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Asymmetric synthesis of a chiral arsinophosphine *via* a metal template promoted asymmetric Diels–Alder reaction between diphenylvinylphosphine and 2-furyldiphenylarsine

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Abstract

The asymmetric Diels–Alder reaction between 2-furyldiphenylarsine and diphenylvinylphosphine was achieved stereospecifically by utilizing an organoplatinum reaction promoter containing the *ortho*-metalated (*R*)-(1-(dimethylamino) ethyl)-naphthalene as the chiral auxiliary. The optically pure (+)-As–P heterobidentate cycloadduct could be liberated from the template product by successive treatment with concentrated hydrochloric acid and aqueous potassium cyanide.

Keywords: Asymmetric Diels–Alder; Chiral metal template; Optically active arsinophosphine; Vinylphosphine; Arsine substituted furan

1. Introduction

Over the past decade, the design, synthesis and applications of chiral phosphines in the field of asymmetric catalysis [1–9] have seen to grow perpetually. In contrast to their phosphine analogues, chiral arsines are less extensively studied due to the technical challenges encountered in their synthesis. Hence, their applications have been scarcely reported even to date [10–13]. Among the various types of chiral phosphines reported in the literatures, much interests are being focused on chiral diphosphines [2,14–21]. On the other hand, the interesting class of chiral bidentate arsinophosphines have been shown to be efficient catalyst supporters [22,23]. Accordingly, the relatively unexplored chemistry of chiral arsinophosphines is an interesting field that should be developed further. Our group has previously prepared various chiral diphosphines containing different functionalities with high efficiency by means of the metal-template promoted asymmetric Diels–Alder reaction [24]. We found that this approach could be applied to the asymmetric synthesis between diphenylvinylphosphine and various cyclic dienes *e.g.* 2-furyldiphenylphosphine promoted by an *ortho*-metalated platinum(II) complex containing the *N*,*N*-dimethyl-1-(1-naphthyl)ethylamine as the chiral auxiliary [25]. By using the same reaction promoter, we hereby report a highly regio- and stereoselective cycloaddition reaction between the diphenylvinylphosphine and 2-furyldiphenylarsine which led to the efficient synthesis of the corresponding optically pure arsinophosphine chelate bearing the oxanorbornene backbone, under mild conditions.

2. Experimental

2.1. Materials and procedures

All reactions involving air-sensitive compounds were performed under a positive pressure of purified nitrogen using standard Schlenk techniques. The solvents were dried over appropriate drying agents and degassed by standard method. Bis(μ-chloro)-bis{(*R*)-1-(dimethylamino)ethyl]-napthyl-C^2,*N*}

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diplatinum (II) (R_c)-**1** [25] and diphenylvinylphosphine [34] were prepared according to literature methods.

A Bruker ACF 300 spectrometer was used to record the ^1H (300 MHz) and $^{31}P\{^1H\}$ (121 MHz) NMR spectra. Optical rotations were measured on the specified solution in a 1-dm cell at 25 °C with a Perkin–Elmer Model 341 polarimeter. Melting points were determined on a Buchi B-545 apparatus. Elemental analyses were performed by the Elemental Analysis laboratory of the Department of Chemistry at the National University of Singapore.

2.2. Preparation of 2-furyldiphenylarsine ligand

Sodium diphenylarsenide was prepared by addition of flatten Na metal (1.00 g, 43.50 mmol) to a stirring solution of diphenylarsine (4.60 g, 20.00 mmol) in dried THF (100 mL) for 16 h. The sodium diphenylarsenide thus prepared was added dropwise (over 1 h) to a solution of 2-bromofuran (3.00 g, 20.41 mmol) in THF (100 mL) at −79 °C (acetone/dry ice bath). The reaction mixture was warmed to room temperature and then further refluxed for 3 h. The solvent was removed under reduced pressure and a saturated ammonium chloride solution (10.00 g in 50 mL of water) was added slowly into the reaction mixture. The product was then extracted with diethyl ether. The organic layer was separated and dried over magnesium sulfate. The solvent was removed and the residue (brownish oil) was distilled (bp 120–130 °C; 0.8 mm Hg) to give the product as a colourless viscous oil: yield 4.47 g (73%); ^1H NMR ($CDCl_3$): δ 6.44 (dd, 1H, $^3J_{HH} = 1.8$ Hz, $^3J_{HH} = 1.2$ Hz, OC=C*H*), 6.52 (d, 1H, $^3J_{HH} = 3.2$ Hz, Ph_2AsC=C*H*), 7.34–7.46 (m, 10H, aromatics), 7.68 (d, 1H, $^3J_{HH} = 1.6$ Hz, OC*H*).

2.3. Synthesis of {R-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-C,N} {(1α,4α,5α(S))-[4-(diphenylarsino)-5-(diphenylphosphino)-7-oxabicyclo[2.2.1] hept-2-ene-As,P} platinum(II) tetrafluoroborate, (R_c)-exo-4a

The dimeric complex (R_c)-**1** (0.68 g, 0.79 mmol) dissolved in dichloromethane (500 mL) was treated with diphenylvinylphosphine (0.34 g, 1.58 mmol) to give the monophosphine complex (R_c)-**2**. This solution was directly treated with silver tetrafluoroborate (0.50 g, 2.57 mmol) in water (2 mL) to generate the cationic complex (R_c)-**3** which was directly treated with 2-furyldiphenylarsine (0.47 g, 1.58 mmol). The resulting mixture was stirred vigorously at room temperature for 2 h, filtered (to remove silver chloride), washed with water, and then dried ($MgSO_4$). The reaction was monitored by ^{31}P NMR spectroscopy and was found to complete in 22 d. Slow addition of diethyl ether to the crude reaction mixture gave complex (R_c)-*exo*-**4a** as pale yellow micro-crystals: (1.09 g, 70%); mp 276–278 °C (decomp.); $[\alpha]_D = +92.9$ (*c* 0.4, CH_2Cl_2); Anal. Calc. for $C_{44}H_{42}NOAsPPtBF_4$: C, 53.4; H, 4.3; N, 1.4; Found C, 53.0; H, 4.4; N, 1.4; ^1H NMR (CD_2Cl_2) δ 1.94 (d, 3H, $^3J_{HH} = 6.4$ Hz, CH*Me*), 1.99–2.10 (m, 1H, $H_{6'}$), 2.37–2.40 (m, 1H, H_6), 2.66 (d, 3H, $^4J_{PH} = 2.1$ Hz, N*Me*), 3.20 (d, 3H, $^4J_{PH} = 3.6$ Hz, N*Me*), 4.80 (qn, 1H, $^3J_{HH} = {}^4J_{PH} = 6.0$ Hz, C*H*Me), 5.10 (dd, 1H, $^3J_{HH} = 4.4$ Hz, $^3J_{HH'} = 1.2$ Hz, H_1), 6.12 (d, 1H, $^3J_{HH} = 5.6$ Hz, H_3), 6.60 (dd, 1H, $^3J_{HH} = 5.8$ Hz, $^3J_{HH'} = 1.2$ Hz, H_2), 6.77 (dd, 1H, $^3J_{HH} = 3.2$ Hz, $^2J_{PH} = 10.1$ Hz, H_5), 7.39–7.93 (m, 26H, aromatics); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 48.0 (s, $J_{PtP} = 3602$ Hz).

2.4. Preparation of dichloro {(1α,4α,5α(S))-[4-(diphenylarsino)-5-(diphenylphosphino)-7-oxabicyclo[2.2.1] hept-2-ene-As,P} platinum(II), (+)-exo-5

The naphthylamine auxillary in the crude reaction product (R_c)-*exo*-**4a** could be chemoselectively removed by the addition of concentrated hydrochloric acid (25 mL) to a solution of the complex (R_c)-*exo*-**4a** (0.30 g, 0.30 mmol) in dichloromethane (60 mL). The mixture was stirred vigorously at room temperature for 12 d, washed with water (3 × 50 mL), and dried ($MgSO_4$). Crystallization of the crude product from dichloromethane–diethyl ether gave pure (+)-*exo*-**5** as white crystals: 0.24 g (89% yield); mp 264–266 °C; $[\alpha]_D = +77.4$ (*c* 0.3, CH_2Cl_2); Anal. Calc. for $C_{30}H_{26}Cl_2OAsPPt$: C, 46.5; H, 3.4; Found C, 46.3; H, 3.3; ^1H NMR (CD_2Cl_2) δ 1.65–1.75 (m, 1H, H_5), 2.04–2.16 (m, 1H, $H_{6'}$), 2.36–2.41 (m, 1H, H_6), 5.24 (dd, $^3J_{HH} = 4.4$ Hz, $^3J_{HH'} = 1.2$ Hz, H_1), 6.19 (d, 1H, $^3J_{HH} = 5.6$ Hz, H_3), 6.57 (dd, 1H, $^3J_{HH} = 4.4$ Hz, $^3J_{HH'} = 1.2$ Hz, H_2), 7.39–8.15 (m, 20H, aromatics); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 48.9 (s, $J_{PtP} = 3476$ Hz).

2.5. Liberation of the free ligand {(1α,4α,5α(S))-[4-(diphenylarsino)-5-(diphenylphosphino)-7-oxabicyclo[2.2.1] hept-2-ene-As,P}, (+)-exo-6

A mixture of the dichloro complex (+)-*exo*-**5** (0.03 g, 0.04 mmol) in dichloromethane (20 mL) and aqueous potassium cyanide (2.00 g, 5 mL) was stirred vigorously for 2 h. The aqueous phase was separated, and the organic layer was washed with water (3 × 10 mL) and dried over magnesium sulfate. Removal of the solvent under vacuum gave ligand (+)-*exo*-**6** as an air-sensitive white solid in 81% yield (0.017 g); $[\alpha]_D = +26.2$ (*c* 0.7, CH_2Cl_2); ^{31}P $\{^1H\}$ NMR ($CDCl_3$): δ −9.7 (s).

3. Results and discussion

The arsine substituted cyclic diene, 2-furyldiphenylarsine was obtained as a colourless oil in 73% yield *via* the nucleophilic addition of diphenylarsenide to 2-bromofuran. In the absence of a transition metal ion, no reaction was observed between diphenylvinylphosphine and 2-furyldiphenylarsine. In the presence of the chiral reaction promoter (R_c)-**1**, however, the asymmetric cycloaddition reaction proceeded smoothly at room temperature. As shown in Scheme 1, the addition of diphenylvinylphosphine to a stoichiometric amount of (R_c)-**1** generated the

monophosphine complex (R_c)-**2**. Treatment of the crude complex (R_c)-**2** with silver tetrafluoroborate removed the kinetically stable chloro ligand to generate the relatively reactive cationic species (R_c)-**3**. In order to optimize the efficiency, the tetrafluoroborato species generated (R_c)-**3** was not isolated in routine synthesis. The diphenylvinylphosphine complex prepared earlier was dissolved in a large volume of dichloromethane [1.02 g (1.58 mmol) in 500 mL] and then treated directly with a stoichiometric quantity of 2-furyldiphenylarsine at room temperature. The Diels–Alder reaction was monitored by the ^{31}P NMR spectroscopy and was found to complete in 22 d. The cycloadduct complex (R_c)-*exo*-**4a** was obtained as pale yellow micro-crystals in 70% isolated yield: $[\alpha]_D = +92.9$ (*c* 0.4, CH_2Cl_2). Prior to purification, the ^{31}P NMR spectrum of the crude cycloadducts in CD_2Cl_2 exhibited a sole singlet signal at δ 48.0 ($J_{PtP} = 3602$ Hz). No other ^{31}P NMR signals could be detected from the 121 MHz NMR spectrum, thus indicating that only a single diastereomer was generated in the Diels–Alder reaction. It is noteworthy that the amount of solvents used in this reaction plays a vital role towards the reaction selectivity. At higher concentration, the reaction became less stereoselective. For example when the reaction was conducted using 0.14 g of (R_c)-**3** and 0.06 g of 2-furyldiphenylarsine in 30 mL of CH_2Cl_2, the ^{31}P NMR spectrum showed that two isomeric products were generated in the ratio of 1:3.

A single crystal X-ray analysis of (R_c)-*exo*-**4a** confirmed the coordination chemistry of the new As–P bidentate chelate. The absolute stereochemistries at C(15), C(18) and C(20) are *S*, *R* and *S*, respectively (Fig. 1). This assignment is based upon both anomalous scattering and by internal reference to the known stereocentre at C(11) of the naphthylamine ligand. The phosphorus atom is positioned *trans* to the σ-donating NMe_2 group while the arsenic analogue is *trans* to the π-accepting naphthalene carbon atom. Such

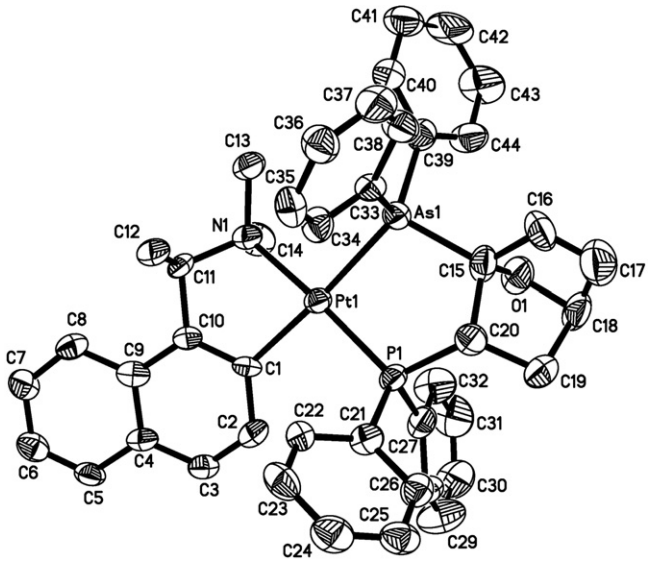
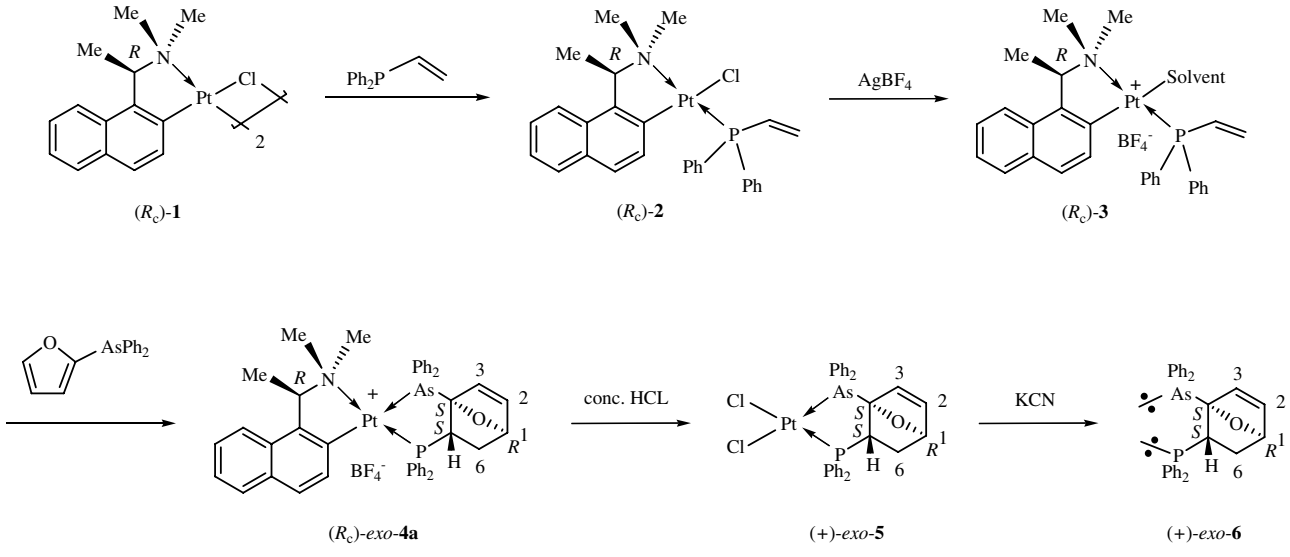


Fig. 1. Molecular structure and absolute stereochemistry of the cationic complex (R_c)-*exo*-**4a**.

regio-selectivity is consistent with a similar P–As complex containing the chiral naphthylamine auxiliary [27]. Selected bond lengths and angles are given in Table 1.The Pt–As(1) and As–C(15) bond distances of 2.436(1) and 1.959(9) Å observed are longer than those recorded for the analogous diphosphine complex in which the Pt–P bond distance is 2.327(2) with the corresponding P–C bond length of 1.850(7) Å [25]. Such phenomenon is clearly attributed to the different electronic properties between the phosphorus and arsenic donors [26]. Additionally, the coordination geometry at the platinum centre is slightly distorted square-planar with angles ranging from 79.6(3)–98.2(2) and 174.0(3)–175.4(2) [28–33]. The bond angle at the bridgehead oxygen [95.8(8)°] is typical of oxanorbornene skeletons [25,28,33].



Scheme 1.

Table 1
Selected bond lengths (Å) and angles (°) for (R_c)-*exo*-4a

Pt–C(1)	2.059(7)	Pt–N(1)	2.113(7)
Pt–P(1)	2.254(2)	Pt–As(1)	2.437(1)
As(1)–C(15)	1.959(9)	P(1)–C(20)	1.877(9)
As(1)–C(33)	1.922(8)	As(1)–C(39)	1.94(1)
P(1)–C(21)	1.82(1)	P(1)–C(27)	1.81(1)
O(1)–C(15)	1.42(1)	O(1)–C(18)	1.48(1)
C(15)–C(16)	1.50(1)	C(15)–C(20)	1.55(3)
C(16)–C(17)	1.32(2)	C(17)–C(18)	1.47(2)
C(18)–C(19)	1.55(2)	C(19)–C(20)	1.53(1)
C(1)–Pt–As(1)	174.0(3)	C(1)–Pt–P(1)	96.4(2)
C(1)–Pt–N(1)	79.6(3)	N(1)–Pt–As(1)	98.2(2)
N(1)–Pt–P(1)	175.4(2)	P(1)–Pt–As(1)	86.03(6)
C(15)–As(1)–Pt	105.6(3)	C(20)–P(1)–Pt	112.9(3)
C(20)–C(15)–As(1)	111.2(6)	C(15)–C(20)–P(1)	113.5(6)
C(16)–C(15)–C(20)	109.3(8)	C(17)–C(16)–C(15)	105.0(12)
C(16)–C(17)–C(18)	107.3(11)	C(17)–C(18)–C(19)	104.7(10)
C(16)–C(17)–C(18)	106.2(5)	C(20)–C(19)–C(18)	102.3(8)
C(19)–C(20)–C(15)	100.6(7)	C(19)–C(24)–C(15)	102.7(4)
C(15)–O(1)–C(18)	95.8(8)		

Table 2
Selected bond lengths (Å) and angles (°) for (+)-***exo*-5**

Pt–As(1)	2.307(6)	Pt–P(1)	2.218(1)
Pt–Cl(1)	2.357(2)	Pt–Cl(2)	2.344(2)
As(1)–C(4)	1.970(6)	As(1)–C(7)	1.920(5)
As(1)–C(13)	1.928(6)	P(1)–C(5)	1.871(6)
P(1)–C(19)	1.833(6)	P(1)–C(25)	1.808 (6)
C(1)–C(2)	1.50(1)	C(1)–C(6)	1.528(9)
C(2)–C(3)	1.309 (9)	C(3)–C(4)	1.496(8)
C(4)–C(5)	1.564(8)	C(5)–C(6)	1.567(8)
C(1)–O(1)	1.574(8)	C(4)–O(1)	1.332(1)
As(1)–Pt–Cl(1)	89.78(5)	As(1)–Pt–Cl(2)	176.59(4)
P(1)–Pt–Cl(1)	176.40(6)	P(1)–Pt–Cl(2)	90.11(5)
P(1)–Pt–As(1)	88.89(4)	Cl(2)–Pt–Cl(1)	91.40(6)
C(4)–As(1)–Pt	106.5(2)	C(5)–P(1)–Pt	111.9(2)
C(5)–C(4)–As(1)	111.7(4)	C(4)–C(5)–P(1)	112.6(4)
C(4)–O(1)–C(1)	95.1(4)	C(2)–C(3)–C(4)	105.9(6)
C(3)–C(4)–C(5)	106.6(5)	C(3)–C(2)–C(1)	105.6(6)
C(2)–C(1)–C(6)	107.2(5)	C(1)–C(6)–C(5)	101.0(5)
C(4)–C(5)–C(6)	99.7(4)		

The chiral naphthylamine auxiliary in (R_c)-*exo*-**4a** could be chemoselectively removed by treatment of the As–P coordination complex with concentrated hydrochloric acid. The neutral dichloro complex (+)-*exo*-**5** thus obtained as white crystals in 89% yield; $[\alpha]_D = +77.4$ (c 0.3, CH_2Cl_2). The ^{31}P NMR spectrum of (+)-*exo*-**5** in CD_2Cl_2 exhibited a singlet resonance at δ 48.9 ($J_{PtP} = 3476$ Hz). The molecular structure of the dichloro complex is shown in Fig. 2. Selected bond lengths and angles are given in Table 2.

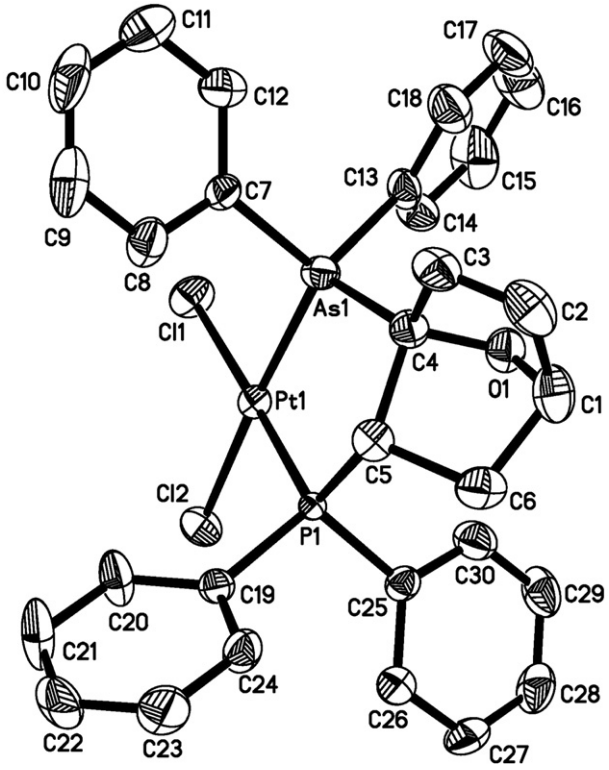


Fig. 2. Molecular structure and absolute stereochemistry of the neutral dichloro complex (+)-*exo*-**5**.

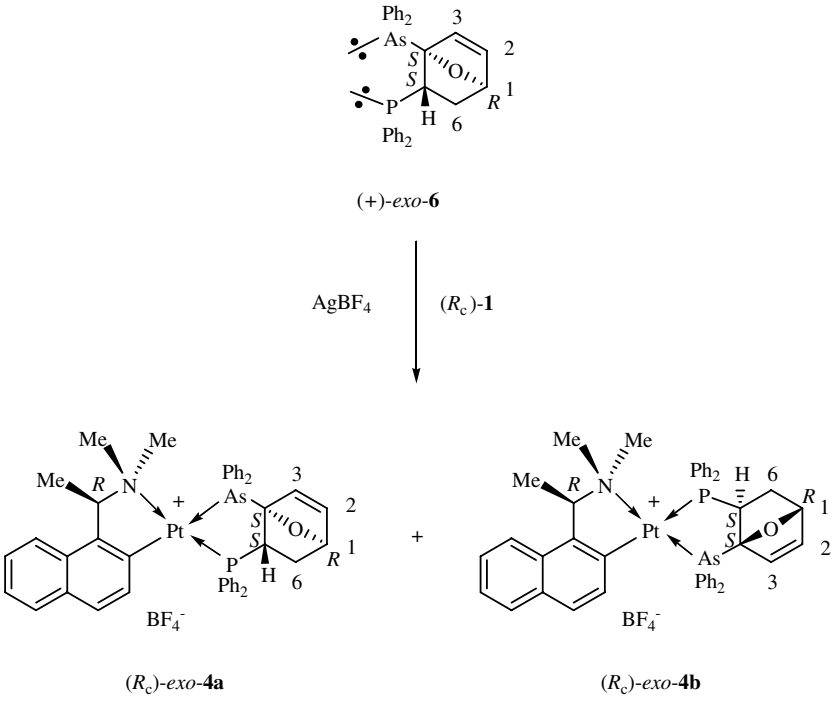
The C(4)–O(1)–C(1) *oxa*-bridgehead angle is recorded as 95.1(4)°. It is noteworthy that the bridgehead C–O bonds in the As–P chelating *exo*-cycloadduct (R_c)-*exo*-**4a**, are not affected by the strong acidic conditions. As desired, the absolute configurations of the three chiral carbon centre at C(1), C(4) and C(5) [*R*, *S* and *S*, respectively] are identical to their counterpart in the original template complex (R_c)-*exo*-**4a** (Table 3).

The optically pure arsinophosphine bidentate ligand could be liberated stereospecifically from (+)-*exo*-**5** by treatment of the dichloro complex with aqueous potassium cyanide. The heterobidentate ligand (+)-*exo*-**6** was thus obtained as an air-sensitive white solid in 81% yield: $[\alpha]_D = +26.2$ (c 0.7, CH_2Cl_2). The ^{31}P NMR spectrum of (+)-*exo*-**6** in $CDCl_3$ exhibited a sharp signal at δ −9.7. In order to establish the optical purity of the liberated ligand, the heterobidentate ligand was re-coordinated to (R_c)-**1**, followed by the treatment with stoichiometric amount of

Table 3
Crystallographic data for complexes (R_c)-*exo*-4a and (+)-*exo*-5

	(R_c)-*exo*-**4a**	(+)-*exo*-**5**
Formula	$C_{44}H_{42}AsBF_4NOPPt$	$C_{30}H_{26}AsCl_2OPPt$
Formula weight	988.58	774.39
Space group	$P2_12_12_1$	$P2_12_12_1$
Crystal system	Orthorhombic	Orthorhombic
a (Å)	11.7784(6)	10.1554(4)
b (Å)	15.6568(8)	15.8084(7)
c (Å)	21.159(1)	17.1282 (8)
V (Å^3)	3901.9(3)	2749.8(2)
Z	4	4
T (K)	223(2)	223(2)
$\rho_{calc.}$ (g cm^{-3})	1.683	1.871
λ (Å)	0.71073 (Mo)	0.71073 (Mo)
μ (mm^{-1})	4.534	6.572
Flack parameters	0.001(10)	0.011(6)
R_1 (obsd data)[a]	0.0756	0.0368
wR_2 (obsd data)[b]	0.1054	0.0659

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



Scheme 2.

silver tetrafluoroborate (Scheme 2). This re-coordination process generated two distinct regioisomers [(R_c)-*exo*-**4a** and (R_c)-*exo*-**4b** (Scheme 2)]. The ^{31}P NMR spectrum of the re-coordination crude products in $CDCl_3$ indeed showed two singlet resonances in equal ratio at δ 48.0 ($J_{PtP} = 3586$ Hz) and 55.2 ($J_{PtP} = 1797$ Hz) respectively. The former being identical to that recorded by (R_c)-*exo*-**4a** and the large Pt–P coupling constant observed is attributed to the *trans* influence exerted by the NMe_2 group. On the other hand, the latter shows a smaller Pt–P coupling constant which is the characteristic indication for this class of platinum complex with the ascribed to the PPh_2 group coordinated *trans* to the strong π-accepting naphthalene carbon atom. Hence the signal at δ 55.2 is unambiguously assigned to the regioisomer (R_c)-*exo*-**4b**, which was not generated directly from the Diels–Alder reaction. Since there are no other ^{31}P signals arising from the other possible diastereomers, this re-coordination process established that the liberated arsinophosphine ligand is optically pure.

In comparison, the cycloaddition reaction between the arsenic cyclic diene with diphenylvinylphosphine is relatively slower than its phosphorus counterpart which requires 6 d to complete the analogous reaction [25]. It is well-established that most classic cycloaddition reactions require activation of the cyclic dienes or dienophiles. The current studies thus provide a direct comparison of the reactivities between a phosphorus substituted furan diene and its arsenic counterpart. In subsequent work, it will be shown that the information obtained in this preliminary study is crucial to the rational utilization of the stereoelectronic properties of the arsenic ligand in some stereochemically highly demanding organic transformations.

4. Supplementary data

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC 608020 for compound (R_c)-*exo*-**4a** and CCDC 608021 for compound (+)-*exo*-**5**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Fax. (int code) +44 (1223) 336 033 or Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

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