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Asymmetric [2+2] Cycloaddition of (*E*)-2-(Diphenylphosphanyl)styrene Promoted by a Chiral Metal Template

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An organoplatinum complex containing the (*S*)-form of orthometalated [1-(dimethylamino)ethyl]naphthalene as the chiral auxiliary promotes the asymmetric [2+2] dimerization of (*E*)-2-(diphenylphosphanyl)styrene to generate two isomeric chelating diphosphanyl-substituted cyclobutane platinum template complexes in the ratio of 6:1. The four substituents on the cyclobutane rings adopt the pseudo-equatorial positions with an *all-trans* arrangement. The naphthylamine auxiliary can be removed chemoselectively from the template products by treatment with concentrated hydrochloric acid to form the corresponding dichloroplatinum(II) complexes, which, upon subsequent ligand displacement with aqueous cyanide, liberate the enantiomerically enriched free diphosphane ligand in high yields. Recomplexation of the liberated diphosphane to the (*R*)-form of the platinum template, followed by fractional crystallization, allows separation of the optically pure platinum template complex containing the diphosphane ligand (1*R*,2*R*,3*R*,4*R*)-1,2-bis(diphenylphosphanyl)-3,4-diphenylcyclobutane, from which the free diphosphane can be subsequently liberated efficiently.

Introduction

The [2+2] cycloaddition reaction is an important method for the synthesis of cyclobutane derivatives.[1] According to the Woodward–Hoffmann rules, concerted thermal $[_{\pi}2_{s}+_{\pi}2_{s}]$ cycloadditions are symmetry-forbidden, but reactions involving $[_{\pi}2_{s}+_{\pi}2_{a}]$ cycloaddition, stepwise addition involving biradical or zwitterionic intermediates, and photocycloaddition are possible.[2] Lewis acids[3] and transition metal complexes[4] have been shown to be useful for the activation of the [2+2] cycloaddition reaction. Recently, it has been reported that the intramolecular [2+2] photochemical dimerization of *trans*-1,2-bis(diphenylphosphanyl)-ethene can be promoted efficiently by platinum and palladium ions.[5] The resultant tetradentate phosphane and other phosphane ligands with the cyclobutane backbone have been successfully applied to many metal-catalyzed reactions.[6]

Over the years, chiral cyclometalated-amine complexes have contributed significantly in many aspects of synthetic chemistry. These organometallic compounds have been used as resolving agents for chiral ligands,[7] clear and reliable references for the NMR assignment of unknown absolute configurations,[7g,8] chiral derivatizing agents (CDAs) for enantiomeric purity determination of chiral compounds,[9] efficient chiral catalysts for asymmetric Claisen rearrangements,[10] reaction promoters for the oxidative coupling between vinylphosphanes and imines,[11] chiral templates for asymmetric Diels–Alder reactions,[12] asymmetric hydroamination,[13] and hydrophosphanylation[14] reactions. In pursing our interest in the application of chiral cyclometalated-amine complexes in asymmetric transformations, we present here the organoplatinum-promoted asymmetric [2+2] dimerization of (*E*)-2-(diphenylphosphanyl)styrene.

Results and Discussion

In the absence of a metal ion, no dimerization of (*E*)-2-(diphenylphosphanyl)styrene is observed upon heating. In principle, the use of the chiral metal promoter (*S*)-**1** for this reaction could be beneficial in several aspects as it could: (a) provide electronic activation, (b) enable the *cis* coordinated vinylphosphane ligands to approach each other closely for the intramolecular cycloaddition reaction, and (c) provide stereochemical induction. Indeed, upon removal of the chloro ligands with silver tetrafluoroborate,[12b,12c,15] the chiral metal template (*S*)-**1** promotes the targeted asymmetric [2+2] cycloaddition reaction of (*E*)-2-(diphenylphosphanyl)styrene (Scheme 1). The reaction is complete after refluxing the mixture in toluene for four days. Prior to purification, the ^{31}P NMR spectrum of the crude reaction mixture in $CDCl_3$ indicated that two major products, together with (*E*)-diphenylstyrylphosphane oxide and trace amounts of other, as-yet unidentified compounds, had formed. The two desired major products − the diastereomeric cycloadducts (*S*)-**2** and (*S*)-**3** − exhibit two pairs of doublet phos-

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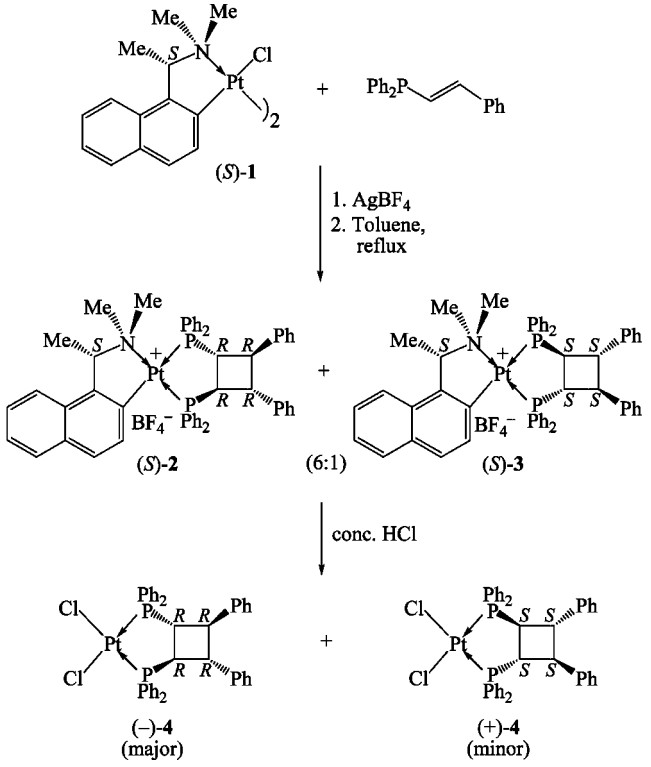
phorus resonance signals at δ = 30.3 ($J_{P,P}$ = 15.3, $J_{Pt,P}$ = 3719 Hz) and 35.2 ppm ($J_{P,P}$ = 15.3, $J_{Pt,P}$ = 1793 Hz) and δ = 29.4 ($J_{P,P}$ = 15.3, $J_{Pt,P}$ = 3780 Hz) and 35.9 ppm ($J_{P,P}$ = 15.3, $J_{Pt,P}$ = 1789 Hz)], respectively, with an intensity ratio of 6:1. It is important to note that this reaction is sensitive to the counterion present. With the tetrafluoroborate or hexafluorophosphate anion, the two desired products, (*S*)-**2** and (*S*)-**3** were formed predominantly. Between the tetrafluoroborate and hexafluorophosphate anions, the use of the former is somewhat more efficient as slightly fewer side-products are formed. However, when perchlorate was used as the counterion, the amount of (*E*)-diphenylstyrylphosphane oxide formed increased significantly, and only trace amounts of the desired cycloadducts were formed (<10%), under identical conditions. The use of a lower reaction temperature also resulted in lower yields of cycloaddition products.



Scheme 1.

The two cycloadducts generated could not, however, be purified by fractional crystallization or column chromatography, hence the naphthylamine auxiliary was removed by treatment with concentrated hydrochloric acid to generate the corresponding dichloro complexes (Scheme 1). After purification by column chromatography and fractional crystallization, an enantiomerically enriched mixture of dichloro complexes **4** [enriched in (–)-**4**] was obtained as colorless crystals. Despite repeated recrystallization, dichloro complex (–)-**4** could not be isolated in its enantiomerically pure state [the optical purity was checked by liberation of the free diphosphane ligand and recoordination to the chiral dimeric complexes (*S*)-**1** and (*R*)-**1** separately, see below]. The X-ray crystallographic analysis of a single crystal from the enantiomeric mixture of dichloro complexes **4** indeed showed that both enantiomers were present in the unit cell. The structure of one of the enantiomers is shown in Figure 1, and selected bond lengths and angles are given in Table 1. The structural analysis confirmed that the tetrasubstituted cyclobutane adducts were formed as depicted in Scheme 1. The cyclobutane ring in **4** is folded with an angle of 142.4° between the C(9)–C(1)–C(2) and C(9)–C(10)–C(2) planes. All the diphenylphosphanyl and phenyl substituents on the cyclobutane ring adopt the pseudo-equatorial positions with an *all-trans* arrangement. The two phosphorus atoms are equivalent as the molecule is C_2-symmetrical, and indeed the ^{31}P NMR spectrum of **4** in $CDCl_3$ exhibits only a singlet at δ = 26.8 ppm ($J_{Pt,P}$ = 3727 Hz).

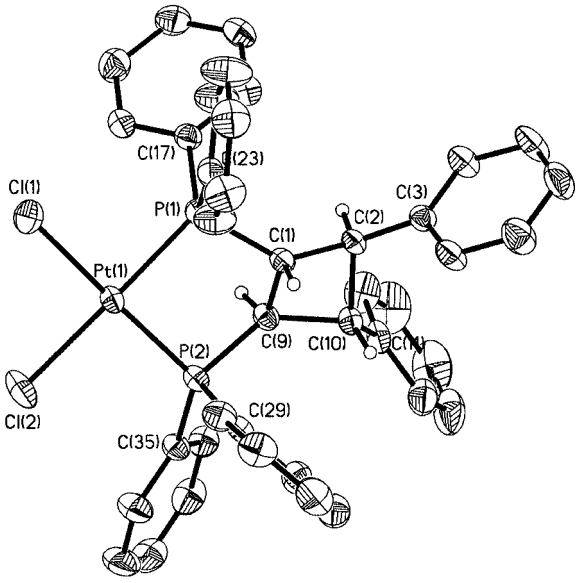


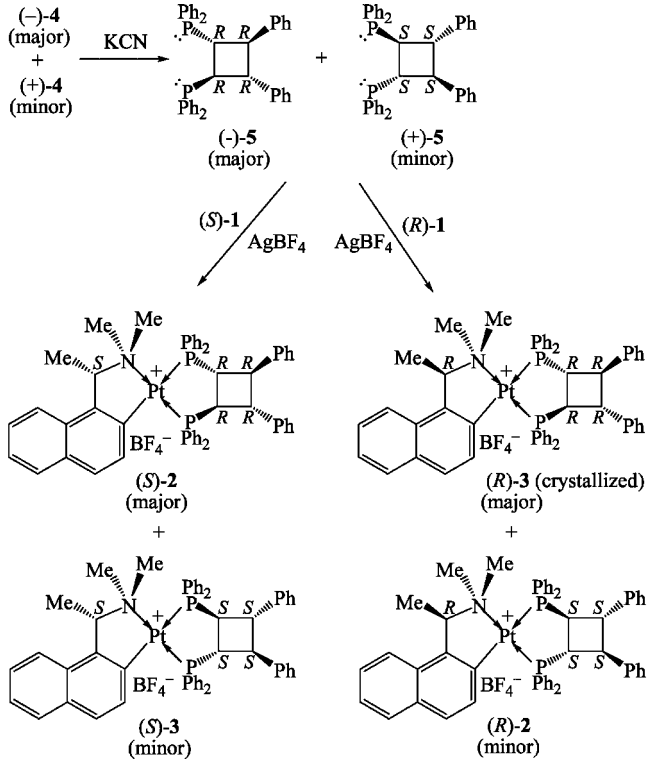
Figure 1. Molecular structure of one of the enantiomers of the dichloro complex **4**.

Table 1. Selected bond lengths [Å] and angles [°] for dichloro complex **4**.

Pt(1)–P(1)	2.2487(8)	P(1)–Pt(1)–P(2)	90.15(3)
Pt(1)–P(2)	2.2431(9)	P(2)–Pt(1)–Cl(1)	176.52(3)
Pt(1)–Cl(1)	2.3426(9)	P(2)–Pt(1)–Cl(2)	91.12(3)
Pt(1)–Cl(2)	2.3446(9)	Pt(1)–P(1)–C(1)	103.1(1)
P(1)–C(1)	1.828(3)	Pt(1)–P(2)–C(9)	101.3(1)
P(2)–C(9)	1.819(3)	P(1)–C(1)–C(9)	108.9(2)
C(1)–C(2)	1.559(4)	P(1)–C(1)–C(2)	135.2(2)
C(2)–C(3)	1.498(4)	P(2)–C(9)–C(1)	107.3(2)
C(2)–C(10)	1.564(5)	P(2)–C(9)–C(10)	135.3(3)
C(10)–C(11)	1.501(5)	C(1)–C(2)–C(3)	122.7(3)
C(9)–C(10)	1.557(4)	C(1)–C(2)–C(10)	86.6(2)
C(1)–C(9)	1.545(4)	C(2)–C(10)–C(11)	119.6(3)
P(1)–Pt(1)–Cl(1)	88.09(3)	C(2)–C(10)–C(9)	86.4(2)
P(1)–Pt(1)–Cl(2)	178.72(3)	C(1)–C(9)–C(10)	87.4(2)

Further treatment of the enantiomerically enriched dichloro complexes **4** with aqueous cyanide liberated an enantiomeric mixture of free diphosphane ligands **5** [enriched

in (–)-**5**] in quantitative yield (Scheme 2). The ^{31}P NMR spectrum of **5** in $CDCl_3$ shows a singlet resonance signal at $\delta = -0.5$ ppm. Recomplexation of the liberated C_2-symmetrical diphosphane ligands **5** to the optically pure dimeric complex (*R*)-**1**, followed by replacement of the chloride counterion with a tetrafluoroborate ion, gave two diastereomeric products, (*R*)-**3** and (*R*)-**2**, in a ratio of 5:1 (Scheme 2), which indicated the presence of both enantiomeric forms of **5** in the liberated diphosphane mixture. Importantly, these two recomplexation products exhibit identical ^{31}P NMR spectra to those recorded for the two cycloadducts generated directly from the asymmetric [2+2] cycloaddition reaction. Eventually, the major recomplexation product, with phosphorus resonance signals at $\delta = 29.4$ ($J_{P,P} = 15.3$, $J_{Pt,P} = 3780$ Hz) and 35.9 ppm ($J_{P,P} = 15.3$, $J_{Pt,P} = 1789$ Hz), could be isolated in a diastereomerically pure form by fractional crystallization from dichloromethane/diethyl ether as colorless crystals in 66% yield {$[\alpha]_D = +148$ (CH_2Cl_2)}. Due to the unique *trans*-electronic influences which originate from the organoplatinum unit, the larger platinum–phosphorus coupling constant observed for the doublet signal at $\delta = 29.4$ ppm is diagnostic of the PPh_2 group coordinated *trans* to the σ-donating nitrogen atom.[12b,12c,15] On the other hand, the doublet at $\delta = 35.9$ ppm, 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. This crystalline product was confirmed by X-ray crystallography to be complex (*R*)-**3**, as shown in Scheme 2 and Figure 2. Selected bond lengths and angles are given in Table 2. The cyclobutane ring in complex (*R*)-**3** is folded with an angle of 141.9° between the C(16)–C(15)–C(18) and C(16)–C(17)–C(18) planes. The absolute configurations at C(11), C(15), C(16), C(17), and C(18) are established to be *R*, *R*, *R*, *R*, and *R*, respectively, with the diphenylphosphanyl and phenyl substituents on the cyclobutane ring adopting the pseudo-equatorial positions in an *all-trans* arrangement. The minor recomplexation product was assigned to complex (*R*)-**2**, which differs from (*R*)-**3** only in the absolute configurations of the C_2-symmetrical diphosphane chelate. It is noteworthy that complexes (*R*)-**3** and (*R*)-**2** are the enantiomeric forms of (*S*)-**3** and (*S*)-**2**, respectively. In the absence of any chiral NMR solvent, the NMR spectra of (*R*)-**3** and (*R*)-**2** would show identical resonance signals to those recorded for their enantiomeric counterparts. Hence from the ^{31}P NMR spectroscopic data it could be established that complex (*S*)-**3** is



Scheme 2.

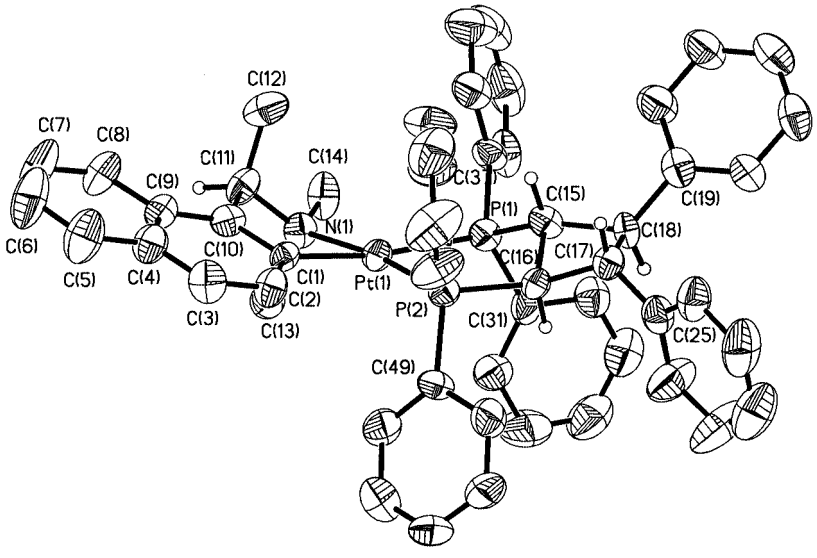


Figure 2. Molecular structure of the cationic complex (*R*)-**3**.

the minor component of the diastereomeric mixture generated directly from the asymmetric dimerization reaction, while complex (*S*)-**2** is the major cycloaddition product formed.

Table 2. Selected bond lengths [Å] and angles [°] for (*R*)-**3**.

Pt(1)–C(1)	2.043(7)	N(1)–Pt(1)–P(1)	100.3(2)
Pt(1)–N(1)	2.127(6)	N(1)–Pt(1)–P(2)	171.1(2)
Pt(1)–P(1)	2.373(2)	P(1)–Pt(1)–P(2)	87.88(7)
Pt(1)–P(2)	2.250(2)	Pt(1)–P(1)–C(15)	99.5(3)
P(1)–C(15)	1.823(6)	Pt(1)–P(2)–C(16)	105.0(2)
P(2)–C(16)	1.816(6)	P(1)–C(15)–C(16)	107.9(4)
C(15)–C(16)	1.51(1)	P(1)–C(15)–C(18)	134.2(6)
C(16)–C(17)	1.567(9)	P(2)–C(16)–C(15)	112.0(5)
C(17)–C(25)	1.48(1)	P(2)–C(16)–C(17)	135.6(5)
C(17)–C(18)	1.58(1)	C(15)–C(16)–C(17)	87.8(5)
C(18)–C(19)	1.52(1)	C(16)–C(17)–C(18)	84.8(5)
C(15)–C(18)	1.541(9)	C(16)–C(17)–C(25)	123.1(7)
C(1)–Pt(1)–P(1)	171.2(2)	C(17)–C(18)–C(15)	86.4(5)
C(1)–Pt(1)–P(2)	93.1(2)	C(17)–C(18)–C(19)	119.6(6)
C(1)–Pt(1)–N(1)	79.4(2)	C(18)–C(15)–C(16)	88.0(5)

Recomplexation of the liberated enantiomerically enriched diphosphane ligands **5** to (*S*)-**1**, followed by treatment with silver tetrafluoroborate, gave the two diastereomeric complexes (*S*)-**2** and (*S*)-**3** in a ratio of 5:1 (Scheme 2). This is in agreement with the earlier assignments of the respective complexes and the presence of both enantiomers of **5** in the liberated diphosphane mixture.

Enantiomerically pure diphosphane ligand (–)-**5** {$[\alpha]_D$ = –108 ($CHCl_3$)}, was obtained in 87% yield by similar treatment of the diastereomerically pure complex (*R*)-**3** with concentrated hydrochloric acid, followed by ligand displacement with aqueous cyanide. Recomplexation of (–)-**5** to (*S*)-**1**, followed by replacement of the chloride counterion with a tetrafluoroborate ion, gave complex (*S*)-**2** as the sole product. This confirmed the optical purity of the diphosphane ligand (–)-**5** and reaffirmed the earlier assignments of the cycloadducts and recomplexation products.

From these recoordination experiments and spectroscopic and crystallographic studies, the two cycloadducts generated by [2+2] cycloaddition reaction of (*E*)-2-(diphenylphosphanyl)styrene promoted by the chiral metal complex [(*S*)-**1**] were established to be complexes (*S*)-**2** and (*S*)-**3** in the ratio of 6:1, respectively. This dimerization reaction proceeds with high stereoselectivity and the substituents on the cyclobutane ring of the cycloadducts generated adopt the pseudo-equatorial positions with an *all-trans* arrangement, while the diastereoselectivity of the reaction is moderately high [(*S*)-**2**:(*S*)-**3** = 6:1]. Similarly, the enantiomeric products (*R*)-**2** and (*R*)-**3** can be obtained in the same ratio of 6:1 when the equally accessible complex (*R*)-**1** is used as the chiral metal promoter for the cycloaddition reaction. As related transition-metal-assisted thermal or photodimerizations of vinylphosphanes and phospholes have been reported to proceed via a stepwise biradical mechanism,[5,16] it is possible that the present chiral organoplatinum-template-promoted dimerization of (*E*)-2-(diphenylphosphanyl)styrene also follows such a biradical pathway. However, a stepwise addition involving zwitterionic intermediates and a concerted pathway cannot be ruled out.

Experimental Section

Reactions involving air-sensitive compounds were performed under a positive pressure of purified nitrogen. NMR spectra were recorded at 25 °C on Bruker ACF 300 and AMX500 spectrometers. The spectral assignments in the ^{1}H NMR spectra are based on selective decoupling of the two types of ^{31}P nucleus, and NOE data from the 2D-ROESY spectrum.[8b] 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 $\gamma B_1/2\pi$ = 5000 Hz and then transformed into 1024 × 1024 points using a sine bell weighting function in both dimensions. Optical rotations were measured on the specified solution in a 0.1-dm cell at 25 °C with a Perkin–Elmer Model 341 polarimeter. Melting points were determined on a Büchi melting point B-540. Elemental analyses were performed by the Elemental Analysis Laboratory of the Department of Chemistry at the National University of Singapore.

(*E*)-2-(diphenylphosphanyl)styrene[17] and dimeric platinum complexes (*S*)- and (*R*)-**1**[12b] were prepared according to literature methods.

Asymmetric Dimerization of (*E*)-2-(Diphenylphosphanyl)styrene and Removal of the Chiral Naphthylamine Auxiliary: An aqueous solution of silver tetrafluoroborate (0.35 g, 1.80 mmol) was added to a solution of (*S*)-**1** (0.546 g, 0.579 mmol) and (*E*)-2-(diphenylphosphanyl)styrene (0.770 g, 2.40 mmol, 90% pure) in dichloromethane (80 mL). The mixture was stirred vigorously at room temperature for 2 h, then filtered through Celite, washed with water (3 × 80 mL), and dried ($MgSO_4$). After removal of dichloromethane from the mixture, it was redissolved in toluene (350 mL) and refluxed for 4 d. After that the toluene was removed under reduced pressure and the reaction mixture was redissolved in dichloromethane (90 mL). The naphthylamine auxiliary was removed by vigorous stirring of the crude reaction mixture with concentrated hydrochloric acid (25 mL) for 14 h. The mixture was washed with water (4 × 100 mL) and dried ($MgSO_4$). The crude product was chromatographed on a silica column with dichloromethane/acetone (20:1) as eluent. Subsequent fractional crystallization from dichloromethane/petroleum ether gave an enantiomerically enriched mixture of dichloro complexes (–)-**4** and (+)-**4** as colorless crystals: 0.273 g (28% yield). $C_{40}H_{34}Cl_2P_2Pt$ (842.7): calcd. C 57.0, H 4.1; found C 57.0, H 4.1. ^{1}H NMR ($CDCl_3$): δ = 2.69–2.79 (m, 2 H, PC*H*), 3.26–3.34 (m, 2 H, PhC*H*), 6.79–8.19 (m, 30 H, aromatics) ppm. ^{31}P NMR ($CDCl_3$): δ = 26.8 (s, $J_{Pt,P}$ = 3727 Hz, 2 P, P^1, P^2) ppm.

Synthesis and Isolation of [{(*R*)-1-[1-(Dimethylamino)ethyl]naphthyl-*C*^{2},*N*}{(1*R*,2*R*,3*R*,4*R*)-1,2-bis(diphenylphosphanyl)-3,4-diphenylcyclobutane-*P*^{1},*P*^{2}}]platinum(II) Tetrafluoroborate [(*R*)-3]: Enantiomerically enriched dichloro complexes **4** (0.129 g, 0.153 mmol) dissolved in dichloromethane (30 mL) were stirred vigorously with a saturated aqueous solution of potassium cyanide (2 g) for 2 h. The organic portion was separated, washed with water (3 × 25 mL), and dried ($MgSO_4$). After that it was added to a solution of (*R*)-**1** (0.068 g, 0.072 mmol) in dichloromethane (10 mL), followed by the addition of aqueous $AgBF_4$ (0.050 g, 0.26 mmol). The mixture was stirred vigorously for 2 h, then filtered through Celite, washed with water (3 × 40 mL), and dried ($MgSO_4$). Recrystallization of the crude product from dichloromethane/diethyl ether gave complex (*R*)-**3** as colorless crystals: m.p. 278–279 °C (decomp.). $[\alpha]_D$ = +148 (*c* = 0.7, CH_2Cl_2); 0.106 g (66% yield). $C_{54}H_{50}BF_4NP_2Pt$ (1056.8): calcd. C 61.4, H 4.8, N 1.3; found C 61.0, H 4.8, N 1.4. ^{1}H NMR ($CDCl_3$): δ = 1.67 (d, $^3J_{H,H}$ = 6.0 Hz, 3 H, CH*Me*), 2.37–2.52 (m, 1 H, H_1), 2.58–2.73 (m, 1 H, H_2), 2.82 (dd, $^4J_{P,H}$ = 4.3, $^4J_{P,H}$ = 2.7 Hz, 3 H, NMe_{eq}), 3.05–3.17 (m, 1 H, H_3), 3.17 (d, $^4J_{P,H}$ =

1.9 Hz, 3 H, NMe_{ax}), 3.26–3.38 (m, 1 H, H_4), 4.92 (quin, $^3J_{H,H}$ = $^4J_{P,H}$ = 6.0 Hz, 1 H, C*H*Me), 6.57–8.14 (m, 36 H, aromatics), ppm. ^{31}P NMR ($CDCl_3$): δ = 29.4 (d, $J_{P,P}$ = 15.3, $J_{Pt,P}$ = 3780 Hz, 1 P, P^1), 35.9 (d, $J_{P,P}$ = 15.3, $J_{Pt,P}$ = 1789 Hz, 1 P, P^2) ppm.

Liberation of (1*R*,2*R*,3*R*,4*R*)-1,2-Bis(diphenylphosphanyl)-3,4-diphenylcyclobutane [(–)-5]: The naphthylamine auxiliary in complex (*R*)-**3** was first removed chemoselectively by stirring a solution of the complex (0.036 g, 0.034 mmol) vigorously in dichloromethane (12 mL) with concentrated hydrochloric acid (4 mL) at room temperature for 7 h. After that more dichloromethane (15 mL) was added and the mixture was washed with water (4 × 20 mL) and dried ($MgSO_4$). The resultant dichloro complex (–)-**4** solution was stirred vigorously with a saturated aqueous solution of KCN (2 g) for 2 h. The organic portion was separated, washed with water (3 × 30 mL), and dried ($MgSO_4$). A white solid was obtained after removal of the solvent: $[\alpha]_D$ = –108 (*c* = 0.6, $CHCl_3$); 0.017 g (87% yield). $C_{40}H_{34}P_2$ (576.7): calcd. C 83.3, H 5.9; found C 82.9, H 6.1. ^{1}H NMR ($CDCl_3$): δ = 3.20–3.37 (m, 4 H, PC*H*, PhC*H*), 6.65–7.44 (m, 30 H, aromatics) ppm. ^{31}P NMR ($CDCl_3$): δ = –0.5 (s, 2 P, P^1, P^2), ppm.

Crystal Structure Determination of Complexes 4 and (*R*)-3: X-ray crystallographic data for complexes **4** and (*R*)-**3** are given in Table 3. The structures were analyzed at the National University of Singapore using a Siemens SMART CCD diffractometer with graphic monochromated Mo-K_α radiation. SADABS absorption corrections were applied for both complexes. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at a fixed distance from carbon atoms and were assigned fixed thermal parameters. The absolute configurations of complex (*R*)-**3** was determined unambiguously using the Flack parameter.[18]

Table 3. Crystallographic data for complexes **4** and (*R*)-**3**.

	4	(*R*)-**3**
Formula	$C_{40}H_{34}Cl_2P_2Pt$	$C_{54}H_{50}BF_4NP_2Pt$
Mol. mass	842.60	1056.79
Space group	$P\bar{1}$	$P2_12_12_1$
Crystal system	triclinic	orthorhombic
a [Å]	9.6147(4)	9.981(2)
b [Å]	11.2803(4)	21.649(5)
c [Å]	16.8636(7)	22.601(5)
α [°]	83.660(1)	90
β [°]	77.750(1)	90
γ [°]	73.856(1)	90
V [Å^3]	1714.3(1)	4883(2)
Z	2	4
T [K]	223(2)	223(2)
$\rho_{calcd.}$ [g cm^{-3}]	1.632	1.437
λ [Å]	0.71073 (Mo)	0.71073 (Mo)
μ [cm^{-1}]	43.70	29.90
Flack parameter	–	0.015(7)
*R*1 (obsd. data)[a]	0.0363	0.0575
*wR*2 (obsd. data)[b]	0.0739	0.0912

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

CCDC-265224 [for (*R*)-**3**] and -265225 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.cdcc.cam.ac.uk/data_request/cif.

Acknowledgments

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