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Synthesis of P-chiral phosphines via chiral metal template promoted asymmetric furan Diels–Alder reaction

Wee-Chuan Yeo [a], Shuli Chen [b], Geok-Kheng Tan [a], Pak-Hing Leung [b,*]

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

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Abstract

The organoplatinum complex containing *ortho*-metalated (*S*)-(1-(dimethylamino)ethyl)-naphthalene as the chiral auxiliary has been used to promote the asymmetric [4+2] Diels–Alder reaction between phenyldivinylphosphine and 2-diphenylphosphinofuran. The reaction was complete in 6 days at room temperature, with the formation of four isomeric diphosphino-substituted oxanorbornene metal complexes in the ratio of 4:2:2:1. Only the *exo*-cycloaddition products were formed. The formation of stereogenic carbon centers within the oxanorbornene skeleton are highly stereoselective, with all four cycloadducts adopting the same absolute configurations. However, the stereocontrol at the external phosphorus stereogenic center is less efficient (S_p:R_p = 2:1 for the template cycloadducts). The chiral naphthylamine auxiliary could be removed chemoselectively by treatment with concentrated hydrochloric acid, and further ligand liberation of the dichloro complexes with aqueous cyanide gave the diphosphino-substituted oxanorbornene ligands. Hydrogenation of the double bonds in the cycloadduct stabilizes the phosphorus stereogenic center of the free diphosphine ligand which otherwise undergoes inversion of absolute configuration.

Keywords: Asymmetric Diels–Alder reaction; Chiral metal template; P-chiral phosphines; Platinum

1. Introduction

The importance of chiral phosphine ligands in asymmetric metal catalysis has been well established [1]. Although the use of P-chiral phosphines are preferred during the initial studies on asymmetric hydrogenation, this class of potentially useful phosphine ligands have received less attention on subsequent investigations in asymmetric catalysis. This can be attributed to the difficulties in the synthesis of highly enantiomerically enriched P-stereogenic phosphines and their configurational instability at high temperatures (especially the diaryl- and triarylphosphines). Generally, P-chiral phosphines have been obtained by resolution or synthesis via precursors such as phosphine oxides, phosphine sulfides, phosphonium salts, phosphine–borane adducts and phosphine–metal complexes [1e,2]. Recently, our group has successfully applied the chiral *ortho*-metalated-amine complexes to asymmetric Diels–Alder reactions for the synthesis of a range of chiral phosphines with the rigid phospha-, oxa- and azanorbornene framework [3]. The introduction of functionalities to the versatile C-chiral bis(diphenylphosphino)-substituted oxa- and azanorbornene ligands using simple organic transformations with metal as protection, has also been achieved [4]. In this paper, we report the chiral metal template promoted asymmetric furan Diels–Alder reaction for the synthesis of diphosphino-substituted oxanorbornene ligands which contain both stereogenic phosphorus and carbon centers. The configurational stability of the stereogenic phosphorus center is also discussed.

* Corresponding author. Tel.: +65 63168905.
E-mail address: pakhing@ntu.edu.sg (P.-H. Leung).

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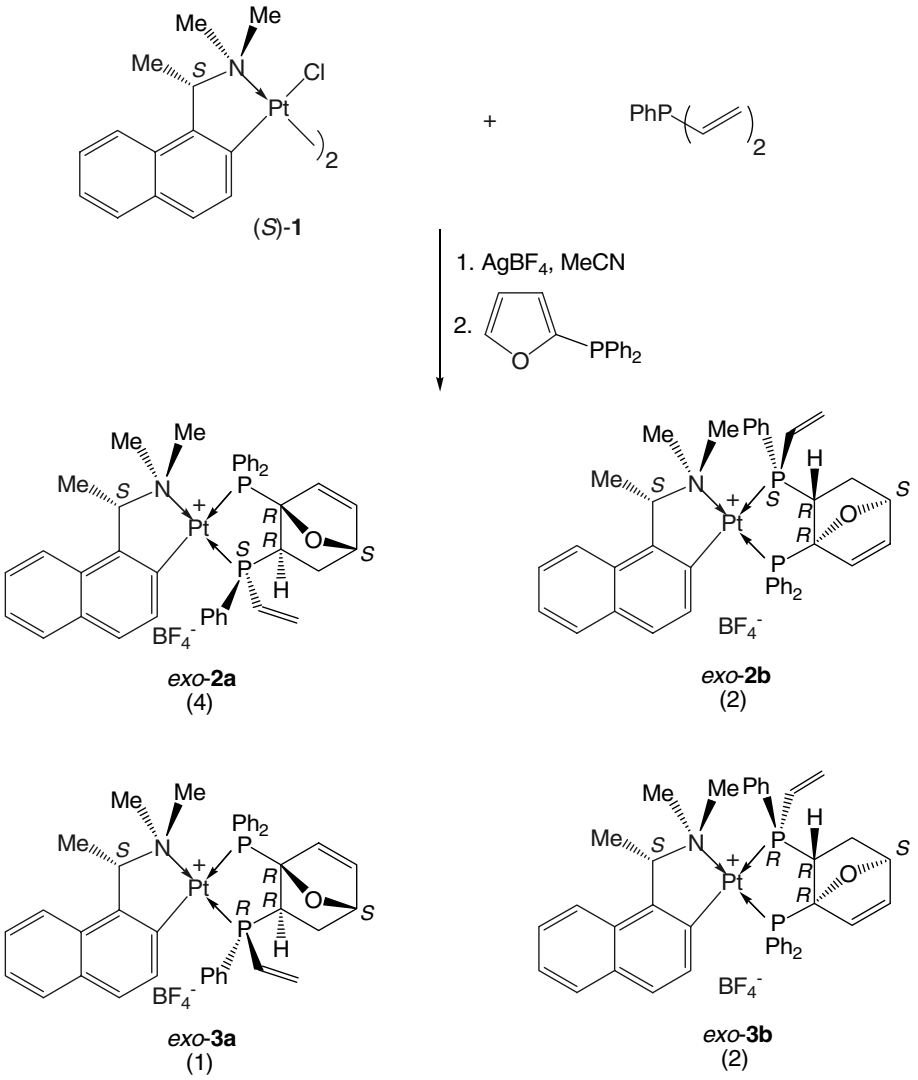
2. Results and discussion

2.1. Asymmetric furan Diels–Alder reaction

Without a metal template, no reaction was observed between phenyldivinylphosphine and 2-diphenylphosphinofuran, even upon prolonged heating. However, with the use of chiral platinum complex (*S*)-**1** (after chloro ligands abstraction with silver tetrafluoroborate [3b,3c]) as the reaction promoter, the corresponding asymmetric Diels–Alder reaction was complete in 6 days at room temperature to generate bidentate diphosphino-substituted cycloadducts which are chelated on the metal template (Scheme 1). In principle, up to sixteen stereochemically distinct template products may be formed as a result of the various sources of diastereoisomerism: (a) the relative regio arrangement of the four nonequivalent donor atoms on the plane; (b) the adoption of either the *endo*- or *exo*-cycloaddition pathways; (c) the adoption of different absolute stereochemistry for the newly generated carbon and phosphorus stereogenic centers. However, the ^{31}P NMR spectrum of the crude reaction mixture in CD_2Cl_2 exhibited four pairs of phosphorus resonance signals in the ratio of 4:2:2:1, indicating that only four out of the possible thirty two stereochemically distinct metal template cycloadducts were formed. Upon purification by silica column chromatography, the least abundant isomer was isolated by repeated fractional crystallization from dichloromethane-petroleum ether as yellow crystals in 3% yield, $[\alpha]_D$ −54° (CH_2Cl_2). The ^{31}P NMR spectrum of this diastereomerically pure product in CD_2Cl_2 showed two singlets at δ 40.0 ($J_{PtP} = 3609$ Hz) and 42.7 ($J_{PtP} = 1816$ Hz). This crystallized product was subsequently confirmed by X-ray crystallography to be complex *exo*-**3a**, as showed in Scheme 1 and Fig. 1. Selected bond distances and angles of *exo*-**3a** are given in Table 1. The geometry at platinum is distorted square planar with cis angles at Pt ranging from 79.1(6)° to 99.5(4)°. The absolute configurations of the newly formed



Scheme 1.

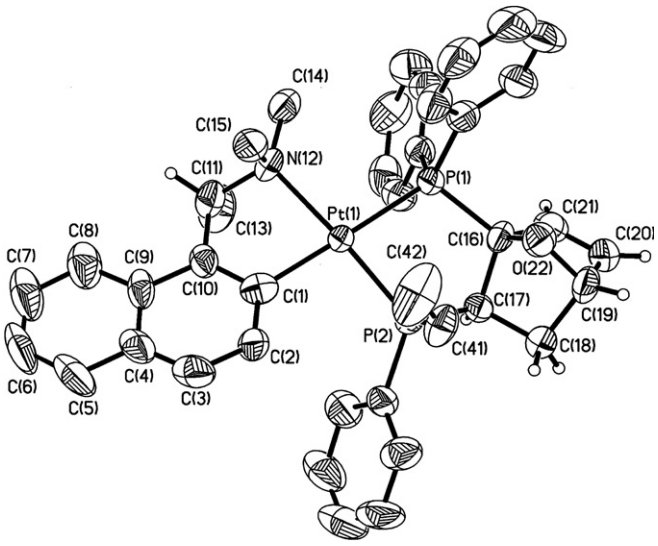


Fig. 1. Molecular structure of the cationic complex *exo*-**3a**.

Table 1
Selected bond lengths (Å) and angles (deg) for *exo*-**3a**

Pt(1)–C(1)	2.04(2)	C(1)–Pt(1)–P(2)	96.5(5)
Pt(1)–N(12)	2.14(1)	C(1)–Pt(1)–N(12)	79.1(6)
Pt(1)–P(1)	2.32(1)	N(12)–Pt(1)–P(1)	99.5(4)
Pt(1)–P(2)	2.23(1)	N(12)–Pt(1)–P(2)	175.3(5)
P(1)–C(16)	1.86(1)	P(1)–Pt(1)–P(2)	85.0(2)
P(2)–C(17)	1.85(1)	P(1)–C(16)–O(22)	112.6(5)
O(22)–C(16)	1.43(1)	P(1)–C(16)–C(17)	112.2(5)
O(22)–C(19)	1.44(1)	P(2)–C(17)–C(16)	108.7(5)
C(16)–C(17)	1.56(1)	P(2)–C(17)–C(18)	114.5(6)
C(16)–C(21)	1.50(1)	C(16)–O(22)–C(19)	96.0(6)
C(17)–C(18)	1.54(1)	C(16)–C(17)–C(18)	101.2(6)
C(18)–C(19)	1.55(1)	C(17)–C(18)–C(19)	101.0(7)
C(19)–C(20)	1.49(2)	C(18)–C(19)–C(20)	106.2(8)
C(20)–C(21)	1.32(1)	C(19)–C(20)–C(21)	106.3(8)
P(2)–C(41)	1.79(1)	C(20)–C(21)–C(16)	105.3(8)
C(41)–C(42)	1.27(2)	C(21)–C(16)–C(17)	107.1(6)
C(1)–Pt(1)–P(1)	175.6(5)	P(2)–C(41)–C(42)	121.8(9)

stereogenic centers at C(16), C(17), C(19) and P(2) are *R*, *R*, *S* and *R* respectively, with the stereogenic phosphorus atom coordinated trans to the NMe_2 group.

The other three more abundant isomeric cycloadduct template complexes could not be isolated in the pure form. Nevertheless, after chromatographic separation, the major product of the furan cycloaddition reaction could be obtained as the predominant species in a diastereomerically enriched mixture, with only small amount of the other isomeric products (<10%). Subsequent treatment of this mixture with concentrated hydrochloric acid effected the chemoselective removal of the chiral naphthylamine auxiliary. Upon recrystallization of the crude product from dichloromethane–diethyl ether, the optically pure dichloro complex *exo*-**4** was obtained as colorless crystals in 34% yield, $[\alpha]_D$ −5° (CH_2Cl_2). The ^{31}P NMR spectrum of this neutral dichloro complex in CD_2Cl_2 exhibited two doublets at δ 37.4 ($J_{PP} = 9.5$ Hz, $J_{PtP} = 3700$ Hz) and 42.7 ($J_{PP} = 9.5$ Hz, $J_{PtP} = 3494$ Hz). The molecular structure and absolute stereochemistry of *exo*-**4** was established by X-ray crystallography (Fig. 2), and selected bond lengths and angles are given in Table 2. The absolute configurations at C(1), C(2), C(5) and P(1) are *R*, *R*, *S* and *S* respectively. A point to note is that the diphosphine ligands in complexes *exo*-**3a** and *exo*-**4** have similar molecular connectivities with identical absolute configurations for the stereogenic carbon centers within the oxanorbornene skeleton, differing only in the absolute stereochemistry of the external phosphorus stereogenic center.

Further treatment of *exo*-**4** with aqueous cyanide liberated the diphosphine-substituted *exo*-cycloadduct (+)-*exo*-**5** (Scheme 2), as white solid in quantitative yield, $[\alpha]_D$ +12° ($CHCl_3$). The ^{31}P NMR spectrum of this diphosphine ligand in $CDCl_3$ revealed two doublets at δ −14.7 and −16.3 ($^3J_{PP} = 68.7$ Hz). The configuration of the phosphorus stereogenic center of (+)-*exo*-**5** is unstable at room temperature both in the solid state and in solution. Diphosphine ligand (+)-*exo*-**5** slowly undergoes inversion of absolute configuration at the phosphorus stereogenic center with the generation of (−)-*exo*-**6** until the equilibrium ratio of 1:3 is reached (in favour of (−)-*exo*-**6**). Hence thermodynamically, (−)-*exo*-**6** is more stable than (+)-*exo*-**5**.

In order to confirm the optical purity of the liberated diphosphine ligand (+)-*exo*-**5** (*i.e.* also the dichloro complex *exo*-**4**) and to establish the identity of the furan cycloaddition products, free ligand (+)-*exo*-**5** was recoordinated separately to (*S*)-**1** and the equally available enantiomeric complex (*R*)-**1**. Recomplexation of (+)-*exo*-**5** to (*S*)-**1**, followed by replacement of the chloride counterion with a tetrafluoroborate ion, gave only a pair of regioisomeric complexes (Scheme 3). The ^{31}P NMR spectrum of the crude reaction mixture in CD_2Cl_2 exhibited two pairs of doublets at δ [40.2 ($J_{PP} = 7.6$ Hz, $J_{PtP} = 3551$ Hz), 43.7

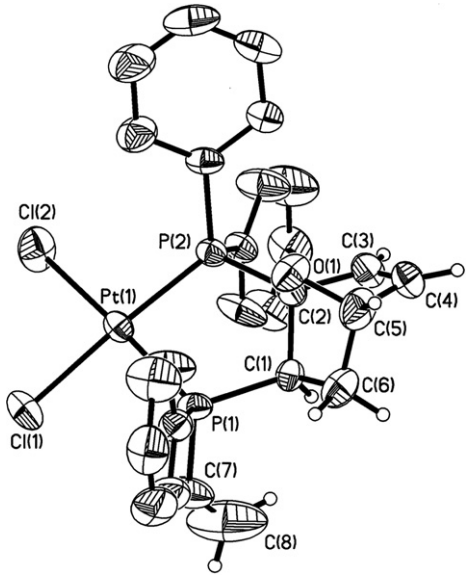


Fig. 2. Molecular structure of the dichloro complex *exo*-**4**.

Table 2
Selected bond lengths (Å) and angles (deg) for *exo*-**4** and *exo*-**9**

	exo-**4**	*exo*-**9**
Pt(1)–P(1)	2.21(1)	2.215(1)
Pt(1)–P(2)	2.21(1)	2.207(1)
Pt(1)–Cl(1)	2.35(1)	2.351(1)
Pt(1)–Cl(2)	2.36(1)	2.359(1)
P(1)–C(1)	1.86(1)	1.858(4)
P(2)–C(2)	1.85(1)	1.850(4)
O(1)–C(2)	1.44(1)	1.442(5)
O(1)–C(5)	1.45(1)	1.453(5)
C(1)–C(2)	1.57(1)	1.554(6)
C(2)–C(3)	1.51(1)	1.530(6)
C(3)–C(4)	1.31(1)	1.543(6)
C(4)–C(5)	1.50(1)	1.514(6)
C(5)–C(6)	1.55(1)	1.543(6)
C(6)–C(1)	1.54(1)	1.550(6)
P(1)–C(7)	1.81(1)	1.817(4)
C(7)–C(8)	1.17(1)	1.530(6)
P(1)–Pt(1)–Cl(1)	88.1(1)	89.3(1)
P(1)–Pt(1)–Cl(2)	175.4(1)	177.1(1)
P(1)–Pt(1)–P(2)	88.5(1)	88.9(1)
P(2)–Pt(1)–Cl(1)	176.4(1)	178.2(1)
P(2)–Pt(1)–Cl(2)	93.4(1)	90.6(1)
P(1)–C(1)–C(2)	109.4(3)	110.5(3)
P(2)–C(2)–C(1)	113.5(3)	113.5(3)
C(2)–O(1)–C(5)	95.1(4)	96.4(3)
C(1)–C(2)–C(3)	106.5(4)	108.8(3)
C(2)–C(3)–C(4)	105.6(5)	101.9(3)
C(3)–C(4)–C(5)	106.1(5)	101.2(4)
C(4)–C(5)–C(6)	106.6(5)	109.2(4)
C(5)–C(6)–C(1)	101.0(4)	101.2(3)
C(6)–C(1)–C(2)	101.0(4)	101.2(3)
P(1)–C(7)–C(8)	132.1(7)	114.1(3)

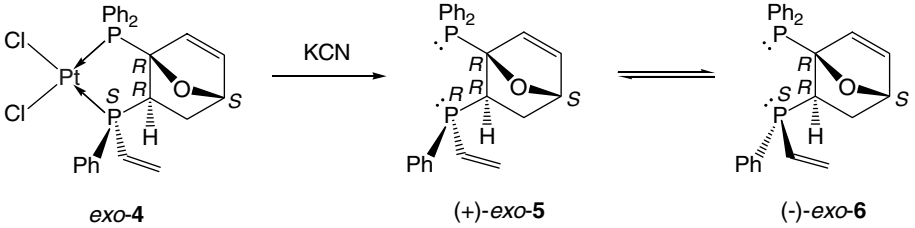
($J_{PP} = 7.6$ Hz, $J_{PtP} = 1839$ Hz)] and [38.0 ($J_{PP} = 7.6$ Hz, $J_{PtP} = 3712$ Hz), 47.5 ($J_{PP} = 7.6$ Hz, $J_{PtP} = 1770$ Hz)] in the ratio of 1:7 respectively. Importantly, these resonance signals for the two recomplexation products are identical to those recorded for the major and one of the isomeric cycloadducts (with relative adundance of 2) in the 4:2:2:1 diastereomeric product mixture obtained directly from the asymmetric furan Diels–Alder reaction. Hence *exo*-**2a** and *exo*-**2b** are two of the cycloadducts originally generated by the furan cycloaddition reaction. The ^{31}P NMR assignment of *exo*-**2a** and *exo*-**2b** could be achieved by comparing the ^{31}P NMR data with that of *exo*-**3a**. It has been well established that, for stereoisomeric chiral diphosphine metal complexes (with this class of *ortho*-metalated-amine unit) which have the same regio arrangements of the four

Scheme 3.

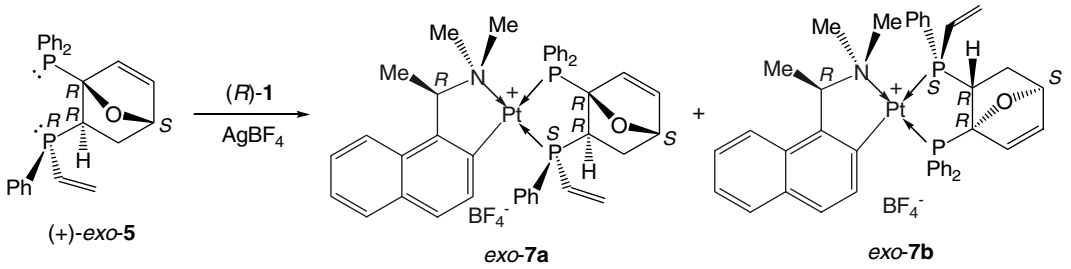
nonequivalent donor atoms but differ in the absolute configurations of the diphosphine chelate, the difference in ^{31}P NMR chemical shifts would be relatively small [3b,3c,5] On the other hand, for isomeric complexes with different regio arrangements of the donor atoms, the difference in ^{31}P NMR chemical shifts would be larger [3b,3c,5]. Hence the pair of doublet phosphorus resonances at δ 40.2 and 43.7 is assigned to *exo*-**2a**, on the basis of the similarity of the chemical shifts to *exo*-**3a**, while the pair of doublet phosphorus signals at δ 38.0 and 47.5 is assigned to *exo*-**2b**.

Recomplexation of (+)-*exo*-**5** to (*R*)-**1**, followed by replacement of the chloride counterion with tetrafluoroborate ion, similarly generated only a pair of regioisomeric complexes (Scheme 4). The ^{31}P NMR spectrum of the crude products in CD_2Cl_2 showed two pairs of doublets at δ [41.8 ($J_{PP} = 7.6$ Hz, $J_{PtP} = 1827$ Hz), 43.0 ($J_{PP} = 7.6$ Hz, $J_{PtP} = 3624$ Hz)] and [38.0 ($J_{PP} = 7.6$ Hz, $J_{PtP} = 3708$ Hz), 46.7 ($J_{PP} = 7.6$ Hz, $J_{PtP} = 1766$ Hz)] in the ratio of 1:4 respectively. Importantly, pairs of phosphorus resonance signals at δ (40.2, 43.7) and (38.0, 47.5) were not observed. This further confirmed the optical purity of the diphosphine ligand (+)-*exo*-**5** and the dichloro complex *exo*-**4**.

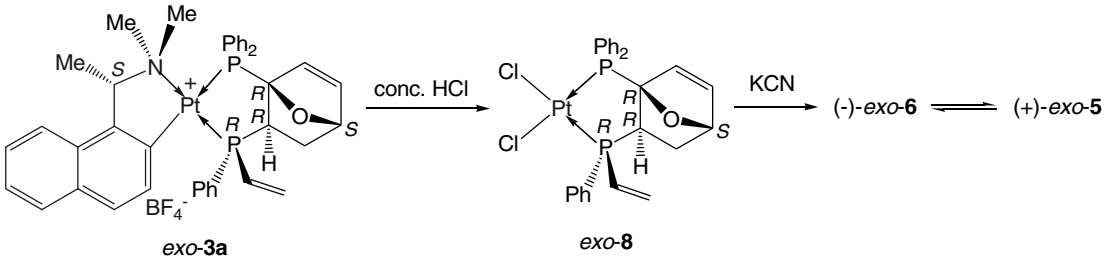
Similarly, the diphosphine ligand (−)-*exo*-**6** could be liberated from *exo*-**3a** by treatment with concentrated hydrochloric acid, followed by ligand displacement with aqueous cyanide (Scheme 5). The free diphosphine ligand was obtained as white solid in 85% yield, $[\alpha]_D$ −85° ($CHCl_3$). The ^{31}P NMR spectrum of (−)-*exo*-**6** in $CDCl_3$ exhibited two doublets at δ −15.3 and −16.7 ($^3J_{PP} = 95.4$ Hz). Similarly, the configuration of the phosphorus stereogenic center of diphosphine ligand (−)-*exo*-**6** is unstable at room temperature. (−)-*exo*-**6** is susceptible to slow inversion of absolute configuration at the phosphorus stereogenic center with the generation of (+)-*exo*-**5** until the same equilibrium ratio of 1:3 is achieved (in favour of (−)-*exo*-**6**).



Scheme 2.

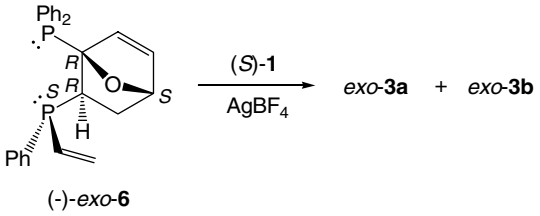


Scheme 4.



Scheme 5.

Recoordination of (−)-*exo*-**6** to (*S*)-**1**, followed by treatment with silver tetrafluoroborate resulted in the formation of two regioisomeric complexes (Scheme 6). The ^{31}P NMR spectrum of the crude product mixture in CD_2Cl_2 exhibited two pairs of singlet phosphorus resonance signals with a pair of them being identical to those recorded previously for *exo*-**3a**. The other two singlets observed at δ 37.3 ($J_{PtP} = 3696$ Hz) and 44.7 ($J_{PtP} = 1793$ Hz), are thus assigned to the regioisomer *exo*-**3 b**. Importantly, this pair of singlet phosphorus resonances is identical to those recorded for the remaining cycloadduct (with relative abundance of 2) in the 4:2:2:1 diastereomeric product mixture obtained directly from the furan cycloaddition reaction. Thus complex *exo*-**3b** is the fourth product of the asymmetric Diels–Alder reaction. In a further test of optical purity of the diphosphine ligand, (−)-*exo*-**6** was similarly recoordinated to (*R*)-**1**. The ^{31}P NMR spectrum of the crude product in CD_2Cl_2 showed two pairs of doublets at δ [41.9 ($J_{PP} = 7.6$ Hz, $J_{PtP} = 3631$ Hz), 42.4 ($J_{PP} = 7.6$ Hz, $J_{PtP} = 1823$ Hz)] and [38.1 ($J_{PP} = 7.6$ Hz, $J_{PtP} = 3692$ Hz), 45.3 ($J_{PP} = 7.6$ Hz, $J_{PtP} = 1778$ Hz)] in the ratio of 1:4 respectively. Since no pairs of phosphorus resonance signals were observed at δ (40.0, 42.7) and (37.3, 44.7), this confirmed the optical purity of the diphosphine ligand (−)-*exo*-**6**.



Scheme 6.

From these recoordination experiments, spectroscopic and crystallographic studies, the four stereoisomeric products generated in the chiral metal template promoted Diels–Alder reaction between phenyldivinylphosphine and 2-diphenylphosphinofuran have been established to be *exo*-**2a**, *exo*-**2b**, *exo*-**3b** and *exo*-**3a** in the ratio of 4:2:2:1 respectively. No *endo*-cycloaddition products were formed. While the organometallic ring is kinetically stable, the monodentate P → M bonds are generally labile, and facile ligand redistribution processes have been frequently observed, particularly when a mixture of nonequivalent phosphine ligands are involved [3b,5e,6]. The ligand redistribution processes usually occur much faster (within seconds) than the Diels–Alder reaction involving vinylphosphines as the dienophiles (ranged from several hours to several days) [3a]. Thus regardless of the sequence of introduction of the phosphino-substituted diene and dienophile to the chiral metal template, regioisomers are still possible due to the faster precursor exchange process. For the current asymmetric Diels–Alder reaction, the regioselectivity is not efficient (2:1). The formation of stereogenic carbon centers within the oxanorbornene skeleton are highly stereoselective, with all four cycloadducts adopting the same absolute configurations. This can be attributed to the distinct stereochemical directing properties of the chiral cyclometalated-amine template via interchelate steric repulsion between the chiral auxiliary and reacting phosphorus substrates [5h,7]. The same absolute stereochemistry of the oxanorbornene backbone is preferably formed irrespective of whether the dienophile is coordinated *trans* to the nitrogen or aromatic carbon of the organometallic ring. For this asymmetric Diels–Alder reaction,

the highly stereoselective formation of the oxanorbornene backbone and its absolute stereochemistry is in accord with the earlier published work using diphenylvinylphosphine as the dienophile [3b]. However, for the current asymmetric Diels–Alder reaction, the stereocontrol at the external phosphorus stereogenic center is not efficient (S_p:R_p = 2:1 for the template cycloadducts).

2.2. Hydrogenation

Both the double bonds in *exo*-**4** could be hydrogenated smoothly with the use of Pd/C as catalyst (Scheme 7). The resultant complex *exo*-**9** was isolated by crystallization from dichloromethane-diethyl ether as colorless crystals in 92% yield, $[\alpha]_D$ +56° (CH_2Cl_2). The ^{31}P NMR spectrum of this hydrogenated product in CD_2Cl_2 revealed two doublets at δ 40.7 (J_{PP} = 7.6 Hz, J_{PtP} = 3708 Hz) and 54.2 (J_{PP} = 7.6 Hz, J_{PtP} = 3494 Hz). The molecular structure and absolute configurations were confirmed by X-ray analysis (Fig. 3). Selected bond distances and angles are given in Table 2. The absolute stereochemistry at C(1), C(2), C(5) and P(1) are established to be *R*, *R*, *R* and *S* respectively. The apparent inversion of configuration at C(5) in the hydrogenated product is merely a consequence of the CIP sequence rules [8]. The optically pure free diphosphine ligand (+)-*exo*-**10** was obtained by ligand displacement of *exo*-**9** with aqueous cyanide (Scheme 7), as white solid in quantitative yield, $[\alpha]_D$ +6° ($CHCl_3$). The ^{31}P NMR spectrum of (+)-*exo*-**10** in $CDCl_3$ showed an apparent doublet at δ −6.5 ($^3J_{PP}$ = 80.1 Hz). In contrast to (+)-*exo*-**5** and (−)-*exo*-**6**, the phosphorus stereogenic center in the saturated diphosphine ligand (+)-*exo*-**10** is shown to be configurationally stable at room temperature by ^{31}P NMR studies. It is noteworthy that the apparent phosphorus inversion at the phosphorus stereogenic center of the free diphosphine ligands (+)-*exo*-**5** and (−)-*exo*-**6** are unusual, as alkylphenylvinylphosphines are known to be configurationally stable at room temperature [9]. Besides the possibility of (+)-*exo*-**5** and (−)-*exo*-**6** having unusually low thermal phosphorus inversion barriers, we could not rule out the possibility that the phosphorus inversion process of the unsaturated diphosphine ligands (+)-*exo*-**5** and (−)-*exo*-**6** could be due to an olefin displacement via an intramolecular cycloaddition pathway.

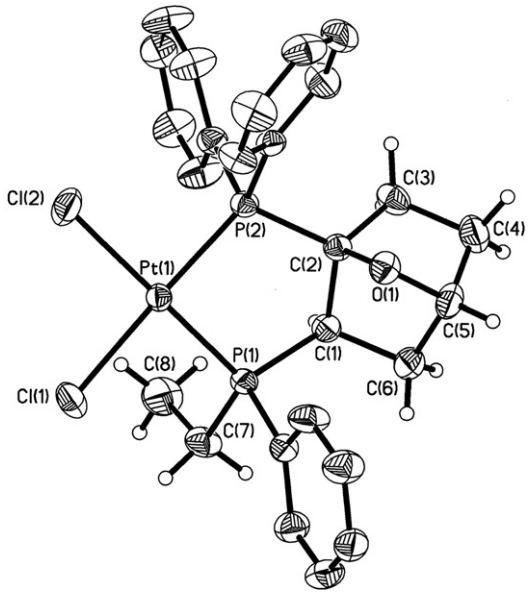


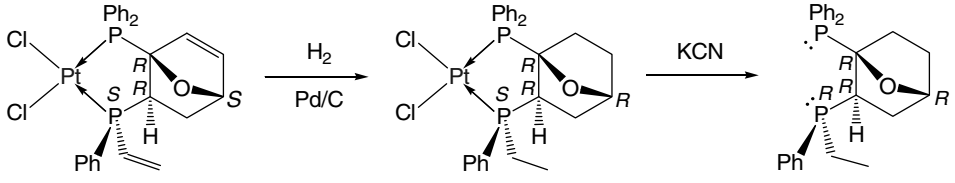
Fig. 3. Molecular structure of the dichloro complex ***exo*-9**.

Further studies are currently underway to look at such a possibility.

In conclusion, the asymmetric furan Diels–Alder reaction involving a prochiral dienophile has been demonstrated for the synthesis of chiral phosphines having both P-stereogenic and C-stereogenic centers. In principle, besides the hydrogenation reaction shown, other organic transformations can be performed on the diphosphine metal complexes for the synthesis of potentially useful functionalized P-chiral phosphine ligands and metal complexes [4].

3. Experimental

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 nucleus, and NOE data from 2D ^1H–^1H ROESY spectra [7a]. 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



exo-**4** *exo*-**9** (+)-*exo*-**10**

Scheme 7.

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 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. Elemental analyses were performed by the Elemental Analysis Laboratory of the Department of Chemistry at the National University of Singapore.

2-Diphenylphosphinofuran [10] and phenyldivinylphosphine [11] were prepared according to standard literature methods. The dimeric platinum complexes (*S*)- and (*R*)-**1** were prepared by the method previously reported by our group [3b].

3.1. Chiral metal template promoted asymmetric furan Diels–Alder reaction

An aqueous solution of silver tetrafluoroborate (1.200 g, 6.160 mmol) was added to a solution of (*S*)-**1** (2.100 g, 2.228 mmol) and phenyldivinylphosphine (0.745 g, 4.59 mmol) in dichloromethane (150 mL) and acetonitrile (15 mL). The mixture was stirred vigorously at room temperature for 2 h, then filtered through Celite (to remove AgCl), washed with water (3×150 mL), and dried ($MgSO_4$). The mixture was subsequently treated with 2-diphenylphosphinofuran (1.157 g, 4.59 mmol) and stirred at room temperature for 6 d. The crude products were purified by silica column chromatography with acetone-chloroform as eluent.

3.2. [SP-4-4-{(S)-1-[1-(dimethylamino)ethyl]naphthyl-C^2,N}{(1S,4R,5R)-4-(diphenylphosphino)-5-(R)-(ethenylphenylphosphino)-7-oxabicyclo[2.2.1]hept-2-ene-P^4,P^5}]platinum(II) tetrafluoroborate, (exo-**3a**)

Compound *exo*-**3a** was obtained by repeated fractional crystallization from dichloromethane-diethyl ether as yellow crystals: mp 238–240 °C (decomp.); $[\alpha]_D$ −54° (*c* 0.5, CH_2Cl_2); 0.124 g (3% yield). Anal. Calcd for $C_{40}H_{40}BF_4NOP_2Pt$: C, 53.7; H, 4.5; N, 1.6. Found: C, 53.2; H, 4.4; N, 1.7%. ^{31}P NMR (CD_2Cl_2) δ 40.0 (s, 1P, $J_{PtP} = 3609$ Hz, P^5), 42.7 (s, 1P, $J_{PtP} = 1816$ Hz, P^4); ^{1}H NMR (CD_2Cl_2) δ 1.71–1.83 (m, 1H, H_{6endo}), 1.79 (d, 3H, $^3J_{HH} = 6.0$ Hz, CH*Me*), 2.40 (dd, 1H, $^3J_{HH} = 8.0$ Hz, $^3J_{HH} = 2.0$ Hz, H_5), 2.60–2.70 (m, 1H, H_{6exo}), 2.71 (d, 3H, $^4J_{PH} = 2.0$ Hz, NMe_{ax}), 2.83 (dd, 3H, $^4J_{PH} = 3.7$ Hz, $^4J_{PH} = 2.9$ Hz, NMe_{eq}), 4.81 (qn, 1H, $^3J_{HH} = {}^4J_{PH} = 6.0$ Hz, C*H*Me), 5.30 (dd, 1H, $^3J_{HH} = 4.7$ Hz, $^3J_{HH} = 1.6$ Hz, H_1), 5.96 (d, 1H, $^3J_{HH} = 5.8$ Hz, H_3), 6.50 (ddd, 1H, $^3J_{PH} = 45.7$ Hz, $^3J_{HH} = 12.0$ Hz, $^2J_{HH} = 1.1$ Hz, PCH=*H*H′), 6.62 (dd, 1H, $^3J_{HH} = 5.8$ Hz, $^3J_{HH} = 1.6$ Hz, H_2), 6.64 (ddd, 1H, $^3J_{PH} = 22.5$ Hz, $^3J_{HH} = 18.3$ Hz, $^2J_{HH} = 1.1$ Hz, PCH=H*H*′), 6.81 (ddd, 1 H, $^3J_{HH} = 18.3$ Hz, $^2J_{PH} = 17.2$ Hz, $^3J_{HH} = 12.0$ Hz, PC*H*=CH_2), 7.21–7.99 (m, 21H, aromatics).

3.3. Isolation of [SP-4-3-{(1S,4R,5R)-dichloro[4-(diphenylphosphino)-5-(S)-(ethenylphenylphosphino)-7- oxabicyclo[2.2.1]hept-2-ene-P^4,P^5]}]platinum(II), (exo-**4**)

The diastereomerically enriched portion (after chromatographic purification) which contained predominantly the major product (*exo*-**2a**) of the furan cycloaddition reaction was stirred vigorously with concentrated hydrochloric acid (20 mL) in dichloromethane (60 mL) for 1 day. After that the mixture was washed with water (4×70 mL), and dried ($MgSO_4$). Recrystallization from dichloromethane–diethyl ether gave the optically pure dichloro complex as colorless crystals: mp 292–294 °C (decomp.); $[\alpha]_D$ −5° (*c* 0.6, CH_2Cl_2); 1.018 g (34% yield, 2 steps combined). Anal. Calcd for $C_{26}H_{24}Cl_2OP_2Pt$: C, 45.9; H, 3.6. Found: C, 45.5; H, 3.4%. ^{31}P NMR (CD_2Cl_2) δ 37.4 (d, 1P, $J_{PP} = 9.5$ Hz, $J_{PtP} = 3700$ Hz, P^4), 42.7 (d, 1P, $J_{PP} = 9.5$ Hz, $J_{PtP} = 3494$ Hz, P^5); ^{1}H NMR (CD_2Cl_2) δ 1.61 (dt, 1H, $^2J_{HH} = {}^3J_{PH} = 11.3$ Hz, $^3J_{HH} = 8.4$ Hz, H_{6endo}), 1.67–1.81 (m, 1H, H_{6exo}), 2.62–2.68 (m, 1H, H_5), 4.86–4.91 (m, 1H, H_1), 6.15 (d, 1H, $^3J_{HH} = 5.6$ Hz, H_3), 6.24 (dd, 1H, $^3J_{PH} = 20.1$ Hz, $^3J_{HH} = 18.9$ Hz, PCH=*H*H′), 6.41 (dd, 1H, $^3J_{PH} = 41.4$ Hz, $^3J_{HH} = 12.5$ Hz, PCH=H*H*′), 6.53 (dt, 1H, $^3J_{HH} = {}^5J_{PH} = 1.4$ Hz, $^3J_{HH} = 5.6$ Hz H_2), 7.06 (ddd, 1H, $^2J_{PH} = 20.5$ Hz, $^3J_{HH} = 18.9$ Hz, $^3J_{HH} = 12.5$ Hz, PC*H*=CH_2), 7.40–8.20 (m, 15H, aromatics).

3.4. Liberation of (1S,4R,5R)-4-(diphenylphosphino)-5-(R)-(ethenylphenylphosphino)-7-oxabicyclo[2.2.1]hept-2-ene, [(+)-exo-**5**]

A solution of *exo*-4 (0.114 g, 0.168 mmol) in dichloromethane (20 mL) was stirred vigorously with a saturated solution of potassium cyanide (2 g) for 30 mins. The organic layer was separated, washed with water (3×20 mL), and dried ($MgSO_4$). Upon removal of the solvent, white solid was obtained: $[\alpha]_D$ +12° (*c* 2.2, $CHCl_3$); 0.066 g (95% yield). ^{31}P NMR ($CDCl_3$) δ −14.7 (d, 1P, $^3J_{PP} = 68.7$ Hz, *P*), −16.3 (d, 1P, $^3J_{PP} = 68.7$ Hz, *P*); ^{1}H NMR ($CDCl_3$) δ 1.40 (ddd, 1H, $^2J_{HH} = 11.6$, $^3J_{HH} = 8.0$ Hz, $^3J_{PH} = 5.2$ Hz, H_{6endo}), 1.55–1.71 (m, 1H, H_{6exo}), 2.32 (ddd, 1H, $^3J_{HH} = 8.0$, $^3J_{HH} = 4.4$ Hz, $^2J_{PH} = 1.2$ Hz, H_5), 4.93 (dd, 1H, $^3J_{HH} = 4.8$, $^3J_{HH} = 1.6$ Hz, H_1), 5.46 (dddd, 1H, $^3J_{HH} = 18.1$ Hz, $^3J_{PH} = 12.8$ Hz, $^2J_{HH} = 2.0$, $J = 0.8$ Hz, PCH=*H*H′), 5.62 (dddd, 1H, $^3J_{PH} = 30.1$ Hz, $^3J_{HH} = 11.6$ Hz, $^2J_{HH} = 2.0$, $J = 0.8$ Hz, PCH=H*H*′), 6.16 (dd, 1H, $^3J_{HH} = 5.6$ Hz, $^3J_{HH} = 1.6$ Hz, H_2), 6.31 (d, 1H, $^3J_{HH} = 5.6$ Hz, H_3), 6.49 (dddd, 1H, $^3J_{HH} = 18.1$ Hz, $^3J_{HH} = 11.6$ Hz, $^2J_{PH} = 8.8$ Hz, $J = 0.8$ Hz, PC*H*=CH_2), 7.22–7.70 (m, 15H, aromatics).

3.5. Liberation of (1S,4R,5R)-4-(diphenylphosphino)-5-(S)-(ethenylphenylphosphino)-7-oxabicyclo[2.2.1]hept-2-ene, [(−)-exo-6]

The naphthylamine auxiliary in *exo*-**3a** was first removed by stirring vigorously a solution of the complex (0.081 g, 0.091 mmol) in dichloromethane (25 mL) with concentrated hydrochloric acid (10 mL) at room temperature for 1 d. The mixture was washed with water (4 × 30 mL), and dried ($MgSO_4$). The resultant dichloro complex *exo*-**8** [^{31}P NMR (CD_2Cl_2) δ 37.8 (d, 1P, $J_{PP} = 7.6$ Hz, $J_{PtP} = 3662$ Hz, P^4), 43.0 (d, 1P, $J_{PP} = 7.6$ Hz, $J_{PtP} = 3540$ Hz, P^5)] in dichloromethane (20 mL) was stirred vigorously with a saturated aqueous solution of KCN (2 g) for 30 mins. The organic portion was separated, washed with water (3 × 20 mL), and dried ($MgSO_4$). White solid was obtained after removal of the solvent: $[\alpha]_D$ −85° (*c* 0.6, $CHCl_3$); 0.032 g (85% yield). ^{31}P NMR ($CDCl_3$) δ −15.3 (d, 1P, $^3J_{PP} = 95.4$ Hz, *P*), −16.7 (d, 1P, $^3J_{PP} = 95.4$ Hz, *P*); ^{1}H NMR ($CDCl_3$) δ 1.50 (ddd, 1H, $^2J_{HH} = 11.3$, $^3J_{HH} = 8.0$ Hz, $^3J_{PH} = 2.8$ Hz, H_{6endo}), 2.05–2.20 (m, 2H, H_{6exo}, H_5), 5.12 (dd, 1H, $^3J_{HH} = 4.4$, $^3J_{HH} = 1.6$ Hz, H_1), 5.62–5.76 (m, 1H, PCH=*H*H′), 5.81–5.98 (m, 1H, PCH=H*H*′), 6.22 (dd, 1H, $^3J_{HH} = 5.6$ Hz, $^3J_{HH} = 1.6$ Hz, H_2), 6.29 (d, 1H, $^3J_{HH} = 5.6$ Hz, H_3), 6.41–6.57 (m, 1H, PC*H*=CH_2), 7.20–7.70 (m, 15H, aromatics).

3.6. Hydrogenation of exo-4. Isolation of [SP-4-3-{(1R,4R,5R)-dichloro[4-(diphenylphosphino)-5-(S)-(ethylphenylphosphino)-7-oxabicyclo[2.2.1]hept-2-ane-P^4, P^5]}]platinum(II), (exo-9)

Hydrogen gas was bubbled slowly into a mixture of *exo*-**4** (0.246 g, 3.62 mmol) and 10% Pd/C (0.172 g) in dichloromethane (35 mL) for 10 h at room temperature and atmospheric pressure. The mixture was filtered through Celite, and *exo*-**9** was isolated from dichloromethane-diethyl ether as colorless crystals: mp 364–365 °C (decomp.); $[\alpha]_D$ +56° (*c* 0.3, CH_2Cl_2); 0.227 g (92% yield). Anal. Calcd for $C_{26}H_{28}Cl_2OP_2Pt$: C, 45.6; H, 4.1. Found: C, 45.4; H, 4.2%. ^{31}P NMR (CD_2Cl_2) δ 40.7 (d, 1P, $J_{PP} = 7.6$ Hz, $J_{PtP} = 3708$ Hz, P^4), 54.2 (d, 1P, $J_{PP} = 7.6$ Hz, $J_{PtP} = 3494$ Hz, P^5); ^{1}H NMR (CD_2Cl_2) δ 1.45 (dt, 3H, $^3J_{PH} = 19.8$ Hz, $^3J_{HH} = 7.5$ Hz, *Me*), 1.48–1.56 (m, 1H, H_{2exo}), 1.63 (ddd, 1H, $^2J_{HH} = 12.0$ Hz, $^3J_{HH} = 8.8$ Hz, $^3J_{HH} = 3.3$ Hz, H_{2endo}), 1.65–1.79 (m, 1H, H_{6exo}), 1.79–1.93 (m, 2H, H_{6endo}, H_{3endo}), 1.95–2.11 (m, 1H, H_{3exo}), 2.21–2.39 (m, 1H, PC*H*H′), 2.60–2.75 (m, 1H, PCH*H*′), 2.70 (dd, 1H, $^3J_{HH} = 8.8$ Hz, $^3J_{HH} = 2.9$ Hz, H_5), 4.42 (t, 1H, $^3J_{HH} = {}^3J_{HH'} = 5.1$ Hz, H_1), 7.42–8.15 (m, 15H, aromatics).

3.7. Liberation of (1R,4R,5R)-4-(diphenylphosphino)-5-(R)-(ethenylphenylphosphino)-7-oxabicyclo[2.2.1]hept-2-ane, [(+)-exo-10]

Diphosphine ligand (+)-*exo*-**10** was similarly obtained from the reaction of *exo*-**9** (0.076 g, 0.11 mmol) and saturated aqueous KCN (2 g), as white solid: $[\alpha]_D$ +6° (*c* 0.3, $CHCl_3$); 0.044 g (95% yield). ^{31}P NMR ($CDCl_3$) δ −6.5 (d, 2P, $^3J_{PP} = 80.1$ Hz, P^4, P^5); ^{1}H NMR ($CDCl_3$) δ 0.78 (dt, 3H, $^3J_{PH} = 16.4$ Hz, $^3J_{HH} = 7.6$ Hz, *Me*), 1.35–1.88 (m, 8H, H_{2exo}, H_{2endo}, H_{3exo}, H_{3endo}, H_{6exo}, H_{6endo}, PC*H*H′, PCH*H*′), 2.50–2.64 (m, 1H, H_5), 4.46–4.52 (m, 1H, H_1), 7.24–7.75 (m, 15H, aromatics).

3.8. Typical procedure used for the recomplexation reactions

Stoichiometric amounts of complex (*S*)-**1** and (+)-*exo*-**5** 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 ($MgSO_4$).

3.9. Crystal structure determination of exo-3a, exo-4 and exo-9

X-ray crystallographic data for all three complexes are given in the Table 3. The structures were analyzed at the National University of Singapore using a Siemens SMART CCD diffractometer with graphic monochromated Mo Kα radiation. For all three complexes, 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

Table 3
Crystallographic data for *exo*-**3a**, *exo*-**4** and *exo*-**9**

	exo-**3a**	*exo*-**4**	*exo*-**9**
Formula	$C_{40}H_{40}BF_4NOP_2Pt$	$C_{26}H_{24}Cl_2OP_2Pt$	$C_{26}H_{28}Cl_2OP_2Pt$
F_w	894.57	680.38	684.41
Space group	$P1$	$P2_12_12_1$	$P2_12_12_1$
Crystal system	Triclinic	Orthorhombic	Orthorhombic
a (Å)	9.4686(7)	11.0811(3)	10.8969(6)
b (Å)	9.8040(7)	14.2889(4)	14.1628(8)
c (Å)	11.1500(8)	15.7217(5)	16.156(1)
α (°)	73.724(2)	90	90
β (°)	81.240(2)	90	90
γ (°)	87.628(2)	90	90
V (Å^3)	982.0(1)	2489.3(1)	2493.3(2)
Z	1	4	4
T (K)	223(2)	295(2)	223(2)
ρ_{calcd} (gcm^{-3})	1.513	1.815	1.823
λ (Å)	0.71073 (Mo)	0.71073 (Mo)	0.71073 (Mo)
μ (cm^{-1})	37.04	59.97	5.988
Flack parameters	0.013(8)	0.001(6)	0.003(5)
R_1 (observed data)[a]	0.0497	0.0274	0.0246
wR_2 (observed data)[b]	0.0939	0.0533	0.0439

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

all chiral complexes were determined unambiguously using the Flack parameter [12].

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Appendix A. Supplementary material

CCDC 631736, 631737 and 631738 contain the supplementary crystallographic data for *exo*-**3a**, *exo*-**4** and *exo*-**9**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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