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Organoplatinum Complex Promoted the Asymmetric *Endo* Stereochemically Controlled Diels−Alder Reaction between 3-Diphenylphosphinofuran and Diphenylvinylphosphine

Fengli Liu, Sumod A. Pullarkat, Kien-Wee Tan, Yongxin Li, and Pak-Hing Leung*

Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637616, Singapore

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The organoplatinum complex containing *ortho*-metalated (*R*)-(1-(dimethylamino)ethyl)-naphthalene as the chiral auxiliary has been used efficiently to promote the asymmetric [4 + 2] Diels−Alder reaction between diphenylvinylphosphine and 3-diphenylphosphinofuran to generate two chelating diphosphine *endo*cycloadducts in the ratio 17:1. The absolute configurations of the three newly generated stereocenters have been assigned by single-crystal X-ray analysis.

Introduction

7-oxabicyclo[2.2.1]heptene derivatives have gained increasing importance as starting material in the synthesis of a large number of natural products, themselves also being valuable intermediates for the synthesis of biologically active compounds.[1] In addition, these compounds are useful building blocks for polymers and other interesting compounds in the field of material science.[2] The development of new methods of change of these compounds into both cyclic and open-chain targets with a high level of stereocontrol is an area of current interest.[3]

Over the past decade, chiral organometalated complexes have been developed as useful reagents in many aspects of synthetic stereochemistry. For example, they have been routinely used as resolving agents for the optical resolution of chiral ligands,[4−9] highly sensitive diamagnetic chiral shift reagents for the determination of optical purities of organic compounds by NMR spectroscopy,[10,11] clear and reliable references for the NMR assignments of absolute configurations of new compounds,[12−16] and efficient catalysts in several stereochemically demanding asymmetric transformations.[17−19]

*To whom correspondence should be addressed. E-mail: pakhing@ntu.edu.sg.

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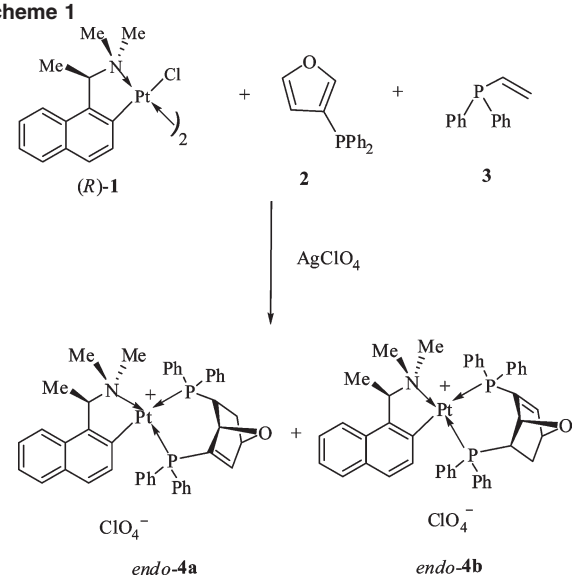
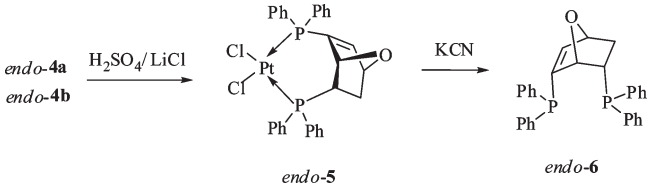
Scheme 1



Scheme 2



Recently, our group has reported the use of cyclometalated-amine complexes as efficient chiral templates for the asymmetric synthesis of chiral phosphines via the asymmetric Diels−Alder reaction between heterocyclic dienes, such as 3,4-dimethyl-1-phenylphosphole (DMPP), 3,4-dimethyl-1-phenylarsole (DMAP), 2-diphenylphosphinofuran, and *N*-diphenylphosphinopyrrole, and a range of dienophiles.[20−23] In general these cyclometalated-amine complexes promoted carbon−carbon bond formation reactions can be related to a common intermediate in which the cyclic diene and the dienophile are coordinated simultaneously to the chiral metal templates during the course of cycloaddition to give the *exo*-cycloadducts. In these asymmetric syntheses, the chiral metal templates not only activate the substrates and provide the desired stereochemical control for the cycloaddition reaction but also stabilize the resulting cycloadducts. However in these intramolecular reactions, we still have not generated *endo*-cycloadducts. In pursuing our interest and extending the scope of this class of metal template promoted cycloaddition reactions, we here present the chiral platinum template promoted asymmetric Diels−Alder reaction between 3-diphenylphosphinofuran and diphenylvinylphosphine.

Results and Discussion

In the absence of a metal ion, no reaction was observed between 3-diphenylphosphinofuran and diphenylvinylphosphine, even upon prolonged heating. However, with the use of chiral platinum complex (*R*)-**1** (after chloro ligands abstraction with silver perchlorate[20,21]) as the reaction promoter, both 3-diphenylphosphinofuran and diphenylvinylphosphine are coordinated simultaneously onto the chiral template and the corresponding asymmetric Diels−Alder reaction was complete in 9 days at 60 °C. Prior to the purification, the $^{31}P\{^{1}H\}$ NMR spectrum of the crude reaction mixture in $CDCl_3$ exhibited two pairs of doublets indicative of the formation of only two stereo chemically distinct products *endo*-**4a** and *endo*-**4b** in the ratio 17:1 (Scheme 1). The two pairs of doublets phosphorus resonance signals were observed at δ 26.2 (J_{PP} = 14.5 Hz, J_{PtP} = 1713 Hz) and −4.6 (J_{PP} = 14.5 Hz, J_{PtP} = 3682 Hz) and δ 27.7 (J_{PP} = 14.7 Hz) and −5.1 (J_{PP} = 14.7 Hz). Interestingly this asymmetric process could not be achieved with the chiral organopalladium complex. Apparently the organopalladium complex is not an efficient promoter for the Diels−Alder reaction.

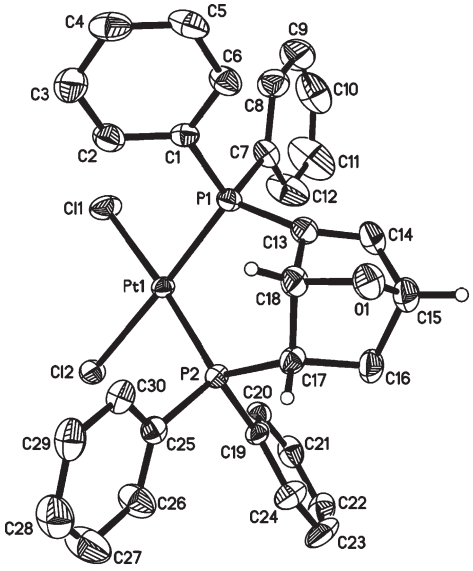


Figure 1. Molecular structure of the dichloro complex *endo*-**5**.

The two cycloadducts generated could not, however, be purified by fractional crystallization or column chromatography; hence, treatment of the perchlorate salt with concentrated sulfuric acid at room temperature removed the naphthylamine auxiliary chemoselectively (Scheme 2). Upon addition of excess lithium chloride into the acidic solution, the dichloro complex *endo*-**5** that precipitated out of solution was recrystallized form dichloromethane-diethyl ether as pale yellow prisms in 70% yield, with $[\alpha]_D$ = +34.7 (*c* 4.0, CH_2Cl_2). The $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture in $CDCl_3$ exhibited one pair of doublets at δ 21.2 (J_{PP} = 14.7 Hz, J_{PtP} = 3577 Hz) and −15.1 (J_{PP} = 14.7 Hz, J_{PtP} = 3411 Hz).

The molecular structure and the absolute configurations of the recrystallized *endo*-**5** were established by a single-crystal X-ray crystallographic analysis (Figure 1). Interestingly, *endo*-**5** crystallized as a pair of crystallographically independent molecules in the unit cell: two independent molecules. However, the two molecules have the same absolute stereochemistry and molecular connectivity and differ only slightly in their bond angles. For clarity, only one molecule (molecule 1) is depicted in Figure 1. Selected bond lengths and bond angles are given in Table 1. The crystallographic study reveals that

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for *endo*-**5**

Molecule **1**		Molecule **2**	
Pt(1)−P(1)	2.231(1)	Pt(2)−P(4)	2.229(1)
Pt(1)−P(2)	2.240 (1)	Pt(2)−P(3)	2.233(1)
Pt(1)−Cl(2)	2.351(1)	Pt(2)−Cl(3)	2.348(1)
Pt(1)−Cl(1)	2.352(1)	Pt(2)−Cl(4)	2.353(1)
P(1)−C(13)	1.800(3)	P(3)−C(43)	1.837(3)
P(2)−C(17)	1.859(3)	P(4)−C(47)	1.783(3)
C(13)−C(14)	1.320(5)	C(43)−C(44)	1.543(4)
C(13)−C(18)	1.526(5)	C(43)−C(48)	1.545(5)
C(14)−C(15)	1.513(5)	C(44)−C(45)	1.549(5)
C(15)−O(1)	1.435(5)	C(45)−O(2)	1.422(4)
C(15)−C(16)	1.539(5)	C(45)−C(46)	1.522(5)
C(16)−C(17)	1.543(4)	C(46)−C(47)	1.347(5)
C(17)−C(18)	1.558(4)	C(47)−C(48)	1.523(5)
C(18)−O(1)	1.428(4)	C(48)−O(2)	1.426(4)
P(1)−Pt(1)−P(2)	97.7(1)	P(4)−Pt(2)−P(3)	97.8(1)
P(1)−Pt(1)−Cl(2)	177.2(1)	P(4)−Pt(2)−Cl(3)	174.8(1)
P(2)−Pt(1)−Cl(2)	84.9(1)	P(3)−Pt(2)−Cl(3)	86.4(1)
P(1)−Pt(1)−Cl(1)	87.5(1)	P(4)−Pt(2)−Cl(4)	86.2(1)
P(2)−Pt(1)−Cl(1)	174.4(1)	P(3)−Pt(2)−Cl(4)	175.6(1)
Cl(2)−Pt(1)−Cl(1)	89.8(1)	Cl(3)−Pt(2)−Cl(4)	89.5(1)
C(18)−C(13)−P(1)	120.7(2)	C(48)−C(43)−P(3)	118.4(2)
C(13)−C(14)−C(15)	106.0(3)	C(43)−C(44)−C(45)	100.9(3)
C(14)−C(15)−C(16)	104.5(3)	C(46)−C(45)−C(44)	103.8(3)
C(15)−C(16)−C(17)	101.4(3)	C(47)−C(46)−C(45)	104.7(3)
C(16)−C(17)−C(18)	100.4(3)	C(46)−C(47)−C(48)	105.0(3)
C(18)−C(17)−P(2)	115.6(2)	C(48)−C(47)−P(4)	122.6(2)
C(13)−C(18)−C(17)	105.7(3)	C(47)−C(48)−C(43)	105.9(3)
C(18)−O(1)−C(15)	96.1(2)	C(45)−O(2)−C(48)	96.7(2)

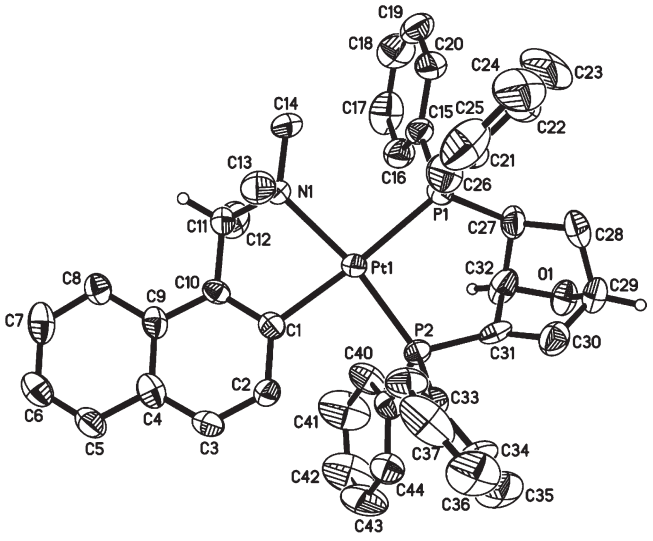
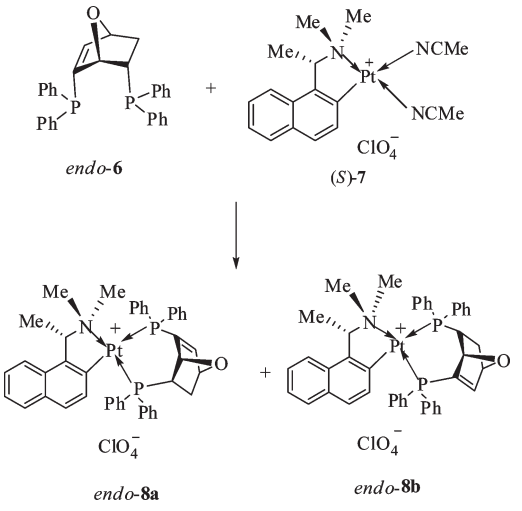


Figure 2. Molecular structure and absolute stereochemistry of the cationic complex *endo*-**8b**.

the cycloaddition reaction between the coordinated 3-diphenylphosphinofuran and diphenylvinylphosphine has resulted in the formation of the *endo*-phosphine. The chiral ligand coordinated as a bidentate chelate via its phosphorus donor atoms to the platinum, with diphenylphosphino group substituted at the *endo* position at C(17). The geometry at platinum is distorted square planar with angles at platinum in the ranges of 84.9(1)−87.5(1) and 174.4(1)−177.2(1)°. The absolute configurations of the three newly generated stereogenic centers at C(15), C(17), and C(18) are *S*, *S*, and *R*, respectively.

The optically active ligand *endo*-**6** can be stereospecifically liberated from the complex *endo*-**5** by treatment of the dichloro complex with aqueous potassium cyanide at room

Scheme 3



temperature. The liberated *endo*-**6** was obtained as an air stable white solid in 80% yield, with $[\alpha]_D = -37.6$ (*c* 1.7, CH_2Cl_2). The $^{31}P\{^1H\}$ NMR spectrum of the free ligand in $CDCl_3$ exhibited two doublets at δ −12.5 (J_{PP} = 77 Hz) and −20.8 (J_{PP} = 77 Hz).

Furthermore, to determine the enantiomeric purity of *endo*-**6** and to establish the identity of the other isomer, the liberated ligand was recoordinated to the easily accessible (*R*)-**7**. This recoordination process generated two regioisomers in the ratio of 12:1. These two recomplexation products exhibited identical $^{31}P\{^1H\}$ NMR spectra to those recorded for the products generated from the original cycloaddition reaction, so the products generated from the original cycloaddition reaction are regioisomers.

As a further check, *endo*-**6** was recoordinated to (*S*)-**7** generated two regioisomers *endo*-**8a** and *endo*-**8b** in the ratio of 1:10. The two pairs of doublets phosphorus resonance signals were observed at δ 22.1 (J_{PP} = 15.2 Hz) and −2.1 (J_{PP} = 15.2 Hz) and δ 27.6 (J_{PP} = 14.5 Hz, J_{PtP} = 1710 Hz) and −6.2 (J_{PP} = 14.5 Hz, J_{PtP} = 3677 Hz). These two recomplexation products exhibited different $^{31}P\{^1H\}$ NMR spectra to those recorded for the two cycloadducts generated directly from the asymmetric cycloaddition reaction thus reaffirming that the liberated product is stereochemically pure. Eventually, the major recomplexation product *endo*-**8b** could be isolated in a diastereomerically pure form by fractional crystallization from dichloromethane/diethyl ether as pale yellow crystals in 85% yield, with $[\alpha]_D = -35°$ (*c* 1.0, CH_2Cl_2). Because of the unique *trans*-electronic influences which originate from the organoplatinum unit, the larger platinum−phosphorus coupling constant observed for the doublet signal at δ −6.2 is diagnostic of the PPh_2 group coordinated *trans* to the σ-donating nitrogen atom.[20,21,23] On the other hand, the doublet at δ 27.6, which shows the smaller platinum−phosphorus coupling constant, is unambiguously assigned to the PPh_2 group that is coordinated *trans* to the strong π-accepting orthometalated carbon atom. The molecular structure and the absolute stereochemistry of *endo*-**8b** were confirmed by X-ray crystallography, as shown in Scheme 3 and Figure 2. Selected bond lengths and angles are given in Table 2. The geometry at platinum is distorted square planar with angles at platinum in the ranges of 79.4(3)−96.5(2) and 169.7(2)−175.2(3)°. The absolute configurations of the

Table 2. Selected Bond Lengths (Å) and Angles (deg) for *endo*-**8b**

Pt(1)−C(1)	2.118(8)	N(1)−Pt(1)−P(2)	169.7(2)
Pt(1)−N(1)	2.196(7)	C(1)−Pt(1)−P(1)	175.2(3)
Pt(1)−P(2)	2.242(2)	N(1)−Pt(1)−P(1)	96.5(2)
Pt(1)−P(1)	2.387(2)	P(2)−Pt(1)−P(1)	93.4(1)
C(27)−C(28)	1.513(15)	C(28)−C(27)−C(32)	101.5(9)
C(27)−C(32)	1.539(15)	C(32)−C(27)−P(1)	112.9(6)
C(27)−P(1)	1.946(11)	C(29)−C(28)−C(27)	102.4(9)
C(28)−C(29)	1.496(15)	C(28)−C(29)−C(30)	105.3(9)
C(29)−O(1)	1.447(13)	C(31)−C(30)−C(29)	107.2(10)
C(29)−C(30)	1.496(15)	C(30)−C(31)−C(32)	103.7(9)
C(30)−C(31)	1.331(13)	C(32)−C(31)−P(2)	120.9(7)
C(31)−C(32)	1.550(14)	C(27)−C(32)−C(31)	105.4(9)
C(31)−P(2)	1.784(9)	C(32)−O(1)−C(29)	97.0(7)
C(32)−O(1)	1.414(12)	C(27)−P(1)−Pt(1)	119.1(3)
C(1)−Pt(1)−N(1)	79.4(3)	C(31)−P(2)−Pt(1)	113.6(3)
C(1)−Pt(1)−P(2)	90.7(2)		

four stereogenic centers at C(11), C(29), C(27), and C(32) are *S*, *S*, *S*, and *R*, respectively. From the X-ray crystallography and the $^{31}P\{^{1}H\}$ NMR spectroscopic data of *endo*-**8b**, the doublet signal at δ −6.2 is diagnostic of the PPh_2 group from 3-diphenylphosphinofuran, while the doublet at δ 27.6 is assigned to PPh_2 group from diphenylvinylphosphine. Hence it could be established that complex *endo*-**4a** is the major component of the mixture generated directly from the asymmetric Diels−Alder reaction, while complex *endo*-**4b** is the minor cycloaddition product formed.

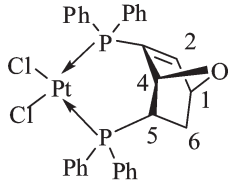
From these recoordination experiments and spectroscopic and crystallographic studies, the two *endo*-cycloadducts generated by asymmetric cycloaddition reaction of diphenylvinylphosphineand and 3-diphenylphosphinofuran promoted by the chiral metal complex (*R*)-**1** were established to be complexes *endo*-**4b** and *endo*-**4b** in the ratio of 17:1, respectively. This reaction proceeds with high stereoselectivity under mild conditions. Studies on the stereodynamic properties of optically pure ligand and the catalytic application of its metal complexes are currently in progress.

Experimental Section

All air-sensitive manipulations were carried out using Schlenk and cannula techniques under a positive pressure of argon. All NMR spectra were recorded at 25 °C on Bruker ACF 300,400, and 500 spectrometers. Optical rotations were measured on the specified solution in a 0.1 dm cell at 25 °C with a Perkin-Elmer model 341 polarimeter. Elemental analyses were performed at the Elemental Analysis Laboratory of the Division of Chemical and Biological Sciences of Nanyang Technological University. High-resolution mass spectra were obtained with a Finnigan MAT 95 XP mass spectrometer (Thermo Electron Corporation). All melting points were measured using the SRS Optimelt Automated Melting Point System, SRS MPA100.

3-Diphenylphosphinofuran was prepared as previously reported.[24] Dimeric platinum template (*R*)-, (*S*)-**1**, and (*S*)-**7** were prepared by an improved method previously reported by our group.[25]

{(1*S*,4*R*,5*S*)-dichloro-[3,5-bis(diphenylphosphino)-7-oxabicyclo-[2.2.1]-hept-2-ene-*P*^{3}, *P*^{5}}Platinum(II), *endo*-5. A solution of silver perchlorate (0.148 g, 0.71 mmol) in water (1 mL) was added to a mixture containing the platinum template (*R*)-**1** (0.255 g, 0.29 mmol), diphenylvinylphosphine (0.126 g, 0.59 mmol), and 3-diphenylphosphinofuran (0.15 g, 0.59 mmol) in dichloromethane (20 mL). The solution was stirred vigorously at room temperature for 1 h. The solution was filtered (to remove silver chloride), washed with water, and then dried ($MgSO_4$). Then we removed dichloromethane and dissolved the reaction mixture into 1,2-dichloroethane . It was further stirred at 60 °C for 9 days. The cationic complex was treated with concentrated sulfuric acid (70%, 3 mL) for 0.5 h, and the acidic solution was poured onto ice (ca. 4 g). Lithium chloride (0.6 g) was then added, and the mixture was stirred for 1 h. Addition of dichloromethane (20 mL) gave a clear yellow organic layer, which was subsequently separated, and the aqueous layer was extracted with dichloromethane. The combined organic layer was washed with water and then dried over anhydrous $MgSO_4$. Subsequently fractional crystallization from dichloromethane-diethyl ether gave complex *endo*-**5** as white prisms: mp 285−286 °C (dec); $[\alpha]_D = +34.7$ (c = 4.0, CH_2Cl_2); 0.303 g (70% yield). Anal. Calcd for $C_{30}H_{26}Cl_2OP_2Pt$: C, 49.3; H, 3.6. Found: C, 49.2; H, 3.6. ^{1}H NMR ($CDCl_3$, δ): 1.08−1.15 (m, 1H, H_5), 2.25−2.37 (m, 1H, $H_{6(exo)}$), 3.43−3.67 (m,1H, $H_{6(endo)}$), 4.98 (d, 1H, $^3J_{HH}$ = 3.9 Hz, H_1), 5.10 (d, 1H, $^3J_{HH}$ = 3.9 Hz, H_4), 6.56 (dd, 1H, $^3J_{PH}$ = 15.3 Hz, $^3J_{HH}$ = 7.0 Hz, H_2), 7.37−8.35 (m, 20H, aromatics). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, δ): 21.2 (d, 1 P, J_{PP} = 14.7 Hz, J_{PtP} = 3577 Hz, P^5), −15.1 (d, 1 P, J_{PP} = 14.7 Hz, J_{PtP} = 3411 Hz, P^3).



endo-**5**

Table 3. Crystallographic Data for Complexes *endo*-**5** and *endo*-**8b**

	endo-**5**	*endo*-**8b**
formula	$C_{30}H_{26}Cl_2OP_2Pt$	$C_{45}H_{44}Cl_3NO_5P_2Pt$
fw	730.44	1042.19
space group	*P*2(1)	*P*2(1)2(1)2(1)
crystal system	monoclinic	orthorhombic
a /Å	11.1119(5)	10.0786(17)
b /Å	17.0141(6)	10.2927(15)
c /Å	14.4999(6)	42.255(7)
V /Å^3	2740.93(19)	4383.4(12)
Z	4	4
T /K	173(2)	296(2) K
ρ_{calcd} /g cm^{-3}	1.770	1.579
λ /Å	0.71073 (Mo)	0.71073 (Mo)
μ/mm^{-1}	5.454	3.502
Flack param	0.003(2)	0.045(10)
R_1 (obsd data)	0.0181	0.0441
wR_2 (obsd data)	0.0381	0.0996

(1*S*,4*R*,5*S*)-3,5-bis(diphenylphosphino)-7-oxabicyclo[2.2.1]-hept-2-ene,*endo*-6 and {(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthyl-*C*, *N*}{(1*S*,4*R*,5*S*)-[3,5-bis(diphenylp- hosphino)-7-oxabicyclo[2.2.1]-hept-2-ene-*P*^{3},*P*^{5}}platinum(II)perchlorate, *endo*-8b. A solution of *endo*-**5** (0.2 g, 0.27 mmol) in dichloromethane (15 mL) was stirred vigorously with a saturated aqueous solution of potassium cyanide (0.2 g) for half an hour. The resulting colorless organic layer was separated, washed with water, and dried ($MgSO_4$). Upon the removal of solvent, a white solid was obtained: $[\alpha]_D = -37.6$ (c = 1.7, CH_2Cl_2); 0.102 g (80% yield). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, δ): −12.5 (d, 1P, $^3J_{PP}$ = 77 Hz, *P*), −20.8 (d, 1P, $^3J_{P,P}$ = 77 Hz, *P*). ESIHRMS: Found: m/z 465.1546. Calcd for $C_{30}H_{26}OP_2$: $(M+H)^+$ 465.1537. Added (R_P)-**6** (0.07 g, 0.15 mmol) to a solution of (*S*)-**7** (0.087 g, 0.15 mmol) in dichloromethane (15 mL) and stirred vigorously for 3 h. Recrystallization of the crude product from dichloromethane-diethyl ether gave complex *endo*-**8b** as pale

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yellow crystals: mp 210−212 °C (dec); $[\alpha]_D = -35°$ (c = 1.0, CH_2Cl_2); 0.134 g (85% yield). ESIHRMS: Found: m/z 857.2401. Calcd for $C_{44}H_{42}NOP_2Pt$: $(M-ClO_4^-)^+$ 857.2390. Anal. Calcd for $C_{44}H_{42}ClNO_5P_2Pt$: C, 55.2; H, 4.4; N, 1.5. Found: C, 54.7; H, 4.9; N, 1.5. ^{1}H NMR ($CDCl_3$, δ): 1.18−1.23 (m,1H, H_5), 1.42 (d, 3H, $^3J_{HH}$ = 6.2 Hz, CH*Me*), 2.18−2.24 (m, 1H, $H_{6(exo)}$), 2.55 (s, 3H, CH*Me*), 2.91 (s, 3H, CH*Me*), 3.37−3.43 (m,1H, $H_{6(endo)}$), 4.69 (qn, 1H, $^3J_{HH} = {}^4J_{PH}$ = 6.1 Hz, C*H*Me), 4.94 (d, 1H, $^3J_{HH}$ = 3.9 Hz, H_1), 5.03 (d, 1H, $^3J_{HH}$ = 3.5 Hz, H_4), 6.48 (d, 1H, $^3J_{HH}$ = 9.1 Hz, H_2), 6.98−8.14 (m, 26H, aromatics). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 27.6 (d, 1 P, J_{PP} = 14.5 Hz, J_{PtP} = 1710 Hz, P^5), −6.2 (d, 1 P, J_{PP} = 14.5 Hz, J_{PtP} = 3677 Hz, P^3).

Crystal Structure Determination of Complexes *endo*-5 and *endo*-8b. X-ray crystallographic data for complex *endo*-**5** and *endo*-**8b** are given in Table 3. Diffraction data were collected on a Bruker X8 CCD diffracto-meter with Mo-*K*α radiation (graphite monochromator). SADABS absorption corrections were applied. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were introduced at calculated positions and refined riding on their carrier atoms. The absolute configurations of the chiral complexes were determined unambiguously by using the Flack parameter.[26]

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Supporting Information Available: Crystallographic data in CIF format for complexes *endo*-**5** and *endo*-**8b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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