Functionalization of Metal-Protected Chiral Phosphines via Simple Organic Transformations

Wee-Chuan Yeo,† Jagadese J. Vittal,† Lip Lin Koh,† Geok Kheng Tan,† and Pak-Hing Leung*,‡

Department of Chemistry, National University of Singapore, Kent Ridge, Singapore 119260, and Division of Chemistry and Biological Chemistry, Nanyang Technological University, Singapore 637616

Received November 10, 2005

With metal as protection, the introduction of functionalities on coordinated chiral phosphines using organic transformations was demonstrated. Bis(diphenylphosphino)-substituted oxa- and azanorbornene metal complexes were subjected to a series of organic transformations including hydrogenation, hydroboration, electrophilic addition, and dihydroxylation reactions. Hydrogenation of the oxanorbornene double bond stabilizes the free diphosphino-substituted oxanorbornene ligand, which is otherwise prone to the retro-cycloaddition reaction. Hydroboration of the oxanorbornenic double bond using borane, followed by oxidation with alkaline hydrogen peroxide, generated two regioisomeric products with the introduction of a hydroxy group at the *exo* position. However, regioselective hydroboration could be achieved with the use of 9-BBN as the hydroborating agent. Stereoselective electrophilic addition of the oxanorbornenic double bond with phenylselenenyl chloride resulted in the formation of a sole anti-addition product. Subsequent oxidative syn-elimination of the resultant selenide product was also shown to proceed regioselectively to give the vinyl chloride complex. Dihydroxylation of the oxa- and azanorbornenic double bond with osmium tetraoxide proceeded stereoselectively with the introduction of two hydroxy group at the *exo* positions. Liberation of the functionalized chiral phosphine ligands from the metal complexes was also illustrated.

Introduction

The application of chiral phosphine ligands in asymmetric metal catalysis has been well established.[1] The presence of functional groups on chiral phosphines can be beneficial in several aspects: (a) secondary interactions between the reacting substrate and functional groups on the chiral phosphine ligand (such as electrostatic, hydrogen-bonding, or $\pi-\pi$ stacking interactions) may result in higher enantioselectivity of the reaction via the more organized transition state;[2] (b) the functional groups can act as hemilabile ligands to the metal center;[3] (c) the functional groups can be coordinated to a second metal for the synthesis of bimetallic catalysts;[4] (d) with the introduction of functional groups, the solubility of the chiral phosphine metal complexes can be controlled (for instance, an increase in water solubility with the presence of ionic or polar hydrophilic groups);[5] (e) immobilization of chiral metal catalysts on solid support can be achieved through the functional groups on the phosphine ligand, which provides an easy means for the separation and recycling of the catalyst.[6]

Generally, functionalized chiral phosphine metal complexes are routinely prepared by coordination of the synthesized phosphine ligand to the metal center.[2−4,5a−d,6] However, organic transformations of a coordinated chiral phosphine ligand (with metal as protection) is not common.[5e,f] Over the past few years, our group has reported the use of cyclometalated-amine complexes as efficient chiral templates for the asymmetric synthesis of chiral phosphines and their metal complexes via

* Corresponding author. E-mail: pakhing@ntu.edu.sg.
† National University of Singapore.
‡ Nanyang Technological University.

(1) (a) Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds. *Comprehensive Asymmetric Catalysis I−III*; Springer-Verlag: Berlin, 1999. (b) Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds. *Comprehensive Asymmetric Catalysis Supplement 1*; Springer-Verlag: Berlin, 2004. (c) Ojima, I., Ed. *Catalytic Asymmetric Synthesis*, 2nd ed.; Wiley-VCH: New York, 2000. (d) Tang, W.; Zhang, X. *Chem. Rev.* **2003**, *103*, 3029.

(2) (a) Sawamura, M.; Ito, Y. *Chem. Rev.* **1992**, *92*, 857, and references therein. (b) Sawamura, M.; Nakayama, Y.; Kato, T.; Ito, Y. *J. Org. Chem.* **1995**, *60*, 1727. (c) Holz, J.; Börner, A.; Kless, A.; Borns, S.; Trinkhaus, S.; Selke, R.; Heller, D. *Tetrahedron: Asymmetry* **1995**, *6*, 1973. (d) Yamada, I.; Yamaguchi, M.; Yamagishi, T. *Tetrahedron: Asymmetry* **1996**, *7*, 3339. (e) Sawamura, M.; Nakayama, Y.; Tang, W. M.; Ito, Y. *J. Org. Chem.* **1996**, *61*, 9090.

(3) (a) Borns, S.; Kadyrov, R.; Heller, D.; Baumann, W.; Spannenberg, A.; Kempe, R.; Holz, J.; Börner, A. *Eur. J. Inorg. Chem.* **1998**, 1291. (b) Gladiali, S.; Alberico, E.; Pulacchini, S.; Kollàr, L. *J. Mol. Catal. A* **1999**, *143*, 155. (c) Nandi, M.; Jin, J.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1999**, *121*, 9899. (d) Verdaguer, X.; Moyano, A.; Pericàs, M. A.; Riera, A.; Maestro, M. A.; Mahía, J. *J. Am. Chem. Soc.* **2000**, *122*, 10242. (e) Börner, A. *Eur. J. Inorg. Chem.* **2001**, 327, and references therein. (f) Kuriyama, M.; Nagai, K.; Yamada, K.; Miwa, Y.; Taga, T.; Tomioka, K. *J. Am. Chem. Soc.* **2002**, *124*, 8932.

(4) (a) Börner, A.; Ward, J.; Kortus, K.; Kagan, H. B. *Tetrahedron: Asymmetry* **1993**, *4*, 2219. (b) Fields, L. B.; Jacobsen, E. N. *Tetrahedron: Asymmetry* **1993**, *4*, 2229. (c) Kimmich, B. F. M.; Landis, C. R.; Powell, D. R. *Organometallics* **1996**, *15*, 4141. (d) Kless, A.; Lefeber, C.; Spannenberg, A.; Kempe, R.; Baumann, W.; Holz, J.; Börner, A. *Tetrahedron* **1996**, *52*, 14599. (e) Quirmbach, M.; Kless, A.; Holz, J.; Tararov, V.; Börner, A. *Tetrahedron: Asymmetry* **1999**, *10*, 1803.

(5) (a) Amrani, Y.; Lecomte, L.; Sinou, D. *Organometallics* **1989**, *8*, 542. (b) Toth, I.; Hanson, B. E.; Davis, M. E. *Tetrahedron: Asymmetry* **1990**, *1*, 913. (c) Sawamura, M.; Kitayama, K.; Ito, Y. *Tetrahedron: Asymmetry* **1993**, *4*, 1829. (d) RajanBabu, T. V.; Yan, Y. Y.; Shin, S. *J. Am. Chem. Soc.* **2001**, *123*, 10207. (e) Holz, J.; Heller, D.; Stürmer, R.; Börner, A. *Tetrahedron Lett.* **1999**, *40*, 7059. (f) Ohe, K.; Morioka, K.; Yonehara, K.; Uemura, S. *Tetrahedron: Asymmetry* **2002**, *13*, 2155.

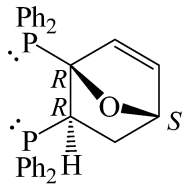
(6) (a) Nagel, U.; Kinzel, E. *J. Chem. Soc., Chem. Commun.* **1986**, 1098. (b) Bayston, D. J.; Fraser, J. L.; Ashton, M. R.; Baxter, A. D.; Polywka, M. E. C.; Moses, E. *J. Org. Chem.* **1998**, *63*, 3137. (c) Uozumi, Y.; Danjo, H.; Hayashi, T. *Tetrahedron Lett.* **1998**, *39*, 8303. (d) Aoki, K.; Shimada, T.; Hayashi, T. *Tetrahedron: Asymmetry* **2004**, *15*, 1771. (e) Steiner, I.; Aufdenblatten, R.; Togni, A.; Blaser, H. U.; Pugin, B. *Tetrahedron: Asymmetry* **2004**, *15*, 2307.

10.1021/om0509645 CCC: $33.50
Publication on Web 01/31/2006

the asymmetric Diels−Alder reaction involving heterocyclic dienes such as 3,4-dimethyl-1-phenylphosphole (DMPP), 2-diphenylphosphinofuran, and *N*-diphenylphosphinopyrrole.[7] In this paper, we demonstrate the facile synthesis of functionalized chiral phosphine metal complexes and the free ligands via the use of simple organic transformations for the introduction of functionalities to chiral phosphines with metal as protection. As the oxa- and azanorbornene skeletons have been shown to be easily derivatized with impressive versatility and selectivity,[8] the bis(diphenylphosphino)-substituted oxa- and azanorbornene metal complexes obtained from the chiral metal template-promoted asymmetric Diels−Alder reactions[7b,c] were subjected to various organic reactions for the introduction of functional groups.

Results and Discussion

Hydrogenation. It has been reported that the free bis(diphenylphosphino)-substituted oxanorbornene ligand (+)-**1** is unstable with respect to the retro-Diels−Alder reaction.[7b] One



(+)-**1**

simple way to deter the undesired cycloreversion reaction is to eliminate the carbon−carbon double bond within the oxanorbornene skeleton.[9] As there is precedence for catalytic hydrogenation of olefin-containing phosphine metal complexes,[7c,10] this reaction was thus attempted with the reported bis(diphenylphosphino)-substituted oxanorbornene platinum complex (−)-**2**. The hydrogenation of complex (−)-**2** proceeded smoothly with the use of Pd/C as catalyst (Scheme 1), and the saturated product (−)-**3** was isolated as yellow crystals from dichloromethane−diethyl ether in 90% yield, $[\alpha]_D$ −64 (CH_2Cl_2). The ^{31}P NMR spectrum of (−)-**3** in CD_2Cl_2 exhibited two doublets at δ 43.5 (J_{PP} = 7.6 Hz, J_{PtP} = 1831 Hz) and 48.8 (J_{PP} = 7.6 Hz, J_{PtP} = 3601 Hz). The molecular structure and absolute configurations of (−)-**3** were confirmed by X-ray crystallography (Figure 1). Selected bond lengths and angles are listed in Table 1. The absolute configurations at C(11), C(16), C(17), and C(19) are *S*, *R*, *R*, and *R*, respectively. It is noteworthy that the apparent inversion of configuration that takes place at C(19) in the hydrogenated product (−)-**3** is merely a consequence of the CIP sequence rules.[11] From the ^{31}P NMR studies, complex (−)-**3** is stable to cycloreversion reaction even upon heating.

The naphthylamine auxiliary could be removed chemoselectively from (−)-**3** by treatment with concentrated hydrochloric acid to generate (−)-**4** (Scheme 1). The neutral dichloro complex was subsequently crystallized from dichloromethane−diethyl ether as colorless crystals in 92% yield, $[\alpha]_D$ −37 (CH_2Cl_2).

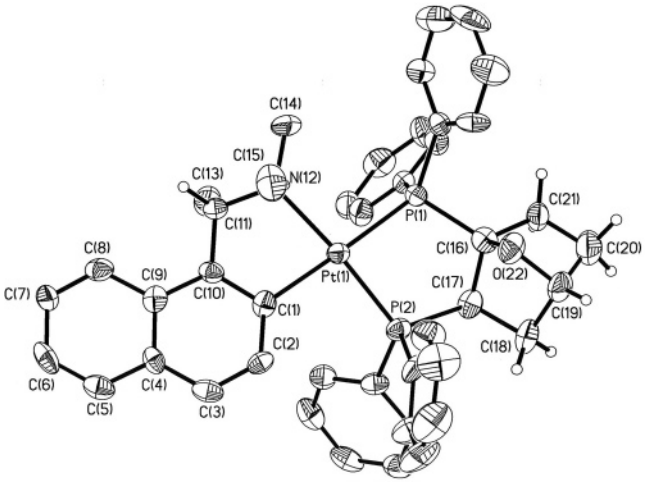


Figure 1. Molecular structure of the cationic complex (−)-**3** (thermal ellipsoids at the 50% probability level).

Scheme 1

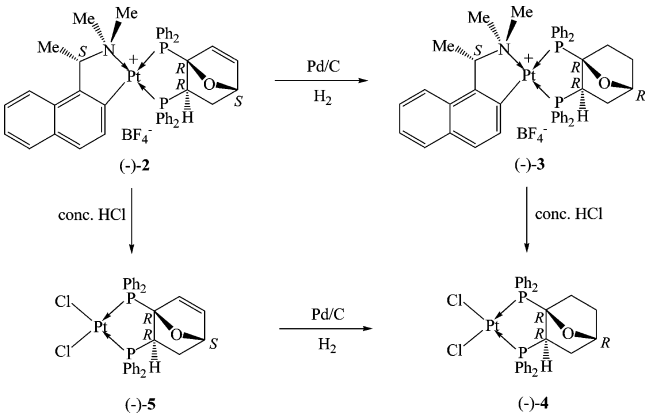


Table 1. Selected Bond Lengths (Å) and Angles (deg) for (−)-3

Pt(1)−C(1)	2.068(8)	C(1)−Pt(1)−N(12)	79.2(3)
Pt(1)−N(12)	2.131(6)	N(12)−Pt(1)−P(1)	100.3(2)
Pt(1)−P(1)	2.323(2)	N(12)−Pt(1)−P(2)	174.4(2)
Pt(1)−P(2)	2.233(2)	P(1)−Pt(1)−P(2)	85.20(8)
P(1)−C(16)	1.839(9)	P(1)−C(16)−O(22)	113.6(5)
P(2)−C(17)	1.861(8)	P(1)−C(16)−C(17)	110.6(5)
O(22)−C(16)	1.444(9)	P(2)−C(17)−C(16)	112.5(5)
O(22)−C(19)	1.45(1)	P(2)−C(17)−C(18)	115.6(6)
C(16)−C(17)	1.52(1)	C(16)−O(22)−C(19)	97.3(6)
C(16)−C(21)	1.54(1)	C(16)−C(17)−C(18)	101.5(7)
C(17)−C(18)	1.55(1)	C(17)−C(18)−C(19)	101.5(7)
C(18)−C(19)	1.53(1)	C(18)−C(19)−C(20)	107.7(8)
C(19)−C(20)	1.52(1)	C(19)−C(20)−C(21)	104.2(8)
C(20)−C(21)	1.51(1)	C(20)−C(21)−C(16)	100.9(7)
C(1)−Pt(1)−P(1)	174.0(3)	C(21)−C(16)−C(17)	112.0(7)
C(1)−Pt(1)−P(2)	95.5(2)		

(7) (a) Leung, P. H. *Acc. Chem. Res.* **2004**, *37*, 169, and references therein. (b) Yeo, W. C.; Vittal, J. J.; White, A. J. P.; Williams, D. J.; Leung, P. H. *Organometallics* **2001**, *20*, 2167. (c) Yeo, W. C.; Vittal, J. J.; Koh, L. L.; Tan, G. K.; Leung, P. H. *Organometallics* **2004**, *23*, 3474.

(8) (a) Katritzky, A. R., Rees, C. W., Bird, C. W., Cheeseman, G. W. H., Eds. *Comprehensive Heterocyclic Chemistry*; Pergamon: Oxford, U. K., 1984; Vol. 4. (b) Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Bird, C. W., Eds. *Comprehensive Heterocyclic Chemistry II*; Pergamon: Oxford, U.K., 1996; Vol. 2. (c) Lipshutz, B. H. *Chem. Rev.* **1986**, *86*, 795. (d) Suami, T. *Pure Appl. Chem.* **1987**, *59*, 1509. (e) Vogel, P.; Fattori, D.; Gasparini, F.; Le Drian, C. *Synlett* **1990**, 173. (f) Lautens, M. *Synlett* **1993**, 177. (g) Chiu, P.; Lautens, M. *Top. Curr. Chem.* **1997**, *190*, 1. (h) Kappe, C. O.; Murphree, S. S.; Padwa, A. *Tetrahedron* **1997**, *53*, 14179. (i) Jiang, S.; Singh, G. *Tetrahedron* **1998**, *54*, 4697. (j) Vogel, P.; Cossy, J.; Plumet, J.; Arjona, O. *Tetrahedron* **1999**, *55*, 13521. (k) Kricka, L. J.; Vernon, J. M. *Adv. Heterocycl. Chem.* **1974**, *16*, 87. (l) Chen, Z.; Trudell, M. L. *Chem. Rev.* **1996**, *96*, 1179.

(9) (a) Schuda, P. F.; Bennett, J. M. *Tetrahedron Lett.* **1982**, *23*, 5525. (b) Gschwend, H. W.; Hillman, M. J.; Kisis, B. *J. Org. Chem.* **1976**, *41*, 104. (c) Ager, D. J.; East, M. B. *Heterocycles* **1994**, *37*, 1789.

(10) Ruwee, J.; Martin-Alvarez, J. M.; Horn, C. R.; Bauer, E. B.; Szafert, S.; Lis, T.; Hampel, F.; Cagle, P. C.; Gladysz, J. A. *Chem. Eur. J.* **2001**, *7*, 3931.

(11) Cahn, R. S.; Ingold, C. K.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385.

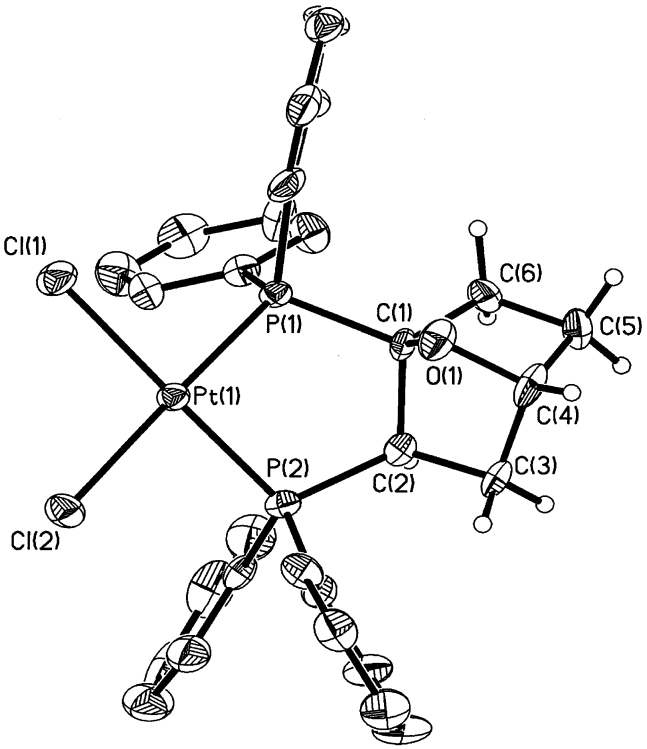


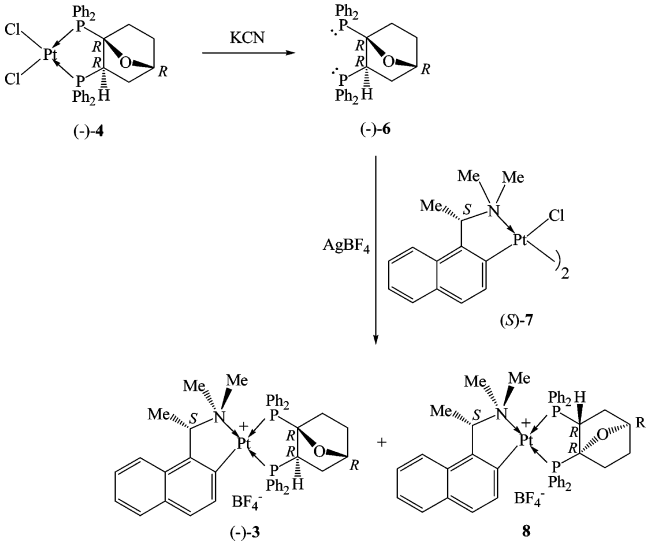
Figure 2. Molecular structure of the dichloro complex (−)-**4** (thermal ellipsoids at the 50% probability level).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for (−)-4

Pt(1)−P(1)	2.207(2)	P(1)−Pt(1)−Cl(1)	89.14(7)
Pt(1)−P(2)	2.218(2)	P(1)−Pt(1)−Cl(2)	177.39(7)
Pt(1)−Cl(1)	2.363(2)	P(1)−Pt(1)−P(2)	87.08(7)
Pt(1)−Cl(2)	2.358(2)	P(2)−Pt(1)−Cl(1)	172.71(8)
P(1)−C(1)	1.870(7)	P(2)−Pt(1)−Cl(2)	91.56(8)
P(2)−C(2)	1.853(8)	P(1)−C(1)−C(2)	111.3(5)
O(1)−C(1)	1.423(9)	P(2)−C(2)−C(1)	112.4(5)
O(1)−C(4)	1.461(9)	C(1)−O(1)−C(4)	95.0(5)
C(1)−C(2)	1.54(1)	C(1)−C(2)−C(3)	99.3(6)
C(2)−C(3)	1.57(1)	C(2)−C(3)−C(4)	101.5(6)
C(3)−C(4)	1.54(1)	C(3)−C(4)−C(5)	109.9(8)
C(4)−C(5)	1.48(1)	C(4)−C(5)−C(6)	101.0(6)
C(5)−C(6)	1.57(1)	C(6)−C(1)−C(2)	111.9(6)
C(6)−C(1)	1.53(1)		

The ^{31}P NMR spectrum of (−)-**4** in CD_2Cl_2 showed a pair of doublets at δ 39.7 (J_{PP} = 9.5 Hz, J_{PtP} = 3647 Hz) and 50.3 (J_{PP} = 9.5 Hz, J_{PtP} = 3559 Hz). The absolute configurations and molecular structure of (−)-**4** were confirmed by X-ray structural analysis (Figure 2). The absolute configurations at C(1), C(2), and C(4) are *R*, *R*, and *R*, respectively. Selected bond lengths and angles are listed in Table 2. Similarly, complex (−)-**4** is stable both in the crystalline state and in solution, as the ^{31}P NMR studies and optical rotation measurement showed that the sample remained unchanged after being kept at room temperature for 3 months. Alternatively, the hydrogenated dichloro complex (−)-**4** could be obtained by hydrogenation of the reported dichloro complex (−)-**5**[7b] with Pd/C as catalyst (Scheme 1). However, this reaction required higher catalyst loading and longer reaction time, compared to the hydrogenation of the template complex (−)-**2**. Nevertheless, hydrogenation of (−)-**5** is feasible and (−)-**4** was isolated in 94% yield. It is noteworthy that the presence of an external catalyst (Pd/C) is essential for the hydrogenation of both platinum complexes (−)-**2** and (−)-**5**, as no reaction was observed without the palladium catalyst.

Scheme 2



Further treatment of (−)-**4** with aqueous cyanide liberated the optically pure free diphosphine ligand (−)-**6** (Scheme 2) as a white solid in 95% yield, $[\alpha]_D$ −26 (CH_2ClCH_2Cl). The ^{31}P NMR spectrum of (−)-**6** in $CDCl_3$ showed two doublets at δ −6.4 and −7.5 ($^3J_{PP}$ = 99.2 Hz). In contrast to (+)-**1**, saturated diphosphine ligand (−)-**6** is stable toward the retro-Diels−Alder reaction, as the ^{31}P NMR studies showed that it remained unchanged after being kept at room temperature in the solid state under inert atmosphere for 6 weeks. Although hydrogenation of the oxanorbornene double bond does not result in the introduction of functionalities, saturation of the double bond indeed stabilizes the free diphosphine ligand, which is otherwise prone to the retro-cycloaddition reaction.

Recoordination of (−)-**6** to the optically pure dimeric complex (*S*)-**7** in the presence of silver tetrafluoroborate generated two regioisomers,[7b,c] (−)-**3** and **8**, in a 1:1 ratio (Scheme 2). The ^{31}P NMR spectrum of the crude reaction mixture in CD_2Cl_2 exhibited two pairs of doublets of equal intensities, with a pair of them being identical to that recorded previously for (−)-**3**. The other pair of doublets was observed at δ 38.4 (J_{PP} = 7.6 Hz, J_{PtP} = 1755 Hz) and 55.3 (J_{PP} = 7.6 Hz, J_{PtP} = 3769 Hz) and could be assigned to the regioisomer **8**. Importantly, this recoordination reaction confirmed that the liberated (−)-**6** retains the same molecular structure as the diphosphine ligand in complex (−)-**3**.

Hydroboration. Apart from hydrogenation, transformation of the double bond to selected functionalities could be accomplished using appropriate organic reactions. However, when such organic transformations are performed on phosphine metal complexes, potential complicating factors must be considered. For example, the hydroboration of allyl and vinylphosphine metal complexes with boranes resulted in various competing reactions such as (a) metal reduction; (b) decomplexation of phosphine ligand from the metal, with the formation of a phosphine-borane adduct; and (c) alkene hydroboration.[12] Despite all these potential competing reactions, interestingly, the hydroboration of the optically pure diphosphine platinum template complex (−)-**2** has been found to proceed chemoselectively to give the desired products. Hydroboration of (−)-**2** with $BH_3{\cdot}SMe_2$, followed by oxidation with alkaline hydrogen peroxide, gave two products (Scheme 3). Prior to purification,

(12) Coles, S. J.; Faulds, P.; Hursthouse, M. B.; Kelly, D. G.; Ranger, G. C.; Toner, A. J.; Walker, N. M. *J. Organomet. Chem.* **1999**, *586*, 234.

Scheme 3

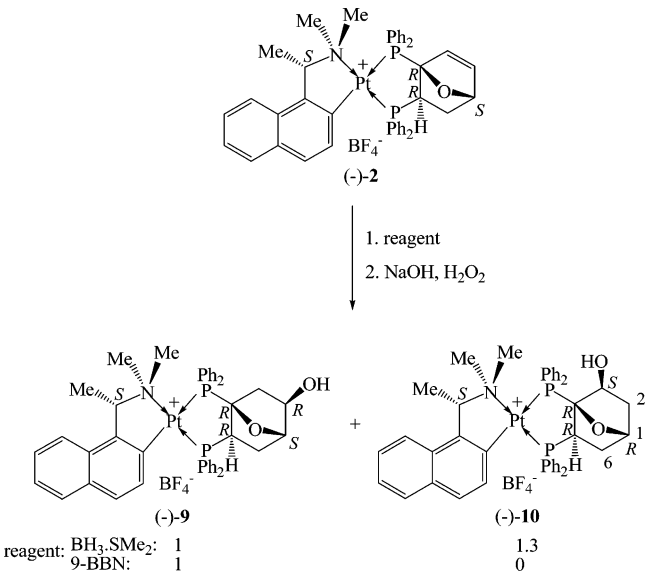


Table 3. Selected Bond Lengths (Å) and Angles (deg) for (−)-9

Pt(1)−C(1)	2.059(8)	C(1)−Pt(1)−N(12)	79.2(3)
Pt(1)−N(12)	2.145(6)	N(12)−Pt(1)−P(1)	99.7(2)
Pt(1)−P(1)	2.323(2)	N(12)−Pt(1)−P(2)	174.7(2)
Pt(1)−P(2)	2.238(2)	P(1)−Pt(1)−P(2)	85.66(7)
P(1)−C(16)	1.837(8)	P(1)−C(16)−O(22)	113.4(5)
P(2)−C(17)	1.880(7)	P(1)−C(16)−C(17)	111.5(5)
O(22)−C(16)	1.441(8)	P(2)−C(17)−C(16)	111.2(5)
O(22)−C(19)	1.48(1)	P(2)−C(17)−C(18)	116.0(6)
C(16)−C(17)	1.55(1)	C(16)−O(22)−C(19)	95.6(6)
C(16)−C(21)	1.53(1)	C(16)−C(17)−C(18)	101.8(6)
C(17)−C(18)	1.54(1)	C(17)−C(18)−C(19)	101.4(7)
C(18)−C(19)	1.54(1)	C(18)−C(19)−C(20)	112.1(8)
C(19)−C(20)	1.49(1)	C(19)−C(20)−C(21)	101.8(7)
C(20)−C(21)	1.50(1)	C(19)−C(20)−O(23)	110.5(9)
C(20)−O(23)	1.43(1)	C(21)−C(20)−O(23)	111.2(8)
C(1)−Pt(1)−P(1)	173.1(2)	C(20)−C(21)−C(16)	103.0(7)
C(1)−Pt(1)−P(2)	95.6(2)	C(21)−C(16)−C(17)	110.2(6)

the ^{31}P NMR spectrum of the crude reaction mixture in CD_2Cl_2 exhibited two pairs of doublets in the ratio of 1.3:1. The two products were separated by silica column chromatography. The minor product (−)-**9** was isolated from dichloromethane−diethyl ether as pale yellow crystals in 30% yield, $[\alpha]_D$ −73 (CH_2Cl_2). The ^{31}P NMR spectrum of this crystallized product in CD_2Cl_2 exhibited two doublets at δ 41.5 (J_{PP} = 7.6 Hz, J_{PtP} = 1835 Hz) and 47.1 (J_{PP} = 7.6 Hz, J_{PtP} = 3605 Hz). The molecular structure of this minor product was subsequently confirmed by X-ray crystallography to be complex (−)-**9**, as depicted in Scheme 3. Selected bond distances and angles are given in Table 3. The geometry at platinum is distorted square planar with cis angles at Pt ranging from 79.2(3)° to 99.7(2)°. The structural analysis affirmed that the bis(diphenylphosphino)-substituted oxanorbornane platinum template structure is intact, with the addition of a hydroxy group at C(20) (Figure 3). The stereogenic centers at C(11), C(16), C(17), C(19), and C(20) are established as adopting the *S*, *R*, *R*, *S*, and *R* absolute configurations, respectively. The ^{1}H and ^{1}H−^{1}H ROESY NMR studies are consistent with the X-ray structural analysis. The absence of coupling between the bridgehead proton H(18) and adjacent endo proton H(19)[13] and the presence of NOE interactions [H(19)−H(18) and H(19)−H(16)] are in agreement with the structure in which the hydroxy group adopts the *exo* position at C(20). This *exo* stereochemistry of the hydroxy group is in accord with the preferential attack of the hydroborating agent on the oxanorbornene double bond from the sterically less hindered *exo* face, followed by stereospecific oxidation with retention of configuration.[14]

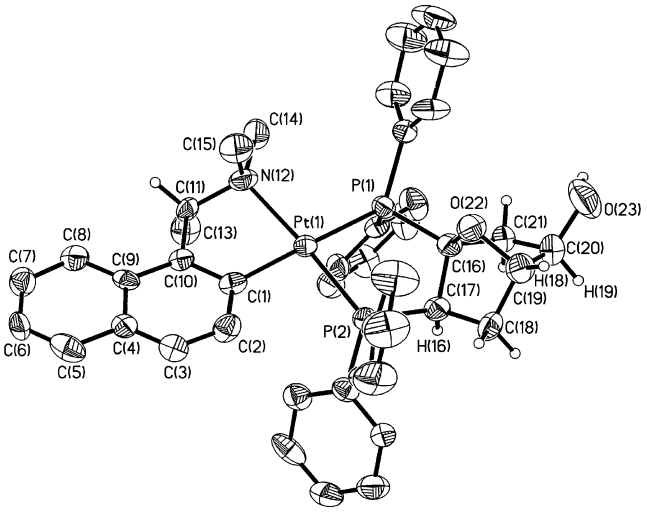


Figure 3. Molecular structure of the cationic complex (−)-**9** (thermal ellipsoids at the 50% probability level).

The major hydroboration product (−)-**10** was subsequently isolated from dichloromethane−diethyl ether as pale yellow crystals in 32% yield, $[\alpha]_D$ −32 (CH_2Cl_2). The ^{31}P NMR spectrum of this crystallized product in CD_2Cl_2 exhibited a pair of doublets at δ 46.7 (J_{PP} = 7.6 Hz, J_{PtP} = 1839 Hz) and 50.3 (J_{PP} = 7.6 Hz, J_{PtP} = 3628 Hz). Although suitable single crystals for X-ray structural analysis could not be obtained despite various efforts, the MS(ESI) (m/z = 875, M^+) analysis for this crystallized product and complex (−)-**9** showed that they are structural isomers. Due to the low steric requirement of borane, the hydroboration of disubstituted internal olefins (steric factors of the substituents have only little effect) is known to proceed with low regioselectivity.[15] Hence it is in concert that two isomeric products, (−)-**9** and (−)-**10** (with hydroxy groups at different carbon atoms, but both adopt the *exo* position due to preferential attack from the *exo* face), were formed in comparable amounts from the hydroboration−oxidation of (−)-**2**. In addition to MS(ESI), the assignment of the major product to (−)-**10** is supported by elemental analysis and ^{1}H, ^{31}P, and ^{1}H−^{1}H ROESY NMR studies. The NOE interactions [H(5)−H(3) (present), H(2*endo*)−H(3) (present), and H(1)−H(3) (absent)] and the presence of coupling between bridgehead proton H(1) and adjacent *exo* proton H(2*exo*)[13] are consistent with the *exo* stereochemistry of the hydroxy group at C(3).

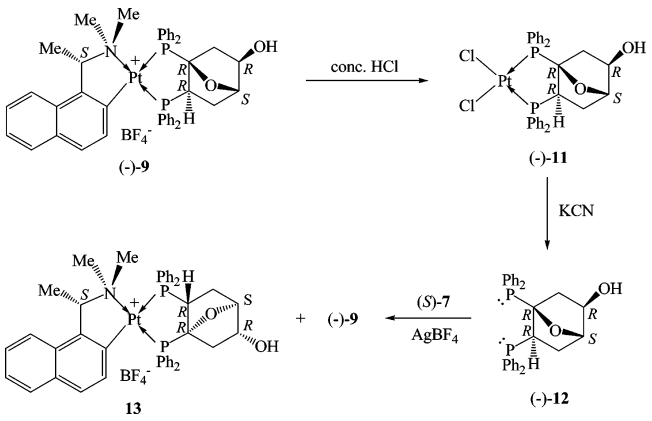
To improve the regioselectivity for the hydroboration of (−)-**2**, the use of a sterically more demanding hydroborating agent was attempted. The hydroborating agent 9-borabicyclo[3.3.1]-nonane (9-BBN) was chosen because of its commercial availability and its remarkable regioselectivity in hydroboration

(13) (a) McCasland, G. E.; Furuta, S.; Durham, L. J. *J. Org. Chem.* **1966**, *31*, 1516. (b) Balthazor, T. M.; Gaede, B.; Korte, D. E.; Shieh, H. S. *J. Org. Chem.* **1984**, *49*, 4547. (c) Fischer, K.; Hünig, S. *J. Org. Chem.* **1987**, *52*, 564. (d) Feringa, B. L.; Gelling, O. J.; Meesters, L. *Tetrahedron Lett.* **1990**, *31*, 7201. (e) Rogers, C.; Keay, B. A. *Can. J. Chem.* **1992**, *70*, 2929. (f) 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.

(14) (a) Brown, H. C.; Kawakami, J. H. *J. Am. Chem. Soc.* **1970**, *92*, 1990. (b) Brown, H. C.; Kawakami, J. H.; Liu, K. T. *J. Am. Chem. Soc.* **1973**, *95*, 2209. (c) Ancerewicz, J.; Vogel, P. *Helv. Chim. Acta* **1996**, *79*, 1415.

(15) (a) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1960**, *82*, 4708. (b) Brown, H. C. *Organic Syntheses via Boranes*; Wiley-Interscience: New York, 1975.

Scheme 4



reactions.[16] Hydroboration of (−)-**2** with 9-BBN, followed by oxidation with alkaline hydrogen peroxide, proceeded regioselectively to give (−)-**9** as the sole product (Scheme 3). Complex (−)-**9** was obtained as pale yellow crystals in 90% yield. Hence with the use of 9-BBN, the hydroboration−oxidation reaction represents an efficient method for the stereoselective introduction of a hydroxy group to the chelating chiral diphosphine in the platinum complex (−)-**2**. Besides the introduction of a hydroxy group from oxidative conversion of the hydroborated intermediate, the versatility of organoboranes in their conversion to other functionalities has been well established.[15b,17] Hence in principle, the introduction of various selected functional groups to the chiral phosphine metal complex could be achieved from the well-developed hydroboration reactions.

Interestingly, unlike the hydrogenation process, the hydroboration reaction is efficient only when applied to the metal template complex (−)-**2**. Hydroboration of the dichloro platinum complex (−)-**5** gave a complicated mixture of products, which is probably the result of various competing reactions.[12] In the presence of the kinetically inert chelating naphthylamine auxiliary, the diphosphine metal template complex (−)-**2** is apparently less susceptible to undesired reactions with the reagents.

Treatment of complex (−)-**9** with concentrated hydrochloric acid resulted in the chemoselective removal of the naphthylamine auxiliary (Scheme 4). The resultant neutral dichloro complex (−)-**11** was isolated from dichloromethane−diethyl ether as colorless crystals in 89% yield, $[\alpha]_D$ −37 (CH_2Cl_2). The ^{31}P NMR spectrum of (−)-**11** in CD_2Cl_2 exhibited a pair of doublets at δ 37.2 (J_{PP} = 9.5 Hz, J_{PtP} = 3658 Hz) and 48.6 (J_{PP} = 9.5 Hz, J_{PtP} = 3563 Hz). Ligand displacement of (−)-**11** with aqueous cyanide liberated the optically pure diphosphine ligand (−)-**12** (Scheme 4) as white solid in quantitative yield, $[\alpha]_D$ −33 ($CHCl_3$). The ^{31}P NMR spectrum of the diphosphine ligand in $CDCl_3$ showed two doublet resonances at δ −7.4 and −9.7 ($^3J_{PP}$ = 95.4 Hz). Free ligand (−)-**12** can be stored at room temperature for at least 2 months without changes under inert atmosphere. Recomplexation of the liberated diphosphine ligand (−)-**12** to (*S*)-**7**, followed by treatment with silver tetrafluoroborate, resulted only in the formation of (−)-**9** and its regioisomer **13** (Scheme 4). Hence it could be confirmed

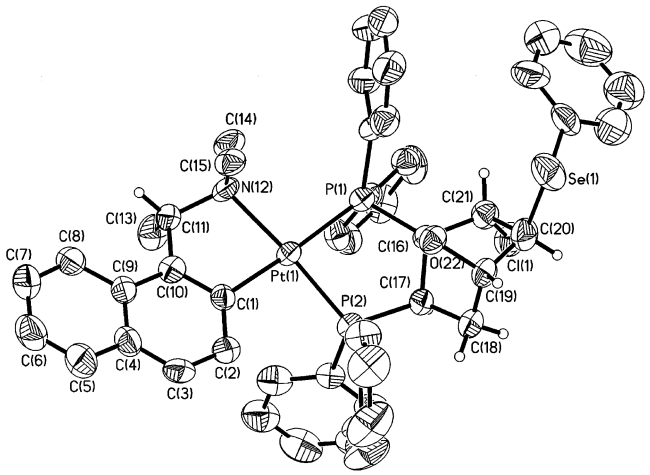
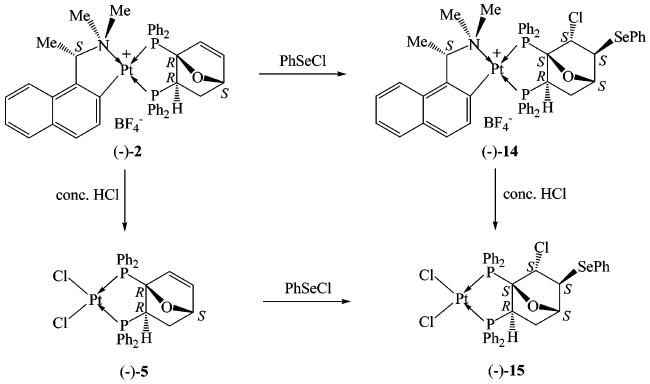


Figure 4. Molecular structure of the cationic complex (−)-**14** (molecule A) (thermal ellipsoids at the 50% probability level).

Scheme 5



that the stereochemistry and molecular structure of the hydroxyphosphine (−)-**12** remain unchanged upon the decomplexation process, which involved treatments with strong acid and cyanide.

Electrophilic Addition. Selenium electrophiles are known to react with olefins to generate, after addition of a nucleophile, the corresponding addition products.[18] Similar to the organic analogues, electrophilic addition of the oxanorbornenic double bond in platinum complex (−)-**2** with phenylselenenyl chloride proceeded smoothly and stereoselectively under mild conditions to give only a single product (Scheme 5). After purification by silica column chromatography, the addition product was isolated from dichloromethane−acetonitrile−petroleum ether as yellow crystals in 84% yield, $[\alpha]_D$ −57 (CH_2Cl_2). In CD_2Cl_2, the ^{31}P NMR spectrum of this isolated product revealed a pair of doublets at δ 42.3 (J_{PP} = 7.6 Hz, J_{PtP} = 1835 Hz) and 46.6 (J_{PP} = 7.6 Hz, J_{PtP} = 3597 Hz). The product was confirmed by X-ray analysis to be complex (−)-**14**, as depicted in Scheme 5. Complex (−)-**14** crystallizes with two crystallographically independent molecules in the asymmetric unit. However, they have identical molecular connectivities and absolute stereochemistries with only slight differences in bond lengths and angles. For simplicity, only one molecule (molecule A) is shown in Figure 4, and selected bond lengths and angles of both molecules are given in Table 4. The stereochemistry at C(11), C(16), C(17), C(19), C(20), and C(21) is established to adopt

(16) (a) Knights, E. F.; Brown, H. C. *J. Am. Chem. Soc.* **1968**, *90*, 5281. (b) Scouten, C. G.; Brown, H. C. *J. Org. Chem.* **1973**, *38*, 4092. (c) Brown, H. C.; Knights, E. F.; Scouten, C. G. *J. Am. Chem. Soc.* **1974**, *96*, 7765. (d) Brown, H. C.; Liotta, R.; Scouten, C. G. *J. Am. Chem. Soc.* **1976**, *98*, 5297.

(17) Matteson, D. S. *Stereodirected Synthesis with Organoboranes*; Springer-Verlag: Berlin, 1995.

(18) (a) Back, T. G., Ed. *Organoselenium Chemistry: A Practical Approach*; Oxford University Press: New York, 1999. (b) Wirth, T., Ed. *Organoselenium Chemistry: Modern Developments in Organic Synthesis*; Springer-Verlag: Berlin, 2000. (c) Clive, D. L. J. *Tetrahedron* **1978**, *34*, 1409. (d) Liotta, D. *Acc. Chem. Res.* **1984**, *17*, 28. (e) Wirth, T. *Angew. Chem., Int. Ed.* **2000**, *39*, 3740.

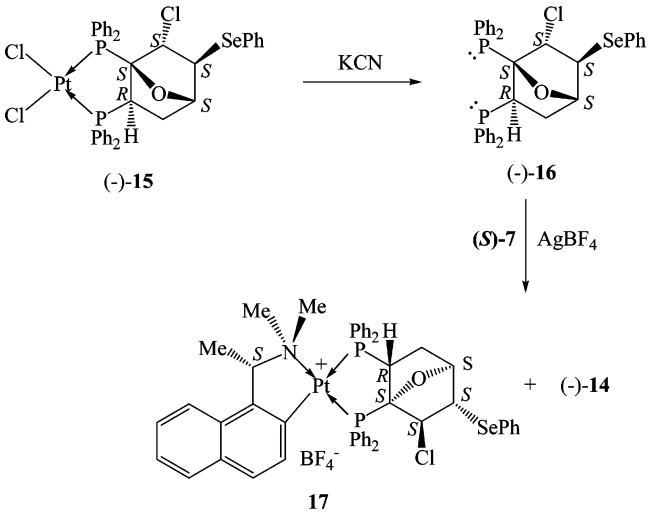
Table 4. Selected Bond Lengths (Å) and Angles (deg) for (−)-14

	molecule A	molecule B
Pt(1)−C(1)	2.075(7)	2.068(6)
Pt(1)−N(12)	2.151(5)	2.155(5)
Pt(1)−P(1)	2.323(2)	2.291(2)
Pt(1)−P(2)	2.249(2)	2.236(2)
P(1)−C(16)	1.843(7)	1.853(7)
P(2)−C(17)	1.862(7)	1.888(6)
O(22)−C(16)	1.434(8)	1.428(8)
O(22)−C(19)	1.451(8)	1.451(8)
C(16)−C(17)	1.582(9)	1.560(9)
C(16)−C(21)	1.55(1)	1.568(9)
C(17)−C(18)	1.53(1)	1.537(9)
C(18)−C(19)	1.54(1)	1.55(1)
C(19)−C(20)	1.51(1)	1.525(9)
C(20)−C(21)	1.53(1)	1.55(1)
C(20)−Se(1)	2.000(8)	1.955(7)
C(21)−Cl(1)	1.794(7)	1.800(7)
C(1)−Pt(1)−P(1)	175.3(2)	171.5(2)
C(1)−Pt(1)−P(2)	97.6(2)	98.1(2)
C(1)−Pt(1)−N(12)	79.2(2)	79.2(2)
N(12)−Pt(1)−P(1)	98.1(2)	97.7(2)
N(12)−Pt(1)−P(2)	176.1(2)	170.2(2)
P(1)−Pt(1)−P(2)	85.27(6)	86.23(6)
P(1)−C(16)−O(22)	111.2(4)	110.5(4)
P(1)−C(16)−C(17)	111.6(5)	112.3(4)
P(2)−C(17)−C(16)	107.6(4)	107.1(4)
P(2)−C(17)−C(18)	115.9(5)	115.9(5)
C(16)−O(22)−C(19)	96.4(5)	96.9(5)
C(16)−C(17)−C(18)	99.2(6)	99.5(5)
C(17)−C(18)−C(19)	102.4(5)	102.3(5)
C(18)−C(19)−C(20)	108.7(7)	111.2(6)
C(19)−C(20)−C(21)	99.7(6)	100.7(5)
C(19)−C(20)−Se(1)	109.7(6)	108.8(5)
C(21)−C(20)−Se(1)	112.4(5)	110.9(5)
C(20)−C(21)−C(16)	103.0(6)	101.4(5)
C(20)−C(21)−Cl(1)	110.3(5)	112.4(5)
C(16)−C(21)−Cl(1)	115.5(5)	112.8(5)
C(21)−C(16)−C(17)	110.4(6)	113.2(5)

the *S*, *S*, *R*, *S*, *S*, and *S* absolute configurations, respectively. The phenylselenenyl group is in the *exo* position at C(20), while the chloro substituent adopts an *endo* stereo arrangement at C(21). Apparently, the reaction is in accord with the preferential attack of the selenium electrophile on the double bond from the sterically less hindered *exo* face with the formation of the three-membered ring seleniranium ion intermediate, which is followed by ring-opening nucleophilic attack by the displaced chloride ion from the *endo* face to give the anti-addition product.[8e,18−20] For complex (−)-**2**, the two-step electrophilic addition reaction proceeds stereoselectively to generate the sterically less hindered addition product (−)-**14** as the sole product.[8e,18−20]

Chemoselective removal of the naphthylamine auxiliary from (−)-**14** was achieved by treatment with concentrated hydrochloric acid (Scheme 5). After purification by silica column chromatography, the neutral dichloro complex (−)-**15** was isolated as a yellow solid in 80% yield, $[\alpha]_D$ −52 (CH_2Cl_2). The ^{31}P NMR spectrum of (−)-**15** in CD_2Cl_2 showed two doublets at δ 37.1 (J_{PP} = 9.5 Hz, J_{PtP} = 3696 Hz) and 46.8 (J_{PP} = 9.5 Hz, J_{PtP} = 3525 Hz). Alternatively, complex (−)-**15** could be obtained by addition of phenylselenenyl chloride to the dichloro platinum complex (−)-**5** (Scheme 5). Similarly, the electrophilic addition reaction proceeded stereoselectively to generate (−)-**15** as the only product, which was isolated in 75% yield. Hence unlike hydroboration, the electrophilic addition reaction with this selenium electrophile is compatible with both the dichloro and template metal complexes.

Scheme 6



Further treatment of (−)-**15** with aqueous cyanide liberated the optically pure diphosphine ligand (−)-**16** (Scheme 6) as a white solid in 95% yield, $[\alpha]_D$ −39 ($CHCl_3$). The ^{31}P NMR spectrum of the diphosphine ligand in $CDCl_3$ exhibited a pair of doublets at δ −12.7 and −14.0 ($^3J_{PP}$ = 49.6 Hz). Recoordination of (−)-**16** to (*S*)-**7** followed by counterion exchange resulted in the formation of complex (−)-**14** and its regioisomer **17** (Scheme 6), which confirmed that the functionalized chiral diphosphine ligand in complex (−)-**14** is stable toward treatments with strong acid and cyanide.

Organic selenides are known to be readily oxidized to selenoxides, which undergo subsequent syn-elimination with the β-hydrogen under mild conditions to generate the corresponding alkenes together with selenenic acid as the byproduct.[18,21] Indeed, reaction of complex (−)-**14** with hydrogen peroxide in dichloromethane−ethanol proceeded smoothly to form the elimination product (−)-**18** (Scheme 7). Complex (−)-**18** was isolated from dichloromethane−acetonitrile−diethyl ether as yellow lumpy crystals in 83% yield, $[\alpha]_D$ −169 (CH_2Cl_2). The ^{31}P NMR spectrum of this crystallized product in CD_2Cl_2 revealed a pair of doublets at δ 49.4 (J_{PP} = 7.6 Hz, J_{PtP} = 3643 Hz) and 51.3 (J_{PP} = 7.6 Hz, J_{PtP} = 1823 Hz). Although suitable single crystals for X-ray crystallography could not be obtained, elemental analysis and MS(ESI) (m/z = 891, M^+) of (−)-**18** are in agreement with the structure as depicted in Scheme 7. From the ^1H and $^1H-^1H$ ROESY NMR studies, the presence of proton−proton coupling and NOE interaction between the bridgehead proton H(1) and the olefinic proton H(2) are also supportive of the vinyl chloride complex (−)-**18**. Such regioselective syn-elimination to form the vinyl halide product is also in accord with the elimination of similar organic oxanorbornane selenoxides reported in the literature.[8e,22]

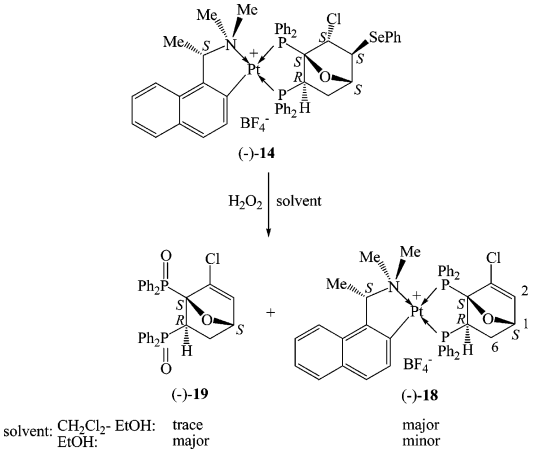
(19) (a) Arjona, O.; De La Pradilla, R. F.; Pérez, R. A.; Plumet, J.; Viso, A. *Tetrahedron Lett.* **1987**, *28*, 5549. (b) Arjona, O.; De La Pradilla, R. F.; Plumet, J.; Viso, A. *Tetrahedron* **1989**, *45*, 4565. (c) Arjona, O.; De La Pradilla, R. F.; Pita-Romero, I.; Plumet, J.; Viso, A. *Tetrahedron* **1990**, *46*, 8199. (d) Arjona, O.; De La Pradilla, R. F.; Plumet, J.; Viso, A. *J. Org. Chem.* **1991**, *56*, 6227. (e) Arjona, O.; De La Pradilla, R. F.; Plumet, J.; Viso, A. *J. Org. Chem.* **1992**, *57*, 772.

(20) (a) Sharpless, K. B.; Lauer, R. F. *J. Org. Chem.* **1974**, *39*, 429. (b) Raucher, S. *J. Org. Chem.* **1977**, *42*, 2950. (c) Raucher, S. *Tetrahedron Lett.* **1977**, 3909. (d) Liotta, D.; Zima, G. *Tetrahedron Lett.* **1978**, 4977. (e) Schmid, G. H.; Garratt, D. G. *Tetrahedron* **1978**, *34*, 2869. (f) Liotta, D.; Zima, G.; Saindane, M. *J. Org. Chem.* **1982**, *47*, 1258. (g) Schmid, G. H.; Garratt, D. G. *J. Org. Chem.* **1983**, *48*, 4169.

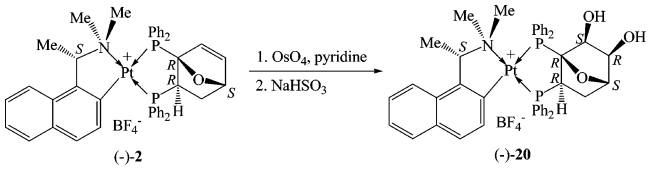
(21) Reich, H. J. *Acc. Chem. Res.* **1979**, *12*, 22.

(22) (a) Fattori, D.; de Guchteneere, E.; Vogel, P. *Tetrahedron Lett.* **1989**, *30*, 7415. (b) Black, K. A.; Vogel, P. *J. Org. Chem.* **1986**, *51*, 5341. (c) Warm, A.; Vogel, P. *J. Org. Chem.* **1986**, *51*, 5348.

Scheme 7



Scheme 8



A point to note is that, when the oxidation of (−)-**14** with hydrogen peroxide was performed in ethanol, the desired product (−)-**18** was formed only in small amount (Scheme 7). The predominant product of this reaction exhibited two singlets in the ^{31}P NMR spectrum ($CDCl_3$), at δ 19.7 and 27.8. The absence of phosphorus−platinum couplings indicates that the phosphorus atoms are not coordinated on platinum. In addition, the MS-(FAB) [m/z = 531, $(M + 1)^+$] analysis of this product, the presence of a P═O absorption band at 1200 cm^{-1} in the infrared spectrum, and the presence of an olefinic proton resonance signal in the ^{1}H NMR spectrum supported the structure of the phosphine oxide (−)-**19** as depicted in Scheme 7. Apparently, oxidation of the diphosphine ligand on the metal complex is a major side reaction for the oxidative syn-elimination reaction of (−)-**14** with H_2O_2 in ethanol.

Dihydroxylation. Dihydroxylation of alkenes with osmium tetraoxide is the most efficient and reliable transformation for the synthesis of cis-diols.[23] Dihydroxylation of complex (−)-**2** using stoichiometric osmium tetraoxide with pyridine, followed by reductive hydrolysis, proceeded stereoselectively to give (−)-**20** as the sole product (Scheme 8). After purification by column chromatography, complex (−)-**20** was isolated by crystallization from dichloromethane−diethyl ether as yellow crystals in 55% yield, $[\alpha]_D$ −18 (CH_2Cl_2). The ^{31}P NMR spectrum of this crystallized product in CD_2Cl_2 revealed a pair of doublets at δ 43.4 (J_{PP} = 7.6 Hz, J_{PtP} = 1839 Hz) and 48.1 (J_{PP} = 7.6 Hz, J_{PtP} = 3647 Hz). The molecular structure and absolute configurations of (−)-**20** were confirmed by X-ray analysis (Figure 5). Selected bond distances and angles are given in Table 5. The geometry at platinum is distorted square planar with cis angles at Pt ranging from 78.1(2)° to 100.3(1)°. The absolute configurations at C(11), C(16), C(17), C(19), C(20), and C(21) are *S*, *R*, *R*, *S*, *R*, and *S*, respectively, with both the hydroxy groups adopting the *exo* stereochemistry. The high stereoselectivity of this dihydroxylation reaction can be attributed again to the preferential attack of the osmium reagent on the oxanorbornene double bond from the sterically less hindered *exo* face, followed by reductive hydrolysis of the resultant osmium(VI) intermediate to form the corresponding *exo* cis-diol.[23a,24] Apart from the stoichiometric reaction, dihydroxylation of (−)-**2** could also be achieved using catalytic osmium tetraoxide with alkaline *tert*-butyl hydroperoxide.[25] However, this catalytic reaction is less efficient, as some other yet unidentified products were also formed. Nevertheless, complex (−)-**20** could be obtained in 20% yield from this catalytic process.

Although the cis-diol complex (−)-**20** could be obtained readily by dihydroxylation, the attempted liberation of the functionalized diphosphine ligand by acid treatment, followed by ligand displacement with aqueous cyanide, resulted in the decomposition of the diphosphine ligand. Another point to note is that, similar to hydroboration, the dihydroxylation reaction is applicable for the template complex (−)-**2**, but not the corresponding dichloro complex (−)-**5**. Similar dihydroxylation of complex (−)-**5** does not result in the formation of the desired product.

Besides complexes (−)-**2** and (−)-**5**, simple organic transformations of the reported bis(diphenylphosphino)-substituted

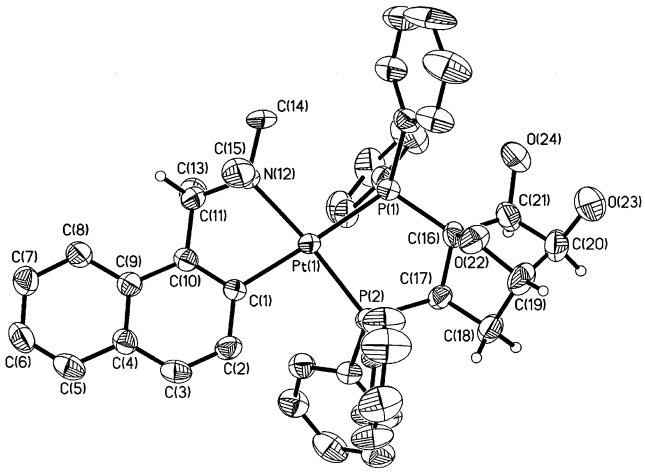


Figure 5. Molecular structure of the cationic complex (−)-**20** (thermal ellipsoids at the 50% probability level).

Table 5. Selected Bond Lengths (Å) and Angles (deg) for (−)-20

Pt(1)−C(1)	2.072(5)	N(12)−Pt(1)−P(1)	100.3(1)
Pt(1)− N(12)	2.133(5)	N(12)−Pt(1)−P(2)	173.8(1)
Pt(1)−P(1)	2.340(2)	P(1)−Pt(1)−P(2)	85.76(5)
Pt(1)−P(2)	2.231(1)	P(1)−C(16)−O(22)	113.3(4)
P(1)−C(16)	1.857(6)	P(1)−C(16)−C(17)	111.3(4)
P(2)−C(17)	1.870(6)	P(2)−C(17)−C(16)	111.8(4)
O(22)−C(16)	1.446(7)	P(2)−C(17)−C(18)	114.5(5)
O(22)−C(19)	1.464(8)	C(16)−O(22)−C(19)	96.1(5)
C(16)−C(17)	1.540(9)	C(16)−C(17)−C(18)	101.8(5)
C(16)−C(21)	1.549(8)	C(17)−C(18)−C(19)	101.0(5)
C(17)−C(18)	1.553(9)	C(18)−C(19)−C(20)	111.0(7)
C(18)−C(19)	1.54(1)	C(19)−C(20)−C(21)	101.2(5)
C(19)−C(20)	1.49(1)	C(19)−C(20)−O(23)	112.4(9)
C(20)−C(21)	1.57(1)	C(21)−C(20)−O(23)	109.7(7)
C(20)−O(23)	1.40(1)	C(20)−C(21)−C(16)	101.0(6)
C(21)−O(24)	1.41(1)	C(20)−C(21)−O(24)	110.7(6)
C(1)−Pt(1)−P(1)	172.8(2)	C(16)−C(21)−O(24)	112.0(6)
C(1)−Pt(1)−P(2)	96.1(2)	C(21)−C(16)−C(17)	109.0(5)
C(1)−Pt(1)−N(12)	78.1(2)		

(23) (a) Schröder, M. *Chem. Rev.* **1980**, *80*, 187. (b) Lohray, B. B. *Tetrahedron: Asymmetry* **1992**, *3*, 1317. (c) Kolb, H. C.; VanNieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483.

(24) (a) Daniels, R.; Fischer, J. L. *J. Org. Chem.* **1963**, *28*, 320. (b) Vieira, E.; Vogel, P. *Helv. Chim. Acta* **1982**, *65*, 1700. (c) Schmidt, R. R.; Beitzke, C.; Forrest, A. K. *J. Chem. Soc., Chem. Commun.* **1982**, 909.

(25) (a) Sharpless, K. B.; Akashi, K. *J. Am. Chem. Soc.* **1976**, *98*, 1986. (b) Akashi, K.; Palermo, R. E.; Sharpless, K. B. *J. Org. Chem.* **1978**, *43*, 2063.

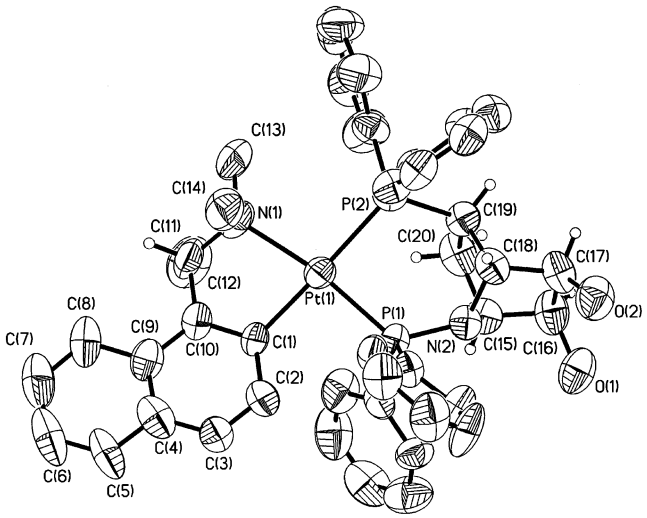


Figure 6. Molecular structure of the cationic complex (+)-**22** (thermal ellipsoids at the 50% probability level).

Scheme 9

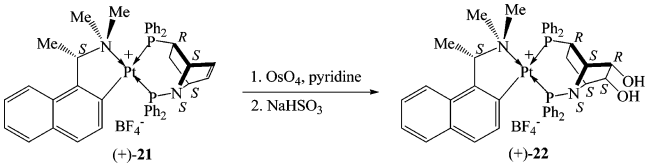


Table 6. Selected Bond Lengths (Å) and Angles (deg) for (+)-22

Pt(1)−C(1)	2.081(8)	P(1)−Pt(1)−P(2)	90.64(8)
Pt(1)−N(1)	2.188(7)	N(1)−Pt(1)−P(1)	170.5(2)
Pt(1)−P(1)	2.237(2)	N(1)−Pt(1)−P(2)	98.7(2)
Pt(1)−P(2)	2.347(2)	N(2)−P(1)−Pt(1)	122.2(3)
P(1)−N(2)	1.679(6)	C(19)−P(2)−Pt(1)	113.1(3)
P(2)−C(19)	1.848(9)	P(1)−N(2)−C(15)	123.2(5)
N(2)−C(15)	1.491(8)	P(1)−N(2)−C(18)	119.7(5)
N(2)−C(18)	1.46(1)	N(2)−C(15)−C(16)	100.1(6)
C(15)−C(16)	1.50(1)	N(2)−C(18)−C(17)	103.1(7)
C(16)−C(17)	1.56(1)	N(2)−C(15)−C(20)	102.0(7)
C(17)−C(18)	1.53(1)	N(2)−C(18)−C(19)	103.9(6)
C(18)−C(19)	1.53(1)	C(15)−C(16)−O(1)	111.0(8)
C(19)−C(20)	1.54(1)	C(17)−C(16)−O(1)	112.6(8)
C(15)−C(20)	1.54(1)	C(18)−C(17)−O(2)	112.9(8)
C(16)−O(1)	1.42(1)	C(16)−C(17)−O(2)	112.6(9)
C(17)−O(2)	1.38(1)	C(15)−C(16)−C(17)	102.7(7)
C(1)−Pt(1)−P(1)	91.9(2)	C(16)−C(17)−C(18)	100.8(7)
C(1)−Pt(1)−P(2)	175.6(2)	C(18)−C(19)−C(20)	100.8(7)
C(1)−Pt(1)−N(1)	78.6(3)	C(15)−C(20)−C(19)	103.3(7)

azanorbornene platinum complex (+)-**21**[7c] are also feasible. Dihydroxylation of (+)-**21** with stoichiometric OsO_4 and pyridine, followed by reductive hydrolysis, proceeded stereoselectively to generate complex (+)-**22** (Scheme 9). After purification by column chromatography, complex (+)-**22** was isolated as yellow crystals from dichloromethane−diethyl ether in 36% yield, $[\alpha]_D$ +8 (CH_2Cl_2). The ^{31}P NMR spectrum of this crystallized product in CD_2Cl_2 showed two doublets at δ 26.6 (J_{PP} = 24.8 Hz, J_{PtP} = 1827 Hz) and 55.2 (J_{PP} = 24.8 Hz, J_{PtP} = 3704 Hz). The molecular structure and absolute stereochemistry were established by X-ray crystallography (Figure 6 and Table 6). The absolute configurations at C(11), C(16), C(17), C(18), C(19), and N(2) are *S*, *S*, *S*, *R*, *S*, *R*, and *S* respectively. For complex (+)-**22**, two new stereogenic centers are created with the introduction of two hydroxy groups. The two cis hydroxy groups adopt the *exo* positions on the azanorbornane skeleton, thus supporting the preferential attack of the osmium reagent from the less hindered *exo* face of the azanorbornyl system.[14]

In conclusion, the use of simple organic transformations such as hydrogenation, hydroboration, electrophilic addition, and dihydroxylation for the synthesis of functionalized chiral phosphine metal complexes and free phosphine ligands has been demonstrated. In principle, with appropriate reaction conditions, many other organic transformations can be utilized for the functionalization of chiral phosphine ligands with metal as protection. This can serve as an alternative general route for the synthesis of functionalized chiral phosphine ligands and metal complexes.

Experimental Section

General Procedures. 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 AMX500 spectrometers. The spectral assignments in the ^1H NMR spectra are based on selective decoupling of the two types of ^{31}P nuclei and NOE data from 2D $^1H-^1H$ ROESY spectra.[26] The phase-sensitive ROESY NMR experiments were acquired into a 1024 × 512 matrix with a 250 ms spin locking time and a spin lock field strength such that $gB_1/2\pi$ = 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 solution in a 0.1 or 1 dm cell at 25 °C with a Perkin-Elmer Model 341 polarimeter. Melting points were determined on a Büchi melting point B-540 apparatus. Elemental and mass spectrometric analyses were performed by the Elemental Analysis Laboratory and the Mass Spectrometry Laboratory of the Department of Chemistry at the National University of Singapore, respectively.

Complexes (−)-**2**, (−)-**5**, (*S*)-**7**, and (+)-**21** were prepared as previously reported by our group.[7b,c] Phenylselenenyl chloride, osmium tetraoxide, $BH_3{\cdot}SMe_2$, and 9-BBN were purchased from Aldrich Chemical Co. and used directly.

Hydrogenation of (−)-2 and Isolation of [*SP*-4-4-{(*S*)-1-[1-(Dimethylamino)ethyl]naphthyl-*C*^{2},*N*}{(1*R*,4*R*,5*R*)-4,5-bis(diphenylphosphino)-7-oxabicyclo[2.2.1]hept-2-ane-*P*^{4},*P*^{5}}]platinum(II) tetrafluoroborate [(−)-3]. Hydrogen gas was bubbled slowly into a mixture of (−)-**2** (0.298 g, 0.315 mmol) and 10% Pd/C (0.030 g) in dichloromethane (30 mL) for 2 h at room temperature and atmospheric pressure. The mixture was then filtered through Celite, and complex (−)-**3** was obtained from dichloromethane−diethyl ether as yellow crystals: mp 366−367 °C (dec); $[\alpha]_D$ −64 (*c* 1.0, CH_2Cl_2); 0.270 g (90% yield). Anal. Calcd for $C_{44}H_{44}BF_4NOP_2Pt$: C, 55.8; H, 4.7; N, 1.5. Found: C, 55.8; H, 4.9; N, 1.4. ^{31}P NMR (CD_2Cl_2) δ 43.5 (d, 1P, J_{PP} = 7.6 Hz, J_{PtP} = 1831 Hz, *P*^{4}), 48.8 (d, 1P, J_{PP} = 7.6 Hz, J_{PtP} = 3601 Hz, *P*^{5}); ^1H NMR (CD_2Cl_2) δ 1.47−1.59 (m, 1H, H_{2exo}), 1.59−1.75 (m, 2H, H_{3endo}, H_{2endo}), 1.88 (d, 3H, $^3J_{HH}$ = 6.0 Hz, CH*Me*), 1.92−2.04 (m, 2H, H_{6exo}, H_{6endo}), 2.04−2.16 (m, 1H, H_{3exo}), 2.49 (d, 3H, $^4J_{PH}$ = 2.4 Hz, NMe_{ax}), 2.65−2.71 (m, 1H, H_5), 2.78 (dd, 3H, $^4J_{PH}$ = 3.9 Hz, $^4J_{PH}$ = 2.9 Hz, NMe_{eq}), 4.55−4.62 (m, 1H, H_1), 4.80 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.0 Hz, C*H*Me), 6.58−8.20 (m, 26H, aromatics).

Hydrogenation of (−)-5 and Isolation of [*SP*-4-3-{(1*R*,4*R*,5*R*)-Dichloro[4,5-bis(diphenylphosphino)-7-oxabicyclo[2.2.1]hept-2-ane-*P*^{4},*P*^{5}]}]platinum(II) [(−)-4]. Hydrogen gas was bubbled slowly into a solution of (−)-**5** (0.052 g, 0.071 mmol) and 10% Pd/C (0.037 g) in dichloromethane (30 mL) for 10 h at room temperature under atmospheric pressure. The mixture was filtered through Celite, and complex (−)-**4** was obtained from dichloromethane−diethyl ether as colorless crystals: mp 371−372 °C

(26) Aw, B. H.; Selvaratnam, S.; Leung, P. H.; Rees, N. H.; McFarlane, W. *Tetrahedron: Asymmetry* **1996**, *7*, 1753.

(dec); $[\alpha]_D$ −37 (*c* 0.8, CH_2Cl_2); 0.049 g (94% yield). Anal. Calcd for $C_{30}H_{28}Cl_2OP_2Pt$: C, 49.2; H, 3.9. Found: C, 49.0; H, 4.0. ^{31}P NMR (CD_2Cl_2) δ 39.7 (d, 1P, J_{PP} = 9.5 Hz, J_{PtP} = 3647 Hz, P^4), 50.3 (d, 1P, J_{PP} = 9.5 Hz, J_{PtP} = 3559 Hz, P^5); ^1H NMR (CD_2Cl_2) δ 1.56−1.81 (m, 3H, H_{2exo}, H_{2endo}, H_{3endo}), 1.88−2.00 (m, 2H, H_{6exo}, H_{6endo}), 2.04−2.18 (m, 1H, H_{3exo}), 2.79−2.86 (m, 1H, H_5), 4.68−4.73 (m, 1H, H_1), 7.33−8.12 (m, 20H, aromatics).

Removal of the Chiral Auxiliary in (−)-3 and Isolation of [*SP*-4-3-{(1*R*,4*R*,5*R*)-Dichloro[4,5-bis(diphenylphosphino)-7-oxabicyclo[2.2.1]hept-2-ane-*P*^{4},*P*^{5}]}]platinum(II) [(−)-4]. Complex (−)-**3** (0.200 g, 0.211 mmol), dissolved in dichloromethane (30 mL), and concentrated hydrochloric acid (10 mL) were stirred vigorously at room temperature for 1 day. The mixture was washed with water (4 × 40 mL) and dried ($MgSO_4$), and complex (−)-**4** was subsequently crystallized from dichloromethane−diethyl ether as colorless crystals, 0.143 g (92% yield).

Liberation of (1*R*,4*R*,5*R*)-4,5-Bis(diphenylphosphino)-7-oxabicyclo[2.2.1]hept-2-ane [(−)-6]. A solution of dichloro platinum complex (−)-**4** (0.111 g, 0.152 mmol) in dichloromethane (25 mL) was stirred vigorously with a saturated aqueous solution of potassium cyanide (2 g) for 3 h. The organic layer was separated, washed with water (3 × 20 mL), and dried ($MgSO_4$). Upon removal of the solvent, a white solid was obtained: $[\alpha]_D$ −26 (*c* 1.2, CH_2ClCH_2Cl); 0.067 g (95% yield). ^{31}P NMR ($CDCl_3$) δ −6.4 (d, 1P, $^3J_{PP}$ = 99.2 Hz, *P*), −7.5 (d, 1P, $^3J_{PP}$ = 99.2 Hz, *P*); ^1H NMR ($CDCl_3$) δ 1.50−1.99 (m, 6H, H_{2exo}, H_{2endo}, H_{3exo}, H_{3endo}, H_{6exo}, H_{6endo}), 2.72 (dd, 1H, $^3J_{HH}$ = 8.8 Hz, $^3J_{HH}$ = 5.6 Hz, H_5), 4.62 (t, 1H, $^3J_{HH}$ = $^3J_{HH}'$ = 1.9 Hz, H_1), 7.13−7.65 (m, 20H, aromatics).

Typical Procedure Used for the Recomplexation Reactions. Stoichiometric amounts of complex (*S*)-**7** and (−)-**6** were dissolved in dichloromethane, followed by the addition of aqueous $AgBF_4$, and stirred vigorously at room temperature for 1 h. The solution was filtered through Celite, washed with water, and dried ($MgSO_4$).

Hydroboration of (−)-2 Using BH_3·SMe_2. A solution of BH_3·SMe_2 in dichloromethane (1.0 M, 1.5 mL, 1.5 mmol) was added to a solution of (−)-**2** (0.401 g, 0.424 mmol) in dichloromethane (120 mL) at −20 °C. It was warmed to room temperature and stirred for 4 h. Then ethanol (40 mL) followed by aqueous NaOH solution (3 M, 1.5 mL, 4.5 mmol) and aqueous H_2O_2 solution (30%, 1.5 mL, 15 mmol) were added, and the mixture was stirred at room temperature for another 3 h. The solvent was removed under reduced pressure, and the reaction mixture was redissolved in dichloromethane (100 mL). The mixture was washed with water (3 × 100 mL), dried ($MgSO_4$), and chromatographed on a silica column with dichloromethane−acetone as eluent. The two isomeric products were subsequently crystallized from dichloromethane−diethyl ether.

[*SP*-4-4-{(*S*)-1-[1-(Dimethylamino)ethyl]naphthyl-*C*^{2},*N*}-{(1*S*,2*R*,4*R*,5*R*)-4,5-bis(diphenylphosphino)-2-hydroxy-7-oxabicyclo[2.2.1]hept-2-ane-*P*^{4},*P*^{5}}]platinum(II) tetrafluoroborate [(−)-9] was obtained as pale yellow crystals: mp > 400 °C; $[\alpha]_D$ −73 (*c* 0.1, CH_2Cl_2); 0.122 g (30% yield). Anal. Calcd for $C_{44}H_{44}BF_4NO_2P_2Pt$: C, 54.9; H, 4.6; N, 1.5. Found: C, 54.4; H, 4.9; N, 1.6. MS(ESI): *m*/*z* = 875, M^+. ^{31}P NMR (CD_2Cl_2) δ 41.5 (d, 1P, J_{PP} = 7.6 Hz, J_{PtP} = 1835 Hz, P^4), 47.1 (d, 1P, J_{PP} = 7.6 Hz, J_{PtP} = 3605 Hz, P^5); ^1H NMR (CD_2Cl_2) δ 1.75−1.87 (m, 2H, H_{3exo}, H_{6endo}), 1.90 (d, 3H, $^3J_{HH}$ = 6.0 Hz, CH*Me*), 1.91−1.99 (m, 1H, H_{6exo}), 2.04 (dd, 1H, $^2J_{HH}$ = 13.7 Hz, $^3J_{HH}$ = 6.4 Hz, H_{3endo}), 2.13 (d, 1H, $^3J_{HH}$ = 6.8 Hz, O*H*), 2.50 (d, 3H, $^4J_{PH}$ = 2.0 Hz, NMe_{ax}), 2.51−2.57 (m, 1H, H_5), 2.80 (dd, 3H, $^4J_{PH}$ = 3.8 Hz, $^4J_{PH}$ = 3.0 Hz, NMe_{eq}), 4.04−4.11 (m, 1H, H_2), 4.40 (d, 1H, $^3J_{HH}$ = 6.0 Hz, H_1), 4.80 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.0 Hz, C*H*Me), 6.56−8.19 (m, 26H, aromatics).

[*SP*-4-4-{(*S*)-1-[1-(Dimethylamino)ethyl]naphthyl-*C*^{2},*N*}-{(1*R*,3*S*,4*R*,5*R*)-4,5-bis(diphenylphosphino)-3-hydroxy-7-oxabicyclo[2.2.1]hept-2-ane-*P*^{4},*P*^{5}}]platinum(II) tetrafluoroborate [(−)-10] was obtained as pale yellow crystals: mp 338−339 °C (dec); $[\alpha]_D$ −32 (*c* 0.1, CH_2Cl_2); 0.129 g (32% yield). Anal. Calcd for $C_{44}H_{44}BF_4NO_2P_2Pt$: C, 54.9; H, 4.6; N, 1.5. Found: C, 55.2; H, 4.9; N, 1.4. MS(ESI): *m*/*z* = 875, M^+. ^{31}P NMR (CD_2Cl_2) δ 46.7 (d, 1P, J_{PP} = 7.6 Hz, J_{PtP} = 1839 Hz, P^4), 50.3 (d, 1P, J_{PP} = 7.6 Hz, J_{PtP} = 3628 Hz, P^5); ^1H NMR (CD_2Cl_2) δ 1.41−1.50 (m, 1H, H_{2exo}), 1.68 (d, 1H, $^3J_{HH}$ = 9.4 Hz, O*H*), 1.83 (d, 3H, $^3J_{HH}$ = 6.2 Hz, CH*Me*), 1.85−1.96 (m, 2H, H_{6exo}, H_{6endo}), 2.22 (dd, 1H, $^2J_{HH}$ = 13.1 Hz, $^3J_{HH}$ = 7.1 Hz, H_{2endo}), 2.44 (d, 3H, $^4J_{PH}$ = 2.0 Hz, NMe_{ax}), 2.62 (dd, 3H, $^4J_{PH}$ = 3.4 Hz, $^4J_{PH}$ = 2.7 Hz, NMe_{eq}), 2.65 (dt, 1H, $^3J_{HH}$ = 8.6 Hz, $^2J_{PH}$ = $^3J_{HH}$ = 3.4 Hz, H_5), 4.09 (ddd, 1H, $^3J_{HH}$ = 9.4 Hz, $^3J_{HH}$ = 7.1 Hz, $^3J_{HH}$ = 2.9 Hz, H_3), 4.68 (t, 1H, $^3J_{HH}$ = $^3J_{HH}'$ = 5.1 Hz, H_1), 4.74 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.2 Hz, C*H*Me), 6.60−8.61 (m, 26H, aromatics).

Hydroboration of (−)-2 Using 9-BBN. Isolation of [*SP*-4-4-{(*S*)-1-[1-(Dimethylamino)ethyl]naphthyl-*C*^{2},*N*}{(1*S*,2*R*,4*R*,5*R*)-4,5-bis(diphenylphosphino)-2-hydroxy-7-oxabicyclo[2.2.1]hept-2-ane-*P*^{4},*P*^{5}}]platinum(II) tetrafluoroborate [(−)-9]. A solution of 9-BBN in hexanes (0.4 M, 5.0 mL, 2.0 mmol) was added to a solution of (−)-**2** (0.590 g, 0.625 mmol) in 1,2-dichloroethane (130 mL) and heated at about 75 °C for 14 h. Then ethanol (40 mL) followed by aqueous NaOH solution (3 M, 2 mL, 6 mmol) and aqueous H_2O_2 solution (30%, 2 mL, 19 mmol) were added, and the mixture was heated at 50 °C for 2 h. The solvent was removed under reduced pressure, and the reaction mixture was redissolved in dichloromethane (120 mL). The mixture was washed with water (3 × 100 mL) and dried ($MgSO_4$), and complex (−)-**9** was subsequently crystallized from dichloromethane−diethyl ether as pale yellow crystals, 0.539 g (90% yield).

Removal of the Chiral Auxiliary and Isolation of [*SP*-4-3-{(1*S*,2*R*,4*R*,5*R*)-Dichloro[4,5-bis(diphenylphosphino)-2-hydroxy-7-oxabicyclo[2.2.1]hept-2-ane-*P*^{4},*P*^{5}]}]platinum(II) [(−)-11]. The naphthylamine auxiliary was similarly removed by reaction of (−)-**9** (0.350 g, 0.364 mmol) and concentrated hydrochloric acid (25 mL) in dichloromethane (80 mL) for 1 day. Complex (−)-**11** was crystallized from dichloromethane−diethyl ether as colorless crystals: mp 250−251 °C (dec); $[\alpha]_D$ −37 (*c* 0.1, CH_2Cl_2); 0.243 g (89% yield). Anal. Calcd for $C_{30}H_{28}Cl_2O_2P_2Pt$: C, 48.1; H, 3.8. Found: C, 48.1; H, 3.9. ^{31}P NMR (CD_2Cl_2) δ 37.2 (d, 1P, J_{PP} = 9.5 Hz, J_{PtP} = 3658 Hz, P^4), 48.6 (d, 1P, J_{PP} = 9.5 Hz, J_{PtP} = 3563 Hz, P^5); ^1H NMR (CD_2Cl_2) δ 1.69−1.94 (m, 4H, H_{6exo}, H_{6endo}, H_{3exo}, O*H*), 2.13 (dd, 1H, $^2J_{HH}$ = 13.7 Hz, $^3J_{HH}$ = 6.4 Hz, H_{3endo}), 2.68 (dt, 1H, $^3J_{HH}$ = 8.4 Hz, $^2J_{PH}$ = $^3J_{HH}$ = 2.8 Hz, H_5), 4.02−4.12 (m, 1H, H_2), 4.45 (d, 1H, $^3J_{HH}$ = 5.6 Hz, H_1), 7.33−8.10 (m, 20H, aromatics).

Liberation of (1*S*,2*R*,4*R*,5*R*)-4,5-Bis(diphenylphosphino)-2-hydroxy-7-oxabicyclo[2.2.1]hept-2-ane [(−)-12]. Diphosphine ligand (−)-**12** was similarly obtained from the reaction of dichloro complex (−)-**11** (0.100 g, 0.134 mmol) and aqueous saturated KCN (2 g), as white solid: $[\alpha]_D$ −33 (*c* 1.3, $CHCl_3$); 0.061 g (95% yield). ^{31}P NMR ($CDCl_3$) δ −7.4 (d, 1P, $^3J_{PP}$ = 95.4 Hz, *P*), −9.7 (d, 1P, $^3J_{PP}$ = 95.4 Hz, *P*); ^1H NMR ($CDCl_3$) δ 1.52−1.61 (m, 1H, H_{3exo}), 1.61−1.73 (m, 1H, H_{6endo}), 1.75−1.89 (m, 1H, H_{6exo}), 2.28 (dd, 1H, $^2J_{HH}$ = 13.6 Hz, $^3J_{HH}$ = 6.4 Hz, H_{3endo}), 2.73 (dd, 1H, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 4.0 Hz, H_5), 3.86 (d, 1H, $^3J_{HH}$ = 6.4 Hz, H_2), 4.36 (d, 1H, $^3J_{HH}$ = 6.0 Hz, H_1), 7.05−7.57 (m, 20H, aromatics).

Addition of Phenylselenenyl Chloride to (−)-2. Isolation of [*SP*-4-4-{(*S*)-1-[1-(Dimethylamino)ethyl]naphthyl-*C*^{2},*N*}-{(1*S*,2*S*,3*S*,4*S*,5*R*)-3-chloro-4,5-bis(diphenylphosphino)-2-phenylselenenyl-7-oxabicyclo[2.2.1]hept-2-ane-*P*^{4},*P*^{5}}]platinum(II) tetrafluoroborate [(−)-14]. Complex (−)-**2** (0.329 g, 0.348 mmol) and phenylselenenyl chloride (0.115 g, 0.660 mmol) were stirred in dichloromethane (60 mL) at room temperature for 16 h. Then aqueous Na_2CO_3 solution (5%, 10 mL) was added and stirred vigorously for 1 h. The organic portion was separated, washed with aqueous Na_2CO_3 (30 mL), followed by water (2 × 30 mL), and dried ($MgSO_4$). The crude product was chromatographed on a silica column with dichloromethane−acetone as eluent. Subsequent

Table 7. Crystallographic Data for Complexes (−)-3, (−)-4, and (−)-9

	(−)-**3**	(−)-**4**	(−)-**9**
formula	$C_{44}H_{44}BF_4NOP_2Pt$	$C_{30}H_{28}Cl_2OP_2Pt$	$C_{44}H_{44}BF_4NO_2P_2Pt$
fw	946.64	732.45	962.64
space group	$P2_12_12_1$	$P2_1$	$P2_12_12_1$
cryst syst	orthorhombic	monoclinic	orthorhombic
a/Å	11.6288(6)	11.6176(5)	11.6519(6)
b/Å	15.7867(8)	8.5768(4)	15.9927(7)
c/Å	21.058(1)	13.8038(6)	21.089(1)
β/deg	90	103.831(1)	90
V/Å^3	3865.8(3)	1335.6(1)	3929.9(3)
Z	4	2	4
T/K	293(2)	323(2)	223(2)
ρ_{calcd}/g cm^{-3}	1.626	1.821	1.627
λ/Å	0.71073 (Mo)	0.71073 (Mo)	0.71073 (Mo)
μ/cm^{-1}	37.68	55.96	37.10
Flack param	−0.018(8)	−0.012(8)	0.001(8)
R_1 (obsd data)[a]	0.0412	0.0355	0.0518
wR_2 (obsd data)[b]	0.0610	0.0806	0.0891

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

crystallization from dichloromethane−acetonitrile−petroleum ether gave complex (−)-**14** as yellow crystals: mp 213-215 °C (dec); $[\alpha]_D$ −57 (*c* 2.2, CH_2Cl_2); 0.331 g (84% yield). Anal. Calcd for $C_{50}H_{47}BClF_4NOP_2SePt$: C, 52.9; H, 4.2; N, 1.2. Found: C, 52.4; H, 4.2; N, 1.4. ^{31}P NMR (CD_2Cl_2) *δ* 42.3 (d, 1P, J_{PP} = 7.6 Hz, J_{PtP} = 1835 Hz, *P*^{4}), 46.6 (d, 1P, J_{PP} = 7.6 Hz, J_{PtP} = 3597 Hz, *P*^{5}); ^{1}H NMR (CD_2Cl_2) *δ* 1.87 (d, 3H, $^3J_{HH}$ = 6.2 Hz, CH*Me*), 2.18 (dddd, 1H, $^3J_{PH}$ = 20.5 Hz, $^2J_{HH}$ = 13.7 Hz, $^3J_{HH}$ = 6.0 Hz, $^3J_{HH}$ = 2.0 Hz, H_{6exo}), 2.27−2.39 (m, 1H, H_{6endo}), 2.47 (d, 3H, $^4J_{PH}$ = 2.4 Hz, N*Me*$_{ax}$), 2.81 (dd, 3H, $^4J_{PH}$ = 3.7 Hz, $^4J_{PH}$ = 3.0 Hz, N*Me*$_{eq}$), 3.44−3.51 (m, 1H, H_5), 3.57 (d, 1H, $^3J_{HH}$ = 1.6 Hz, H_2), 4.31 (dd, 1H, $^3J_{PH}$ = 2.4 Hz, $^3J_{HH}$ = 1.6 Hz, H_3), 4.51 (d, 1H, $^3J_{HH}$ = 6.0 Hz, H_1), 4.82 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.2 Hz, C*H*Me), 6.59−8.30 (m, 31H, aromatics).

Addition of Phenylselenenyl Chloride to (−)-5. Isolation of [*SP*-4-3-{(1*S*,2*S*,3*S*,4*S*,5*R*)-Dichloro[3-chloro-4,5-bis(diphenylphosphino)-2-phenylselenenyl-7-oxabicyclo[2.2.1]hept-2-ane-*P*^{4},*P*^{5}]}]-platinum(II) [(−)-15]. Complex (−)-**5** (0.252 g, 0.345 mmol) and PhSeCl (0.135 g, 0.705 mmol) were stirred in dichloromethane (50 mL) at room temperature for 16 h. Then aqueous Na_2CO_3 solution (5%, 10 mL) was added and stirred vigorously for 1 h. The organic portion was separated, washed with aqueous Na_2CO_3 (40 mL), followed by water (2 × 40 mL), and dried ($MgSO_4$). The crude product was chromatographed on a silica column with chloroform−acetone as eluent. Upon removal of solvent and drying under vacuum, a pale yellow solid was obtained: mp 208−210 °C (dec); $[\alpha]_D$ −52 (*c* 0.1, CH_2Cl_2); 0.240 g (75% yield). Anal. Calcd for $C_{36}H_{31}Cl_3OP_2SePt$: C, 46.9; H, 3.4. Found: C, 47.1; H, 3.5. ^{31}P NMR (CD_2Cl_2) *δ* 37.1 (d, 1P, J_{PP} = 9.5 Hz, J_{PtP} = 3696 Hz, *P*^{4}), 46.8 (d, 1P, J_{PP} = 9.5 Hz, J_{PtP} = 3525 Hz, *P*^{5}); ^{1}H NMR (CD_2Cl_2) *δ* 1.97−2.27 (m, 2H, H_{6exo}, H_{6endo}), 3.53 (d, 1H, $^3J_{HH}$ = 2.0 Hz, H_2), 3.64 (dt, 1H, $^3J_{HH}$ = 8.4 Hz, $^2J_{PH}$ = $^3J_{HH}$ = 3.4 Hz, H_5), 4.35−4.43 (m, 1H, H_3), 4.61 (d, 1H, $^3J_{HH}$ = 5.6 Hz, H_1), 7.20−8.28 (m, 25H, aromatics).

Removal of the Chiral Auxiliary in (−)-14 and Isolation of [*SP*-4-3-{(1*S*,2*S*,3*S*,4*S*,5*R*)-Dichloro[3-chloro-4,5-bis(diphenylphosphino)-2-phenylselenenyl-7-oxabicyclo[2.2.1]hept-2-ane-*P*^{4},*P*^{5}]}]-platinum(II) [(−)-15]. The naphthylamine auxiliary was similarly removed by reaction of (−)-**14** (0.150 g, 0.132 mmol) and concentrated hydrochloric acid (10 mL) in dichloromethane (30 mL) for 6 h. The crude product was chromatographed on a silica column with chloroform−acetone as eluent. Upon removal of solvent and drying under vacuum, a pale yellow solid was obtained, 0.097 g (80% yield).

Liberation of (1*S*,2*S*,3*S*,4*S*,5*R*)-3-Chloro-4,5-bis(diphenylphosphino)-2-phenylselenenyl-7-oxabicyclo[2.2.1]hept-2-ane [(−)-16]. Diphosphine ligand (−)-**16** was similarly obtained from the reaction of dichloro complex (−)-**15** (0.101 g, 0.110 mmol) and saturated aqueous KCN (2 g), as a white solid: $[\alpha]_D$ −39 (*c* 0.5, $CHCl_3$); 0.068 g (95% yield). ^{31}P NMR ($CDCl_3$) *δ* −12.7 (d, 1P, $^3J_{PP}$ = 49.6 Hz, *P*), −14.0 (d, 1P, $^3J_{PP}$ = 49.6 Hz, *P*); ^{1}H NMR ($CDCl_3$) *δ* 1.54−1.89 (m, 2H, H_{6exo}, H_{6endo}), 3.23 (d, 1H, $^3J_{HH}$ = 4.0 Hz, H_2), 3.82−3.94 (m, 2H, H_3, H_5), 4.55 (d, 1H, $^3J_{HH}$ = 5.2 Hz, H_1), 7.14−7.80 (m, 25H, aromatics).

Isolation of [*SP*-4-4-{(*S*)-1-[1-(Dimethylamino)ethyl]naphthyl-*C*^{2},*N*}{(1*S*,4*S*,5*R*)-3-chloro-4,5-bis(diphenylphosphino)-7-oxabicyclo[2.2.1]hept-2-ene-*P*^{4},*P*^{5}}]platinum(II) tetrafluoroborate [(−)-18]. Complex (−)-**14** (0.150 g, 0.132 mmol) and aqueous H_2O_2 solution (30%, 0.4 mL, 4 mmol) were stirred vigorously in dichloromethane (20 mL) and ethanol (8 mL) under an ice-bath for 1 h. After that the reaction mixture was warmed to room temperature and stirred for 16 h. More dichloromethane (35 mL) was added to the mixture, which was subsequently washed with aqueous Na_2CO_3 (30 mL), followed by water (2 × 30 mL), and dried ($MgSO_4$). Crystallization from dichloromethane−acetonitrile−diethyl ether gave complex (−)-**18** as lumpy yellow crystals: mp 258−259 °C (dec); $[\alpha]_D$ −169 (*c* 0.3, CH_2Cl_2); 0.107 g (83% yield). Anal. Calcd for $C_{44}H_{41}BClF_4NOP_2Pt$: C, 54.0; H, 4.2; N, 1.4. Found: C, 53.8; H, 4.1; N, 1.6. MS(ESI): *m*/*z* = 891, M$^+$. ^{31}P NMR (CD_2Cl_2) *δ* 49.4 (d, 1P, J_{PP} = 7.6 Hz, J_{PtP} = 3643 Hz, *P*^{5}), 51.3 (d, 1P, J_{PP} = 7.6 Hz, J_{PtP} = 1823 Hz, *P*^{4}); ^{1}H NMR (CD_2Cl_2) *δ* 1.55 (d, 3H, $^3J_{HH}$ = 6.2 Hz, CH*Me*), 2.04−2.24 (m, 2H, H_{6exo}, H_{6endo}), 2.89 (dd, 3H, $^4J_{PH}$ = 3.6 Hz, $^4J_{PH}$ = 2.8 Hz, N*Me*$_{eq}$), 2.91 (d, 3H, $^4J_{PH}$ = 2.4 Hz, N*Me*$_{ax}$), 3.08 (ddd, 1H, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 2.8 Hz, $^2J_{PH}$ = 1.4 Hz, H_5), 4.76 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.2 Hz, C*H*Me), 4.81 (dd, 1H, $^3J_{HH}$ = 4.0 Hz, $^3J_{HH}$ = 1.6 Hz, H_1), 6.46 (d, 1H, $^3J_{HH}$ = 1.6 Hz, H_2), 6.65−8.24 (m, 26H, aromatics).

With ethanol as the solvent, the reaction procedure was similar to that above.

(1*S*,4*S*,5*R*)-3-Chloro-4,5-bis(diphenylphosphinyl)-7-oxabicyclo[2.2.1]hept-2-ene [(−)-19]. MS(FAB): *m*/*z* = 531, (M + 1)$^+$. ^{31}P NMR ($CDCl_3$) *δ* 19.7 (s, 1P, *P*), 27.8 (s, 1P, *P*); ^{1}H NMR ($CDCl_3$) *δ* 1.52 (ddd, 1H, $^2J_{HH}$ = 11.6 Hz, $^3J_{HH}$ = 8.3 Hz, $^3J_{PH}$ = 4.2 Hz, H_{6endo}), 2.54−2.63 (m, 1H, H_{6exo}), 3.08 (dd, 1H, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 5.6 Hz, H_5), 5.29 (br d, 1H, $^3J_{HH}$ = 4.2 Hz, H_1), 6.16 (d, 1H, $^3J_{HH}$ = 1.9 Hz, H_2), 7.28−8.02 (m, 20H, aromatics).

Dihydroxylation Using Stoichiometric OsO_4. Isolation of [*SP*-4-4-{(*S*)-1-[1-(Dimethylamino)ethyl]naphthyl-*C*^{2},*N*}-{(1*S*,2*R*,3*S*,4*R*,5*R*)-4,5-bis(diphenylphosphino)-2,3-dihydroxy-7-oxabicyclo[2.2.1]hept-2-ane-*P*^{4},*P*^{5}}]platinum(II) tetrafluoroborate [(−)-20]. A solution of osmium tetraoxide in *tert*-butyl alcohol (2.5 wt %, 3.85 mL, 0.307 mmol) was added to a mixture of complex (−)-**2** (0.286 g, 0.303 mmol) and pyridine (2 mL) in dichloromethane (30 mL). The reaction mixture was stirred at room temperature for 16 h, followed by the addition of aqueous $NaHSO_3$

Table 8. Crystallographic Data for Complexes (−)-14, (−)-20, and (+)-22

	(−)-**14**	(−)-**20**	(+)-**22**
formula	$C_{50}H_{47}BClF_4NOP_2SePt$	$C_{44}H_{44}BF_4NO_3P_2Pt$	$C_{44}H_{45}BF_4N_2O_2P_2Pt$
fw	1136.14	978.64	977.66
space group	*R*3	$P2_12_12_1$	$C222_1$
cryst syst	rhombohedral	orthorhombic	orthorhombic
a/Å	21.6188(5)	11.6888(7)	10.4452(6)
b/Å	21.6188(5)	15.999(1)	18.448(1)
c/Å	54.139(3)	21.015(1)	42.096(2)
γ/deg	120	90	90
V/Å^3	21913(1)	3930.0(4)	8111.4(8)
Z	18	4	8
T/K	223(2)	223(2)	293(2)
ρ_{calcd}/g cm^{-3}	1.550	1.654	1.601
λ/Å	0.71073 (Mo)	0.71073 (Mo)	0.71073 (Mo)
μ/cm^{-1}	38.01	37.13	35.97
Flack param	0.002(4)	0.008(7)	0.001(9)
R_1 (obsd data)[a]	0.0345	0.0345	0.0451
wR_2 (obsd data)[b]	0.0757	0.0774	0.0908

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

solution (10%, 5 mL) and ethanol (4 mL). The mixture was stirred vigorously for 2 h, then washed with aqueous $NaHSO_3$ (25 mL), followed by water (2 × 25 mL), and dried ($MgSO_4$). The crude product was purified by column chromatography on a silica column with acetone−dichloromethane as eluent. Subsequent crystallization from dichloromethane−diethyl ether gave complex (−)-**20** as yellow crystals: mp > 400 °C; $[\alpha]_D$ −18 (*c* 0.1, CH_2Cl_2); 0.162 g (55% yield). Anal. Calcd for $C_{44}H_{44}BF_4NO_3P_2Pt$: C, 54.0; H, 4.5; N, 1.4. Found: C, 53.4; H, 4.6; N, 1.6. ^{31}P NMR (CD_2Cl_2) δ 43.4 (d, 1P, J_{PP} = 7.6 Hz, J_{PtP} = 1839 Hz, *P*[4]), 48.1 (d, 1P, J_{PP} = 7.6 Hz, J_{PtP} = 3647 Hz, *P*[5]); ^{1}H NMR (CD_2Cl_2) δ 1.76−2.00 (m, 2H, *H*$_{6endo}$, *H*$_{6exo}$), 1.86 (d, 3H, $^3J_{HH}$ = 6.0 Hz, CH*Me*), 2.42 (d, 3H, $^4J_{PH}$ = 2.0 Hz, N*Me*$_{ax}$), 2.56−2.62 (m, 1H, *H*$_5$), 2.65 (dd, 3H, $^4J_{PH}$ = 3.9 Hz, $^4J_{PH}$ = 2.7 Hz, N*Me*$_{eq}$), 3.40 (d, 1H, $^3J_{HH}$ = 7.6 Hz, O*H*), 3.49 (d, 1H, $^3J_{HH}$ = 5.2 Hz, O*H*), 3.95 (dd, 1H, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 6.0 Hz, *H*$_3$), 4.08 (dd, 1H, $^3J_{HH}$ = 6.0 Hz, $^3J_{HH}$ = 5.2 Hz, *H*$_2$), 4.43 (d, 1H, $^3J_{HH}$ = 5.6 Hz, *H*$_1$), 4.73 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.0 Hz, C*H*Me), 6.58−8.71 (m, 26H, aromatics).

Dihydroxylation Using Catalytic OsO_4. Isolation of [*SP*-4-4-{(*S*)-1-[1-(Dimethylamino)ethyl]naphthyl-*C*^{2},*N*}{(1*S*,2*R*,3*S*,4*R*,5*R*)-4,5-bis(diphenylphosphino)-2,3-dihydroxy-7-oxabicyclo[2.2.1]-hept-2-ane-*P*^{4},*P*^{5}}]platinum(II) tetrafluoroborate [(−)-20]. Aqueous tetraethylammonium hydroxide solution (20 wt %, 0.07 mL, 0.1 mmol) and aqueous *tert*-butyl hydroperoxide solution (70 wt %, 0.12 mL, 0.87 mmol) were added to a solution of complex (−)-**2** (0.389 g, 0.412 mmol) in dichloromethane (30 mL) and acetone (40 mL). The reaction mixture was cooled under an ice-bath, and a solution of osmium tetraoxide in *tert*-butyl alcohol (2.5 wt %, 0.16 mL, 0.013 mmol) was added. The reaction mixture was stirred under an ice-bath for 1 h, then it was warmed to room temperature and further stirred for 2 days. After that, aqueous $NaHSO_3$ solution (10%, 5 mL) was added and stirred vigorously for 2 h. The solvent was removed and the reaction mixture was redissolved in dichloromethane (50 mL), washed with water (3 × 40 mL), and dried ($MgSO_4$). The crude product was chromatographed on a silica column with dichloromethane−acetone as eluent. Subsequent crystallization from dichloromethane−diethyl ether gave complex (−)-**20** as yellow crystals, 0.079 g (20% yield).

A similar result was obtained with the use of tetraethylammonium acetate as the base instead of tetraethylammonium hydroxide.

Dihydroxylation of (+)-21. Isolation of [*SP*-4-3-{(*S*)-1-[1-(Dimethylamino)ethyl]naphthyl-*C*^{2},*N*}{(1*S*,2*S*,3*R*,4*S*,5*R*,7*S*)-2,3-dihydroxy-5,7-bis(diphenylphosphino)-7-azabicyclo[2.2.1]hept-2-ane-*P*^{5},*P*^{7}}]platinum(II) tetrafluoroborate [(+)-22]. A solution of osmium tetraoxide in *tert*-butyl alcohol (2.5 wt %, 0.95 mL, 0.076 mmol) was added to a mixture of (+)-**21** (0.069 g, 0.073 mmol) and pyridine (2 mL) in dichloromethane (30 mL). The reaction mixture was stirred for 16 h, followed by the addition of aqueous $NaHSO_3$ solution (10%, 5 mL) and ethanol (4 mL). The mixture was stirred vigorously for 2 h, washed with aqueous $NaHSO_3$ (20 mL), then with water (2 × 20 mL), and dried ($MgSO_4$). The crude product was purified by column chromatography on a silica column with acetone−dichloromethane as eluent. Subsequent crystallization from dichloromethane−diethyl ether gave complex (+)-**22** as yellow crystals: mp > 390 °C; $[\alpha]_D$ +8 (*c* 0.5, CH_2Cl_2); 0.026 g (36% yield). Anal. Calcd for $C_{44}H_{45}BF_4N_2O_2P_2Pt$: C, 54.1; H, 4.6; N, 2.9. Found: C, 53.6; H, 4.8; N, 2.6. ^{31}P NMR (CD_2Cl_2) δ 26.6 (d, 1P, J_{PP} = 24.8 Hz, J_{PtP} = 1827 Hz, *P*[5]), 55.2 (d, 1P, J_{PP} = 24.8 Hz, J_{PtP} = 3704 Hz, *P*[7]); ^{1}H NMR (CD_2Cl_2) δ 1.60−1.74 (m, 1H, *H*$_{6endo}$), 1.95 (d, 3H, $^3J_{HH}$ = 6.2 Hz, CH*Me*), 2.30−2.44 (m, 2H, *H*$_{6exo}$, *H*$_5$), 2.43 (dd, 3H, $^4J_{PH}$ = 4.0 Hz, $^4J_{PH}$ = 2.4 Hz, N*Me*$_{eq}$), 2.74 (d, 3H, $^4J_{PH}$ = 1.6 Hz, N*Me*$_{ax}$), 2.98 (dt, 1H, $^3J_{PH}$ = 9.8 Hz, $^3J_{PH}$ = $^4J_{HH}$ = 2.2 Hz, *H*$_4$), 3.05 (d, 1H, $^3J_{HH}$ = 5.2 Hz, *H*$_{2endo}$), 3.49 (br s, 1H, O*H*), 3.64 (br s, 1H, O*H*), 3.67−3.75 (m, 2H, *H*$_1$, *H*$_{3endo}$), 4.71 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.2 Hz, C*H*Me), 6.82−8.64 (m, 26H, aromatics).

Crystal Structure Determination of (−)-3, (−)-4, (−)-9, (−)-14, (−)-20, and (+)-22. X-ray crystallographic data for all six complexes are given in Tables 7 and 8. The structures were analyzed at the National University of Singapore using a Siemens SMART CCD diffractometer with graphite-monochromated Mo Kα radiation. For all six complexes, SADABS 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.[27]

Acknowledgment. We are grateful to the National University of Singapore for support of this research, and a research scholarship to W.C.Y.

Supporting Information Available: For complexes (−)-**3**, (−)-**4**, (−)-**9**, (−)-**14**, (−)-**20**, and (+)-**22**, 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.

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

OM0509645