**8a** and Pt-*exo*-**8b** should show identical resonance signals as those recorded for their enantiomeric counterparts. By analying the ^{31}P NMR spectra of the crude products obtained from the recomplexation process (Scheme 3) and those recorded directly from the cycloaddition reaction (Scheme 1), it is thus possible to determine if Pt-*exo*-**3a** and Pt-*exo*-**3b** are among the cycloadducts that were generated directly from the Diels−Alder reaction.

The ^{31}P NMR spectrum of the crude reaction mixture in CD_2Cl_2 indicated that both regioisomers of Pt-*exo*-**8** were generated as a 1.3:1 mixture in the recomplexation process. The major isomer showed a pair of doublets at δ 41.0 ($J_{P-P'}$ = 7.6 Hz, J_{P-Pt} = 1827 Hz) and 48.6 ($J_{P-P'}$ = 7.6 Hz, J_{P-Pt} = 3631 Hz) and the two doublets of the minor isomer was observed at δ 38.0 ($J_{P-P'}$ = 7.6 Hz, J_{P-Pt} = 3662 Hz) and 53.2 ($J_{P-P'}$ = 7.6 Hz, J_{P-Pt} = 1778 Hz). It is important to note that the major re-coordination product exhibits NMR signals identical to those observed for the second minor isomer in the original 1:2:10 product mixture obtained directly from the Diels−Alder reaction. The absolute regiochemistry of the two

re-coordination products can be established by comparing their NMR signals with those of closely related compounds. It has been well established that when a pair of enantiomeric diphosphine are coordinated to this particular optically pure *ortho*-metalated naphthylamine unit, the two resulting diastereomers will show ^{31}P NMR signals of similar patterns, coupling constants and differ only slightly in their chemical shifts. On the other hand, when an optically pure asymmetric P−P′ diphosphine is coordinated to the same chiral organometallic unit, the two resulting regioisomers invariably exhibit signals with rather different patterns and, particularly, in the chemical shifts. In agreement with these literature findings, the pair of regioisomers Pt-*exo*-**2a** and Pt-*exo*-**2b** indeed show rather distinct signal patterns in their ^{31}P NMR spectra. Thus, by a careful examination of the ^{31}P NMR signals recorded for the two re-coordination products, it is noted that signals due to the major isomer occurred at the positions similar to those recorded for Pt-*exo*-**2a** and the signals arising from the minor isomer are similar to those obtained for Pt-*exo*-**2b**. Accordingly, the major and the minor re-coordination products are assigned to be Pt-*exo*-**8a** and Pt-*exo*-**8b**, respectively. Furthermore, from these re-coordination reactions and spectroscopic investigations, it is possible to deduce that isomers Pt-*exo*-**2a**, Pt-*exo*-**2b**, and Pt-*exo*-**3a** were the three stereoisomeric complexes generated in the cycloaddition reaction, in the ratio of 10:1:2, respectively. It is noteworthy that the platinum complex promoted Diels−Alder reaction could be accelerated to completion in 16 h by heating the reaction mixture at 65 °C. Under this stronger reaction condition, however, the stereoselectivity of the cycloaddition is somewhat lower. The three product isomers Pt-*exo*-**2a**, Pt-*exo*-**2b**, and Pt-*exo*-**3a** were obtained as a 5:1:1.5 mixture in similar overall yield. Due to the poorer selectivity, the isolation of the major product Pt-*exo*-**2a** from this faster reaction was found to be somewhat less efficient. Nevetheless, no *endo*-cycloadducts were produced despite the fact that the reaction is less stereoselective at 65 °C.

Interestingly, when the platinum template Pt−(*S*)-**1** was replaced by the analogous chiral palladium complex Pd−(*S*)-**1**, the cycloaddition reaction proceeded at a significantly slower rate with a lower degree of stereoselectivity. At room temperture, the reaction proceed very slowly with about 30% of the precursors having undergone the cycloaddition reaction after 5 days. At 65 °C, however, the palladium template promoted cycloaddition reaction was found to complete in 16 h. In CD_2Cl_2, the ^{31}P NMR spectrum of the crude product obtained from the accelerated reaction exhibited three pairs of doublets in the ratio of 1:1.2:1.6 which indicated that three diastereomeric complexes were generated in similar quantities. Isolation of these cationic diastereomeric complexes was found to be rather difficult and inefficient. Nevertheless, after purification by preparative silica column chromatography and repeated fractional crystallization, one of the isomer was eventually isolated in its pure form as pale yellow prisms in 11% yields, $[\alpha]_{365}$ −222° (CH_2Cl_2). The ^{31}P NMR spectrum of this crystallized isomer in CD_2Cl_2 showed the two doublets at δ 37.4 ($J_{P-P'}$ = 32.4 Hz) and 69.3 ($J_{P-P'}$ = 32.4 Hz). These doublets correspond to the most intense signals observed in the ^{31}P NMR spectrum of the original 1:1.2:1.6 diastereomeric mixture. This crystallized isomer was subsequently confirmed by X-ray crystallography to be isomer Pd-*exo*-**2a** (Figure 2). The X-ray structural analyses established the C(11)*S*, (16)*R*, (17)*R*, and (19)*S* absolute configurations and the PPh_2 moiety at C(17) is coordinated trans to the NMe_2 group. The palladium complex Pd-*exo*-**2a** and its platinum analogue Pt-*exo*-**2a** are isostructural with each other. The optically pure diphosphine ligand (+)-*exo*-**7** was liberated similarly from Pd-*exo*-**2a** by successive treatments with hydrochloric acid and aqueous cyanide as previously described.

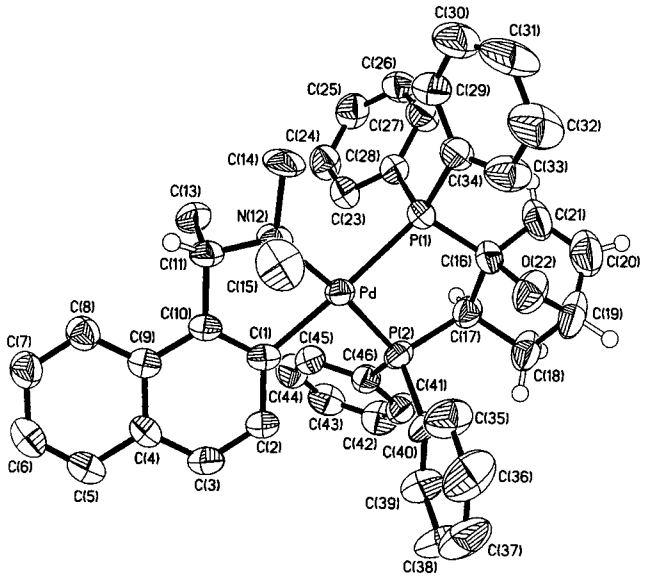


Figure 2. Molecular structure and absolute stereochemistry of the cationic complex Pd-*exo*-**2a**.

To determine if the regioisomer Pd-*exo*-**2b** was among the reaction products generated in the cycloaddition reaction, liberated (+)-*exo*-**7** was re-coordinated to Pd−(*S*)-**1**. After the treatment with silver tetrafluoroborate, the ^{31}P NMR spectrum of the crude reaction mixture in CD_2Cl_2 indicated that both the regioisomers, Pd-*exo*-**2a** and Pd-*exo*-**2b**, were generated as a 1:1 mixture. The new regioisomer showed a pair of doublets at δ 48.3 ($J_{P-P'}$ = 32.4 Hz) and 57.6 ($J_{P-P'}$ = 32.4 Hz). These doublet signals indeed correspond to those recorded for an isomer (with the relative adundance of 1.2) in the original 1:1.2:1.6 diastereomeric mixture obtained from the cycloaddition reaction. It is noteworthy that, individual regioisomers could not be separated efficiently from this 1:1 stereoisomeric mixture.

To identify the third isomer in the palladium template synthesis, a similar approach to that used for the platinum complex assisted reaction was adopted. Thus, the recoordination of liberated (+)-*exo*-**7** to the enantiomeric dimeric complex Pd−(*R*)-**1** followed by the treatment with silver tetrafluoroborate generated a 3:1 mixture of the two regio isomers Pd-*exo*-**8a** and Pd-*exo*-**8b**. In CD_2Cl_2, the major isomer showed a pair of doublets at δ 34.4 ($J_{P-P'}$ = 32.4 Hz) and 69.2 ($J_{P-P'}$ = 32.4 Hz) and the two doublets of the minor isomer was observed at δ 46.7 ($J_{P-P'}$ = 32.4 Hz) and 55.5 ($J_{P-P'}$ = 32.4 Hz). A comparison of these NMR signals with those recorded for Pd-*exo*-**2a** and Pd-*exo*-**2b** revealed that the major and the minor recomplexation products are Pd-

exo-**8a** and Pd-*exo*-**8b**, respectively. The signals observed for Pd-*exo*-**8a** are identical to those recorded for the least abundant isomer in the original 1:1.2:1.6 diastereomeric mixture obtained from the cycloaddition reaction. Accordingly, it is clear that the three isomers Pd-*exo*-**2a**, Pd-*exo*-**2b**, and Pd-*exo*-**3a** were generated in the ratio of 1.6:1.2:1 respectively in the palladium complex assisted Diels−Alder reaction. The other five possible isomers were not formed in any detectable amount in this asymmetric synthesis. The stereoselectivity of the palladium complex promoted cycloaddition reaction can be somewhat improved if the reaction was carried out at room temperature and allowed to reach completion by stirring for about 3 weeks. Under this milder reaction condition, the ^{31}P NMR spectrum of the crude reaction mixture in CD_2Cl_2 indicated that isomers Pd-*exo*-**2a**, Pd-*exo*-**2b**, and Pd-*exo*-**3a** were generated in the ratio of 2.1:1.6:1, respectively. Despite this minor improvement in the stereoselectivity, however, it is our judgment that the palladium template Pd−(*S*)-**1** is less exalted than its platinum counterpart for this series of cycloaddition reaction. The lower chemical reactivity and stereoselectivity offered by Pd−(*S*)-**1** in the cycloaddition reaction had indeed imposed more technical problems in the product isolation process.

Stabilities of the Optically Active Cycloadduct, (+)-*exo*-7. Oxanorbornenes are frequently considered to be unstable compounds as they can undergo the retro Diels−Alder reaction readily to regenerate the corresponding cyclic dienes and dienophiles.[12,13] A similar instability was observed for the liberated diphosphine (+)-*exo*-**7**. For instance, after a pure solid sample of the optically active diphosphine ligand had been kept at room temperature under an inert atmosphere for six weeks, the ^{31}P NMR spectrum of this sample in $CDCl_3$ indicated that approximately 20% of the cycloadduct had reverted back to the original cycloadduct precursors, ie diphenylvinylphosphine and 2-diphenylphosphinofuran. However, this undesired cycloreversion reaction can be prevented by means of metal complexation. Thus, for the purpose of protection and storage, the liberated chiral diphosphophosphine ligand was routinely re-coordinated to $[Pd(MeCN)_2Cl_2]$ or $[Pt(MeCN)_2Cl_2]$ to form M-*exo*-**6**. The dichloro complexes were obtained in practically quantitative yields. Pd-*exo*-**6** was obtained as pale yellow prisms by crystallization from dichloromethane-diethyl ether, $[\alpha]_{365}$ −89° (CH_2Cl_2). The ^{31}P NMR spectrum of Pd-*exo*-**6** in CD_2Cl_2 exhibited two doublets at δ 61.1 (d, $J_{P-P'} = 7.6$ Hz) and 73.6 (d, $J_{P-P'} = 7.6$ Hz). It is noteworthy that Pd-*exo*-**6** obtained by this recoordination process using the free diphosphine ligand synthesized from the superior Pt template Diels−Alder reaction, is more efficient than by the direct Pd template Diels−Alder route. Once formed, the diphosphine metal complexes are stable, both in the solid state and in solution. For example, the optical rotation measurement and the ^{31}P NMR studies of Pt-*exo*-**6** and Pd-*exo*-**6** showed that the samples were unchanged after being kept at room temperature for 3 months. Apparently, the diphosphine-metal complexes are both kinetically and thermodynamically stable.

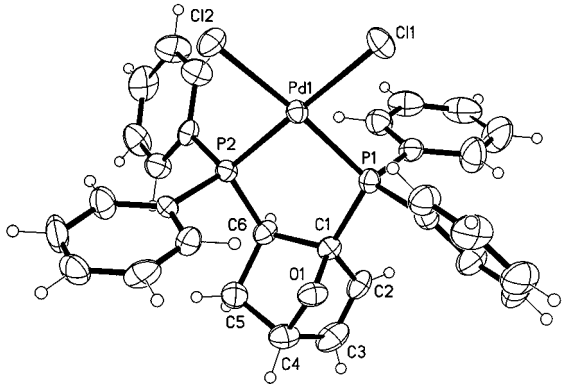


Figure 3. Molecular structure of the dichloro complex Pd-*exo*-**6**.

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

Pd(1)−P(1)	2.224(1)	P(1)−Pd(1)−Cl(1)	89.4(1)
Pd(1)−P(2)	2.223(1)	P(1)−Pd(1)−Cl(2)	175.4(1)
Pd−Cl(1)	2.344(1)	P(1)−Pd(1)−P(2)	88.2(1)
Pd−Cl(2)	2.351(1)	P(2)−Pd(1)−Cl(1)	173.8(1)
P(1)−C(1)	1.857(4)	P(2)−Pd(1)−Cl(2)	88.6(1)
P(2)−C(6)	1.863(4)	Cl(1)−Pd(1)−Cl(2)	94.1(1)
O(1)−C(1)	1.416(5)	P(1)−C(1)−C(6)	113.4(3)
O(1)−C(4)	1.463(5)	P(2)−C(6)−C(1)	110.5(2)
C(1)−C(2)	1.499(5)	C(1)−O(1)−C(4)	96.3(3)
C(2)−C(3)	1.309(6)	C(1)−C(2)−C(3)	105.3(4)
C(3)−C(4)	1.483(6)	C(2)−C(3)−C(4)	107.2(4)
C(4)−C(5)	1.531(6)	C(3)−C(4)−C(5)	106.0(4)
C(5)−C(6)	1.547(5)	C(4)−C(5)−C(6)	101.2(3)
C(6)−C(1)	1.560(5)	C(6)−C(1)−C(2)	106.4(3)

Differences between the Electronic Properties of Pd−(*S*)-1 or Pt−(*S*)-1. It is interesting to note that, the P−P′ coupling of the Pd dichloro complex, Pd-*exo*-**6**, is small (7.6 Hz) when compared with those recorded for complexes Pd-*exo*-**2**, **3**, and **8** (32.4 Hz). It has been established that the P−P′ coupling of dissymmetrical five-membered bidentate phosphine P−P′ metal chelates are invariably small (0−10 Hz) as the "through-the-backbone" and the "through-the-metal" contributions are nearly equal but of opposite signs.[14] Hence the P−P′ coupling is larger for the free ligand (+)-exo-**7** than its metal complexes. All the P−P′ couplings recorded for Pd-*exo*-**6** (7.6 Hz), the dichloro platinum complex, Pt-*exo*-**6** (9.5 Hz) and all the stereoisomeric platinum template complexes (7.6 Hz) may be considered to be within the expected value. The coupling observed for the palladium template complexes Pd-*exo*-**2**, **3** and **8** (32.4 Hz), therefore, may be considered as unusually large. A further examination of the stereochemical environment of the diphosphine chelates in complexes Pd-*exo*-**6** (Figure 3 and Table 2), Pd-*exo*-**2a** and Pt-*exo*-**2a** by single crystal X-ray structural crystallography revealed that the coordination chemistry and the general structural features of the diphosphine metal chelate in all three complexes are similar. Thus, the unusually large P−P′ coupling observed in complexes Pd-*exo*-**2**, **3,** and **8** must be due to the strong electronic influences originating from the *ortho*-palladated naphthylamine unit. These electronic influences, however, are not

(13) Danishefsky, S.; Tsuzuki, K. *J. Am. Chem. Soc.* **1980**, *102*, 6893. Klein, L. L. *J. Org. Chem.* **1985**, *50*, 1770. Lipshutz, B. H. *Chem. Rev.* **1986**, *86*, 795. Grieco, P. A.; Nunes, J. J.; Gaul, M. D. *J. Am. Chem. Soc.* **1990**, *112*, 4595. Cook, M. J.; Cracknell, S. J. *Tetrahedron* **1994**, *50*, 12125. Dauben, W. G.; Lam, J. Y. L.; Guo, Z. R. *J. Org. Chem.* **1996**, *61*, 4816. Fraile, J. M.; Garcia, J. I.; Gracia, D.; Mayoral, J. A.; Pires, E. *Org. Chem.* **1996**, *61*, 9479. Kappe, C. O.; Murphree, S. S.; Padwa, A. *Tetrahedron* **1997**, *53*, 14179.

(14) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

observed in the analogous platinum complexes containing similar *ortho*-platinated naphthylamine rings. Clearly, in addition to their similar steric features, the electronic properties of Pd−(*S*)-**1** and Pt−(*S*)-**1** also play an important role in the activation and stereoselectivity of the corresponding cycloaddition reaction. Investigation on the electronic effects of these metal templates on other hetero-cycloaddition reactions are currently in progress.

Experimental Section

Reactions involving air-sensitive compounds were performed under a positive pressure of purified nitrogen. NMR spectra were recorded at 25 °C on Bruker ACF 300 and AMX 500 spectrometers. Optical rotations were measured on the specified solution in a 1-dm cell at 25 °C with a Perkin-Elmer Model 341 polarimeter. Elemental analyses were performed by the Elemental Analysis Laboratory of the Department of Chemistry at the National University of Singapore.

2-Diphenylphosphinofuran was prepared according to standard literature methods.[15] The enantiomerically pure form of Pd−(*S*)-**1** was prepared as previously described.[2−8] The platinum template Pt−(*S*)-**1** was prepared by an improved method previously reported by our group.[16]

The Improved Method for the Synthesis of the Platinum Template. Synthesis of Bis(*μ*-chloro)bis[(*S*)-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C,N*]-diplatinum-(II). [Pt−(*S*)-1]. A solution of *N,N*-dimethyl[1-(1-naphthyl)-ethyl]amine (2.1 g) in methanol (25 mL) was added to a stirring solution of potassium tetrachloroplatinate (2.0 g) in water (25 mL) at room temperature. The reaction was allowed to stir vigorously at the same temperature for 3 d. The crude product was isolated by filtration and washed with water (to remove KCl and any excess K_2PtCl_4) and then redissolved in boiling benzene and dried ($MgSO_4$). The solvent was removed under reduced pressure to give a brownish residue. This material was chromatographed on a silica column with chloroform as the elute. The compound was subsequently crystallized from dichloromethane−hexane as yellow prisms, 1.5 g (70% yield), the physical and spectroscopic properties of the product are identical to those reported previously.[16]

The excess naphthylamine ligand can be recovered efficiently in its optically pure form from the filtrate by neutralization with aqueous sodium hydroxide.[17]

Asymmetric Diels−Alder Reactions. Isolation of {(*S*)-1-[1-(Dimethylamino)ethyl]naphthyl-*C*²,*N*}{(1α,4α,5α(*R*))-[4,5-bis(diphenylphosphino)-7-oxabicyclo[2.2.1]hept-2-ene-*P*⁴,*P*⁵}platinum(II) tetrafluoroborate, [Pt-*exo*-2a]. A solution of silver tetrafluoroborate (0.82 g) in water (2 mL) was added to a mixture containing the platinum template [Pt−(*S*)-**1**] (1.26 g), diphenylvinylphosphine (0.58 g), and 2-diphenylphosphinofuran (0.68 g) in dichloromethane (75 mL). The solution was stirred vigorously at room temperature for 3 h. The solution was filtered (to remove silver chloride), washed with water, and then dried ($MgSO_4$). The dried reaction mixture was further stirred at room temperature for 5 d. Upon slow addition of diethyl ether to the mixture, [Pt-*exo*-**2**a] was obtained as pale yellow prisms: mp 261−262 °C (decomp.); $[\alpha]_D$ −97° (*c* 0.5, CH_2Cl_2); 1.77 g (70% yield). Anal. Calcd for $C_{44}H_{42}BF_4NOP_2Pt$: C, 55.9; H, 4.5; N, 1.5. Found C, 55.6; H, 4.5; N, 1.8. ^{31}P NMR (CD_2Cl_2) δ 42.8 (d, 1 P, J_{PP} = 7.6 Hz, J_{PtP} = 1846 Hz, P^4), 47.8 (d, 1 P, J_{PP} = 7.6 Hz, J_{PtP} = 3624 Hz, P^5); ^{1}H NMR (CD_2Cl_2) δ 1.85 (d, 3 H, $^3J_{HH}$ = 6.0 Hz, CH*Me*), 1.96−2.11 (m, 1 H, $H_{6(exo)}$), 2.51−2.55 (m, 1 H, $H_{6(endo)}$), 2.56 (d, 3 H, $^4J_{PH}$ = 2.4 Hz, N*Me*), 2.86 (dd, 3 H, $^4J_{PH}$ = 3.7 Hz, $^4J_{P'H}$ = 3.0 Hz, N*Me*), 4.80 (qn, 1 H, $^3J_{HH}$ = $^4J_{PH}$ = 6.0 Hz, C*H*Me), 5.03 (br dd, 1 H, $^3J_{HH}$ = 4.4 Hz, $^3J_{H'H}$ = 1.2 Hz, H_1), 6.15 (d, 1 H, $^3J_{HH}$ = 5.6 Hz, H_3), 6.61 (dd, 1 H, $^3J_{HH}$ = 5.6 Hz, $^3J_{H'H}$ = 1.2 Hz, H_2), 6.73−6.79 (m, 1 H, H_5), 7.07−8.11 (m, 26 H, aromatics).

{(*S*)-1-[1-(Dimethylamino)ethyl]naphthyl-*C*²,*N*}-{(1α,4α,5α(*R*))-[4,5-bis(diphenylphosphino)-7-oxabicyclo-[2.2.1]hept-2-ene-*P*⁴,*P*⁵}palladium(II) Tetrafluoroborate, [Pd-*exo*-2a]. The palladium template promoted cycloaddition reaction was performed similarly from [Pd−(*S*)-**1**] (0.68 g), diphenylvinylphosphine (0.43 g), and 2-diphenylphosphinofuran (0.50 g) at 65 °C in 1,2-dichloroethane for 16 h. This palladium template promoted reaction was found to be more efficient when the second phosphine ligand was added after the chloro abstraction process. The crude product was chromatographed on a silica column with acetone−dichloromethane as eluent and then repeatedly crystallized from dichloromethane-diethyl ether forming pale yellow prisms: Mp 222−223 °C (decomp.); $[\alpha]_D$ −78° (*c* 0.5, CH_2Cl_2); 0.18 g (11% yield). Anal. Calcd for $C_{44}H_{42}BF_4NOP_2Pd$: C, 61.7; H, 4.9; N, 1.6. Found C, 61.6; H, 4.5; N, 1.8. ^{31}P NMR (CD_2Cl_2) δ 37.4 (d, 1 P, J_{PP} = 32.4 Hz, P^4), 69.3 (d, 1 P, J_{PP} = 32.4 Hz, P^5); ^{1}H NMR (CD_2Cl_2) δ 1.85 (d, 3 H, $^3J_{HH}$ = 6.0 Hz, CH*Me*), 2.06−2.18 (m, 1 H, $H_{6(exo)}$), 2.49 (dd, 3 H, $^4J_{PH}$ = 4.0 Hz, $^4J_{P'H}$ = 3.7 Hz, N*Me*), 2.63 (d, 3 H, $^4J_{PH}$ = 1.6 Hz, N*Me*), 2.62−2.67 (m, 1 H, $H_{6(endo)}$), 4.45 (qn, 1 H, $^3J_{HH}$ = $^4J_{PH}$ = 6.0 Hz, C*H*Me), 5.01 (br dd, 1 H, $^3J_{HH}$ = 4.8 Hz, $^3J_{H'H}$ = 1.2 Hz, H_1), 6.16 (d, 1 H, $^3J_{HH}$ = 5.6 Hz, H_3), 6.50−6.57 (m, 1 H, H_5), 6.58 (ddd, 1 H, $^3J_{HH}$ = 5.6 Hz, $^3J_{H'H}$ = $^5J_{PH}$ = 1.2 Hz, H_2), 7.03−8.02 (m, 26 H, aromatics).

[SP-4-2-[(1α,4α,5α(*R*))]]-Dichloro[4,5-bis(diphenylphosphino)-7-oxabicyclo[2.2.1]hept-2-ene-*P*⁴,*P*⁵]platinum-(II) [Pt-*exo*-6]. The naphthylamine auxiliary in [Pt-*exo*-**2a**] was removed chemoselectively by adding concentrated hydrochloric acid (12 mL) to a solution of the complex (0.44 g) in dichloromethane (40 mL). The reaction mixture was stirred vigorously for 3 d at room temperature. The reaction mixture was then washed with water (4 × 20 mL), dried ($MgSO_4$), and subsequently crystallized from dichloromethane-diethyl ether as white prisms: mp 297−298 °C (decomp); $[\alpha]_D$ −53° (*c* 0.5, CH_2Cl_2); 0.32 g (95% yield). Anal. Calcd for $C_{30}H_{26}Cl_2OP_2Pt$: C, 49.3; H, 3.6. Found C, 49.0; H, 3.5. ^{31}P NMR (CD_2Cl_2) δ 37.9 (d, 1 P, J_{PP} = 9.5 Hz, J_{PtP} = 3677 Hz, *P*), 49.1 (d, 1 P, J_{PP} = 9.5 Hz, J_{PtP} = 3570 Hz, *P*); ^{1}H NMR (CD_2Cl_2) δ 1.68−1.79 (m, 1 H, H_5), 2.01−2.13 (m, 1 H, $H_{6(exo)}$), 2.66−2.70 (m, 1 H, $H_{6(endo)}$), 5.10−5.12 (m, 1 H, H_1), 6.23 (d, 1 H, $^3J_{HH}$ = 5.6 Hz, H_3), 6.55 (ddd, 1 H, $^3J_{HH}$ = 5.6 Hz, $^3J_{H'H}$ = $^5J_{PH}$ = 1.4 Hz, H_2), 7.41−8.16 (m, 20 H, aromatics).

[SP-4-2-[(1α,4α,5α(*R*))]]-Dichloro[4,5-bis(diphenylphosphino)-7-oxabicyclo[2.2.1]hept-2-ene-*P*⁴,*P*⁵]palladium-(II) [Pd-*exo*-6]. The neutral dichloro palladium complex was obtained similarily from [Pd-*exo*-**2a**] (0.13 g). The crude product was crystallized from dichloromethane−diethyl ether as pale yellow prisms: mp 238−239 °C (decomp.); $[\alpha]_D$ −46° (*c* 0.5, CH_2Cl_2); 0.09 g (92% yield). Anal. Calcd for $C_{30}H_{26}Cl_2OP_2Pd$: C, 56.1; H, 4.1. Found C, 56.5; H, 3.9. ^{31}P NMR (CD_2Cl_2) δ 61.1 (d, 1 P, J_{PP} = 7.6 Hz, *P*), 73.6 (d, 1 P, J_{PP} = 7.6 Hz, *P*); ^{1}H NMR (CD_2Cl_2) δ 1.68−1.79 (m, 1 H, H_5), 2.07−2.20 (m, 1 H, $H_{6(exo)}$), 2.78−2.82 (m, 1 H, $H_{6(endo)}$), 5.09 (dd, 1 H, $^3J_{HH}$ = 4.8 Hz, $^3J_{HH'}$ = 1.5 Hz, H_1), 6.30 (d, 1 H, $^3J_{HH}$ = 5.6 Hz, H_3), 6.54 (ddd, 1 H, $^3J_{HH}$ = 5.6 Hz, $^3J_{H'H}$ = $^5J_{PH}$ = 1.5 Hz, H_2), 7.41−8.17 (m, 20 H, aromatics).

Alternatively, the dichloro complex [Pd-*exo*-**6**] can be generated quantitatively by recoordination of the liberated diphosphine ligand (+)-*exo*-**7** to [$Pd(MeCN)_2Cl_2$] using dichloromethane as the solvent.

Liberation of Diphosphine Cycloadduct. Isolation of 4,5-Bis(diphenylphosphino)-7-oxabicyclo[2.2.1]hept-2-

(15) Ramanathan, V.; Levine, R. *J. Org. Chem.* **1962**, *27*, 1216. Allen, D. W.; Hutley, B. G.; Rich, T. C. *J. Chem. Soc., Perkin Trans. 2* **1973**, 820.

(16) Chooi, S. Y. M.; Ranford, J. D.; Leung. P. H.; Mok, K. F. *Tetrahedron: Asymmetry* **1994**, *5*, 1805.

(17) Barclay, C. E.; Deeble, G.; Doyle, R. J.; Elix, S. A.; Salem, G.; Jones, T. L.; Wild, S. B.; Willis, A. C. *J. Chem. Soc., Dalton Trans.* **1995**, 57.

Table 3. Crystallographic Data for Complexes Pt-*exo*-2a, Pd-*exo*-2a, and Pd-*exo*-6

	Pt-*exo*-**2a**	Pd-*exo*-**2a**	Pd-*exo*-**6**
formula	$C_{44}H_{42}BF_4NOP_2Pt$	$C_{44}H_{42}BF_4NOP_2Pd$	$C_{30}H_{26}Cl_2OP_2Pd$
fw	944.63	855.94	641.75
space group	$P2_{12121}$	$P2_12_12_1$	$P2_12_12_1$
crystal system	orthorhombic	orthorhombic	orthorhombic
a/Å	11.721(1)	11.798(2)	10.063(1)
b/Å	15.721(1)	15.730(4)	15.697(1)
c/Å	21.129(1)	21.179(4)	17.089(2)
V/Å^3	3893(1)	3930(2)	2699(1)
Z	4	4	4
T/K	293	293	223
ρ_{calcd}/g cm^{-3}	1.612	1.447	1.579
λ/Å	0.71073 (Mo)	1.54178 (Cu)	0.71073 (Mo)
μ/cm^{-1}	37.4	50.3	10.3
Flack params	0.01(1)	0.00(1)	−0.03(2)
R_1 (obsd data)[a]	0.0407	0.044	0.040
wR_2 (obsd data)[b]	0.0692	0.112	0.064

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

ene [(+)-*exo*-7]. A solution of [Pt-*exo*-**6**] (0.23 g) in dichloromethane (20 mL) was stirred vigorously with a saturated aqueous solution of potassium cyanide (1 g) for 16 h. The resulting colorless organic layer was separated, washed with water, and dried ($MgSO_4$). Upon the removal of solvent, a white solid was obtained: $[\alpha]_D$ +0.6° (*c* 0.5, CH_2ClCH_2Cl); 0.14 g (95% yield). ^{31}P NMR ($CDCl_3$) δ −11.2 (d, 1 P, J_{PP} = 80.1 Hz, *P*), −15.2 (d, 1 P, J_{PP} = 80.1 Hz, *P*); ^{1}H NMR ($CDCl_3$) δ 1.53−1.61 (m, 1 H, H_5), 1.86−1.96 (m, 1 H, $H_{6(exo)}$), 2.58 (dd, 1 H, $^3J_{HH}$ = 4.4 Hz, $^3J_{HH'}$ = 8.0 Hz, $H_{6(endo)}$), 5.02 (dd, 1 H, $^3J_{HH}$ = 4.4 Hz, $^3J_{HH'}$ = 1.6 Hz, H_1), 6.20 (dd, 1 H, $^3J_{HH}$ = 6.0 Hz, $^3J_{HH'}$ = 1.6 Hz, H_2), 6.34 (d, 1 H, $^3J_{HH}$ = 6.0 Hz, H_3), 7.20−7.56 (m, 20 H, aromatics).

Crystal Structure Determination of [Pt-*exo*-2a], [Pd-*exo*-2a] and [Pd-*exo*-6]. Crystal data for all three complexes and a summary of the crystallographic analyses are given in Table 3. The palladium (II) complex [Pd-*exo*-**2a**] was analyzed at the Imperial College using a Siemens P4/PC diffractometer with Cu Kα radiation (graphite monochromator) using ω-scans. The other two structures were analyzed at the National University of Singapore using a Siemens SMART CCD diffractometer with graphic monochromated Mo Kα radiation. For all three complexes, semiempirical absorption corrections were applied. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at fixed distance from carbon atoms and were assigned fixed thermal parameters. The absolute configurations of all chiral complexes were determined unambiguously using the Flack parameter.[18]

Acknowledgment. We are grateful to the National University of Singapore for support of this research (Grant No. RP 979905) and a research scholarship to W.C.Y.

Supporting Information Available: For Pt-*exo*-**2a**, Pd-*exo*-**2a**, and Pd-*exo*-**6** tables of crystal data, data collection, solution and refinement, final positional parameters, bond distances and angles, thermal parameters of non-hydrogen atoms and calculated hydrogen parameters. This material is available free of charge via the Internet at http://pubs.acs.org

OM001063T

(18) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.