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Asymmetric hydroarsination reactions toward synthesis of alcohol functionalised C-chiral As–P ligands promoted by chiral cyclometallated complexes

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ABSTRACT

The asymmetric hydroarsination reactions between diphenylarsine and 3-diphenylphosphanyl-but-3-en-1-ol and 2-diphenylphosphanyl-prop-2-en-1-ol have been achieved using the organopalladium complex containing ortho-metallated (*R*)-[1-(dimethylamino)ethylnaphthalene as the chiral reaction template in high stereoselectivities under mild conditions. Hydroarsination of 3-diphenylphosphanyl-but-3-en-1-ol with diphenylarsine generated only one stereoisomer as five-membered As–P bidentate chelate on chiral naphthylamine palladium template. Using the same chiral metal template, similar hydroarsination reaction was carried out on 2-diphenylphosphanyl-prop-2-en-1-ol which gave two different products in the ratio of 2.6 to 1. The major isomer was identified as the expected five-membered As–P bidentate ligand and the minor isomer was identified as the elimination product. The naphthylamine auxiliary could be removed chemoselectively by treatment with concentrated hydrochloric acid. Optically pure As–P ligands containing the hydroxy groups at the chiral carbon centres were prepared by ligand displacement. The absolute configuration and coordination properties of the complexes have been established by single crystal X-ray analysis.

1. Introduction

Organoarsenic compounds are found to be useful in various aspects of enantioselective catalysis. They have been found to be more effective than phosphines in catalyzing a number of organic reactions [1]. However available methods to prepare arsine ligands are limited [2] and the number of reports on the addition of As–H moiety to a C–C double bond of an unsaturated compound is not vastly reported [3]. Applying chiral cyclometallated complexes as efficient chiral auxiliaries, our group has recently published reports on the synthesis of an optically active As–P heterobidentate ligand via Diels–Alder cycloaddition [4] and asymmetric hydroarsination reaction [5]. Keto and ester- functionalised chiral pyridyl-arsines has also been synthesised via a similar reaction by our group [6]. To our knowledge, no other example of metal complex activated hydroarsination reactions involving diphenylarsine whereby a series of chiral bidentate As–P ligands bearing diphenylphosphino moiety with chirality residing on carbon backbone carrying various functional groups has been reported.

In continuation of our exploration of chiral As–P ligands, we herein report a protocol for the synthesis of two chiral alcohol-functionalised As–P ligands promoted by chiral cyclometallated-amine complexes of a hydroarsination reaction involving diphenylarsine and phosphine functionalised alkenols, 3-diphenylphosphanyl-but-3-en-1-ol and 2-diphenylphosphanyl-prop-2-en-1-ol. This work is part of our efforts to understand the differences in P and As reactivity.

2. Results and discussion

2.1. Asymmetric hydroarsination of 3-diphenylphosphanyl-but-3-en-1-ol

The monodentate 3-diphenylphosphanyl-but-3-en-1-ol was coordinated to the palladium complex (*Rc*)-**1** via a regiospecific bridge splitting process (Scheme 1) [7]. It is known that the chloro ligand in the template complex (*Rc*)-**2a** is kinetically and thermodynamically stable and is not readily displaced by incoming monodentate arsine ligands [8]. Therefore to provide an empty coordination site for the incoming arsine ligand, complex (*Rc*)-**2a** was treated with silver perchlorate.

The perchlorato complex (*Rc*)-**3a** was then treated with diphenylarsine at −78 °C and the reaction mixture was then left to stir for 24 h. The reported conditions are the optimum condition for this reaction and have also been used extensively in our previous works

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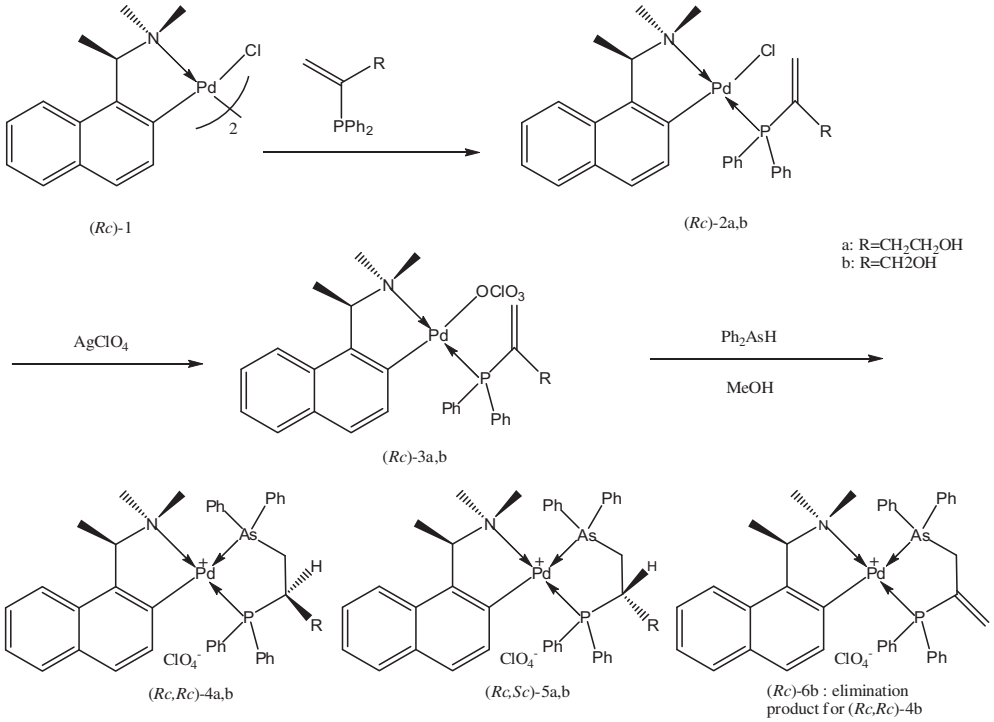


Scheme 1. Chiral cyclometallated promoted asymmetric hydroarsination reactions of diphenylarsine and phosphine functionalised alkenols.

on asymmetric hydrophosphination [9] and hydroarsination reactions [5]. The ^{31}P NMR spectrum showed a singlet at δ 77.6 indicating that only one diastereomer was generated out of the two possible diastereomers. Unlike the addition of the analogous secondary phosphine which resulted in cis-trans regioisomers of the products [7,9], introduction of diphenylarsine in this reaction is regiospecific. The P atom occupies the coordination site trans to the N atom of the chiral auxiliary. Such high regioselectivity case has been previously observed for other P–As ligands [10]. The high stereoselectivity has also been observed for the analogous hydrophosphination reactions. As described previously, the formation of the favoured diastereomer is mainly due to steric factors [5–7]. The crude mixture was then purified by column chromatography and the product was obtained as a white solid in 55% isolated yield.

The single-crystal X-ray analysis of the crystallized pure product (*Rc,Rc*)-**4a** showed that the expected five-membered P–As bidentate ligand has been formed (Fig. 1). A new stereogenic centre at C(28) was generated which adopts the *R* absolute configuration while as expected the absolute configuration of the stereocentres at C(11) remained unchanged. The geometry at the Pd centre is distorted square planar with angle of 80.8(1)–100.2(1)° and 174.6(1)–178.6(1)° (Table 1). The five-membered P–As chelate adopts the λ ring configuration with the CH_2CH_2OH substituent at C(28) occupying an equatorial position [7.9g]. The P and As donor atoms of the new heterobidentate are bonded regiospecifically to the metal centre with the softer P atom occupying the position trans to NMe_2 group Table 1.

Treatment with strong acid is a standard method to remove the naphthylamine auxiliary. As shown in Scheme 2 the chiral naphthylamine in (*Rc,Rc*)-**4a** can be removed chemoselectively from the palladium template by treatment with concentrated hydrochloric acid in dichloromethane. The resultant neutral dichloro complex (*Rc*)-**7a** was obtained as yellow prisms in 83% yield. The ^{31}P NMR spectum showed a singlet at δ 77.5.

The optically active P–As chiral bidentate (*Rc*)-**8a** could be liberated from (*Rc*)-**7a** $[\alpha]_D = -37.9$ (c 0.5, CH_2Cl_2) by treatment of the dichloro complex with potassium cynanide at room temperature for ½ h. It is necessary to destroy the chiral template as there is no other stronger chelating ligand suitable to displace the template without destroying the structural integrity and stereochemistry of the ligand other than potassium cyanides [4d,5]. The liberated optically pure ligand (*Rc*)-**8a** $[\alpha]_D = +62.3$ (c 0.5, CH_2Cl_2) was obtained as white solid in 88% yield (Scheme 2). The ^{31}P NMR spectrum showed a singlet at δ −1.2 and the liberated ligand could be recoordinated back to the same metal template without loss of optical purity.

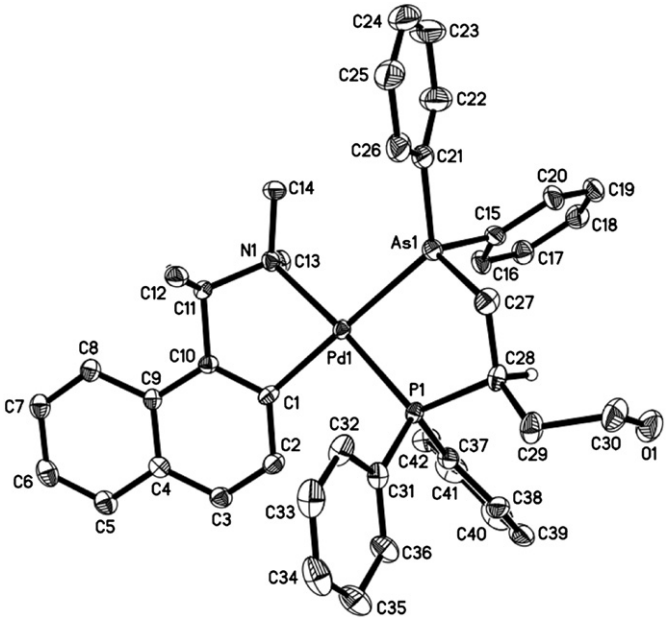


Fig. 1. Molecular structure of complex (*Rc,Rc*)-**4a**.

Table 1
Selected bond lengths [Å] and angles [°] of (*Rc,Rc*)-**4a**.

Pd(1)–C(1)	2.043(3)	C(1)–Pd(1)–N(1)	80.8 (1)
Pd(1)–N(1)	2.132(2)	C(1)–Pd(1)–P(1)	94.0(1)
Pd(1)–P(1)	2.261(1)	N(1)–Pd(1)–P(1)	174.6(1)
Pd(1)–As(1)	2.443(1)	C(1)–Pd(1)–As(1)	178.6(1)
As(1)–C(15)	1.922(3)	N(1)–Pd(1)–As(1)	100.2(1)
As(1)–C(21)	1.940(3)	P(1)–Pd(1)–As(1)	82.1(1)
As(1)–C(27)	1.947(3)	C(28)–P(1)–Pd(1)	112.4(1)
P(1)–C(28)	1.885 (3)	C(27)–As(1)–Pd(1)	102.4(1)
P(1)–C(31)	1.818(3)	C(29)–C(28)–C(27)	111.2(3)
P(1)–C(37)	1.821(3)	C(29)–C(28)–P(1)	113.4(2)
C(27)–C(28)	1.535(5)	C(28)–C(27)–As(1)	110.1(1)
C(28)–C(29)	1.532(4)	C(27)–C(28)–P(1)	111.7(2)

2.2. Asymmetric hydroarsination of 2-diphenylphosphanyl-prop-2-en-1-ol

The 2-diphenylphosphanyl-prop-2-en-1-ol ligand which was obtained by hydrophosphination of propargyl alcohol [9g] was coordinated to the dimeric ortho-metalled palladium complex (*Rc*)-**1** as shown in Scheme 1. The chloro complex (*Rc*)-**2b** was subsequently converted to the perchlorato complex by treatment with aqueous silver perchlorate. The perchlorato complex (*Rc*)-**3b** was dissolved in methanol and reacted with diphenylarsine at −78 °C. The ^{31}P NMR spectrum showed two singlets at δ 66.3 and 55.6 in the ratio of 2.6 to 1 respectively. The ratio of the two signals did not change with different concentration of diphenylarsine. After purification by silica gel chromatography the major product (*Rc,Rc*)-**4b** was crystallised from acetonitrile-diethyl ether as air-stable white crystals.

The single crystal X-ray diffraction analysis of the complex revealed that the expected five-membered P–As bidendate chelate has been formed (Fig. 2). A new stereogenic centre at C(28) was generated which adopts the *R* absolute configuration while the absolute configuration of the stereocentre at C(11) remained unchanged. The geometry at the palladium is distorted square planar with angle at palladium in the range 80.3(1)–103.0(1)° and 170.9(1)–174.6(1)° (Table 2). Similar to diastereomeric complex

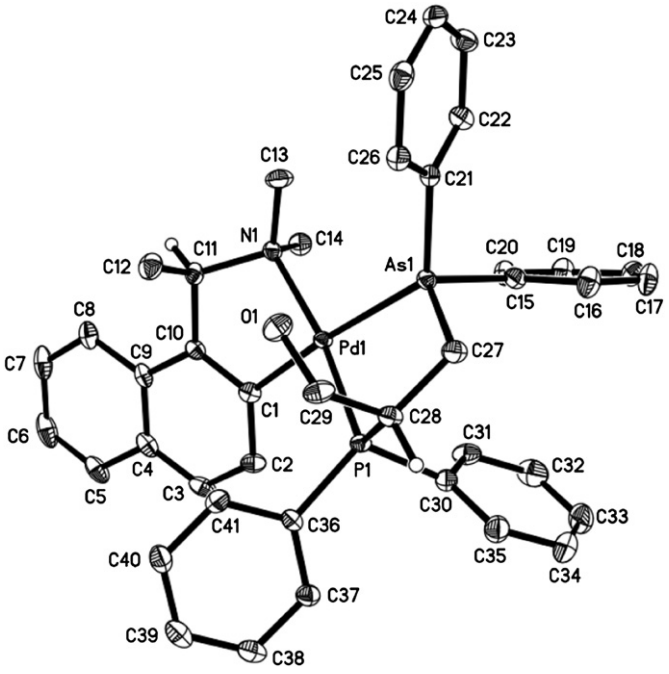
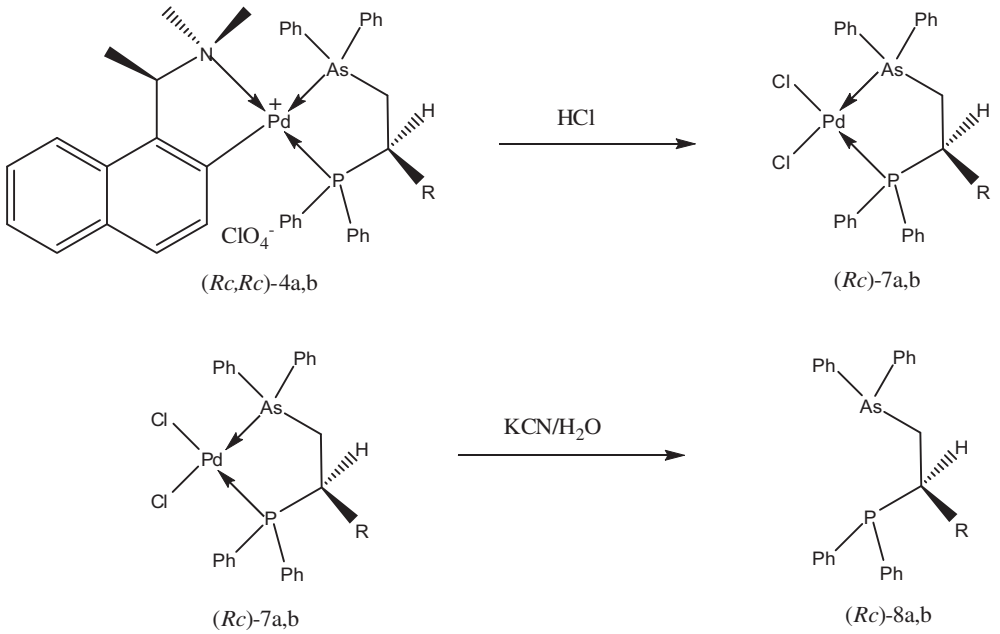


Fig. 2. Molecular structure of complex (*Rc,Rc*)-**4b**.

(*Rc,Rc*)-**4a** in the five-membered P–As bidentate chelate system the CH_2OH substituent at C(28) occupies an equatorial position [9a,9g].

The treatment of complex (*Rc,Rc*)-**4b** with concentrated hydrochloric acid generated (*Rc*)-**7b** (Scheme 2). The dichloro complex was subsequently crystallised from dicholoromethane-dietyl-ether as yellow prisms in 88% yield, $[\alpha]_D = -120$ (c 0.5, CH_2Cl_2). Further treatment of (*Rc*)-**7b** with aqueous cyanide liberated the optically pure (*Rc*)-**8b** in 79% yield, $[\alpha]_D = +30$ (c 0.3, CH_2Cl_2) (Scheme 2). The recoordination of the free ligand to the metal template employing the same protocol confirmed that (*Rc*)-**8b** is optically pure.



Scheme 2. Liberation of optically active As–P ligands.

Table 2
Selected bond lengths [Å] and angles [°] of (*Rc*,*Rc*)-**4b**

Pd(1)–C(1)	2.031(3)	C(1)–Pd(1)–N(1)	80.3 (1)
Pd(1)–N(1)	2.138(2)	C(1)–Pd(1)–P(1)	94.9(1)
Pd(1)–P(1)	2.253(1)	N(1)–Pd(1)–P(1)	170.9(1)
Pd(1)–As(1)	2.463(1)	C(1)–Pd(1)–As(1)	174.6(1)
As(1)–C(15)	1.950(3)	N(1)–Pd(1)–As(1)	103.0(1)
As(1)–C(21)	1.954(3)	P(1)–Pd(1)–As(1)	82.4(1)
As(1)–C(27)	1.980(3)	C(28)–P(1)–Pd(1)	108.0(1)
P(1)–C(28)	1.863 (3)	C(27)–As(1)–Pd(1)	105.1(1)
P(1)–C(30)	1.815(3)	C(29)–C(28)–C(27)	113.2(2)
P(1)–C(36)	1.818(3)	C(29)–C(28)–P(1)	113.0(2)
C(27)–C(28)	1.541(4)	C(28)–C(27)–As(1)	111.2(1)
C(28)–C(29)	1.523(4)	C(27)–C(28)–P(1)	108.2(2)

Table 3
Selected bond lengths [Å] and angles [°] of (*Rc*)-**6b**

Pd(1)–C(1)	2.046(6)	C(1)–Pd(1)–N(1)	80.3 (2)
Pd(1)–N(1)	2.130(6)	C(1)–Pd(1)–P(1)	95.0(2)
Pd(1)–P(1)	2.247(1)	N(1)–Pd(1)–P(1)	174.3(2)
Pd(1)–As(1)	2.461(1)	C(1)–Pd(1)–As(1)	177.5(2)
As(1)–C(15)	1.940(8)	N(1)–Pd(1)–As(1)	99.9(1)
As(1)–C(21)	1.958(8)	P(1)–Pd(1)–As(1)	84.9(5)
As(1)–C(27)	1.940(8)	C(28)–P(1)–Pd(1)	109.5(3)
P(1)–C(28)	1.837 (8)	C(27)–As(1)–Pd(1)	104.6(2)
P(1)–C(30)	1.817(7)	C(29)–C(28)–C(27)	124.0(7)
P(1)–C(36)	1.825(7)	C(29)–C(28)–P(1)	122.8(6)
C(27)–C(28)	1.499(11)	C(28)–C(27)–As(1)	113.1(6)
C(28)–C(29)	1.347(12)	C(27)–C(28)–P(1)	104.6(2)

The minor product isolated from silica gel chromatography was crystallised from dichloromethane-diethyl ether. The single-crystal X-ray diffraction revealed that it was (*Rc*)-**6b** (Fig. 3). The ^{31}P NMR spectrum showed a singlet at δ 55.6. The single-crystal X-ray crystallographic analysis clearly established that the hydroxyl functional group has dissociated. The C28–C29 bond distance [1.35(1) Å] is consistent with a typical C–C double bond (Table 3). A possible explanation to the presence of the elimination product could be found by analysing the structure of the coordination complex (*Rc*)-**2b**. It was reported that upon coordination of the vinylic phosphine entity to the metal template, crystallographic data revealed that the oxygen atom of the –OH group was oriented in such a way that in was in close proximity to the Pd metal centre [9g]. This Pd–O interaction can activate the O–C bond which then underwent a cleavage assisted by the presence of uncoordinated diphenylarsine. From the previous analogous hydrophosphination reaction on 2-diphenylphosphanyl-prop-2-en-1-ol ligand, the elimination product was not observed [9g]. This indicated the presence of uncoordinated diphenylphosphine couldn't assist the O–C cleavage. Phosphines are softer than arsines and generally show higher affinity to bind to the platinum metal ions than arsines [13]. The reason why loss of H_2O is not observed with phosphine is because in the intermediate, the excess phosphine will approach all possible coordination cites of the metal centre thus not allowing oxygen to be chelated to the metal. Hence, no C–O activation can occur. However for arsine which is a harder donor than phosphine, oxygen is allowed to bind to the metal centre and hence C–O activation can occur.

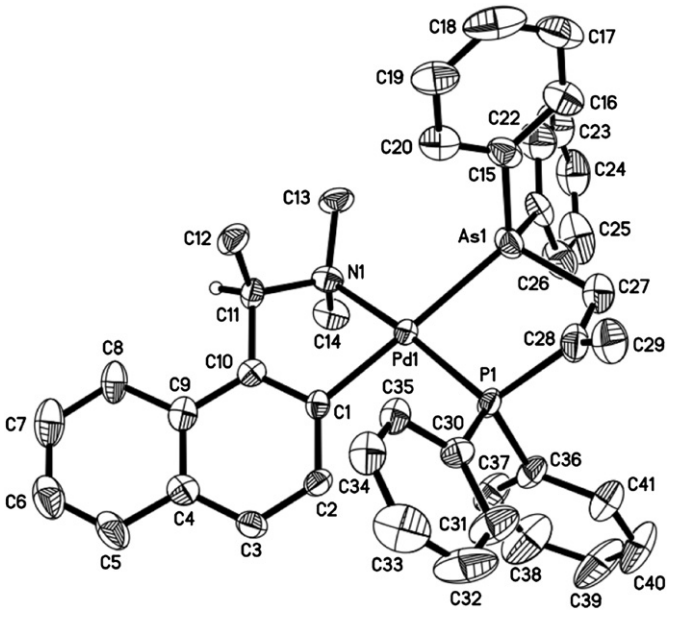


Fig. 3. Molecular structure of complex (*Rc*)-**6b**.

Table 4
Crystallographic data for complexes of (*Rc*,*Rc*)-**4a**, (*Rc*,*Rc*)-**4b**, (*Rc*)-**6b**.

	(*Rc*,*Rc*)-**4a**	(*Rc*,*Rc*)-**4b**	(*Rc*)-**6b**
Formula	$C_{43}H_{46}AsCl_3NO_5PPd$	$C_{42.33}H_{44}AsNClO_5PPd$	$C_{41}H_{40}AsClNO_4PPd$
fw	975.45	903.87	858.48
Space group	P2(1)2(1)2(1)	P2(1)2(1)2(1)	P2(1)2(1)2(1)
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
a[Å]	10.0282(10)	16.3768(4)	8.8780(4)
b[Å]	18.8206(3)	21.2060(6)	12.7264(8)
c[Å]	22.8781(4)	33.9413(8)	35.0996(2)
a[°]	90	90	90
b[°]	90	90	90
g[°]	90	90	90
V[Å^3]	4317.94(11)	11787.(5)	3792.1(4)
Z	4	12	4
T[K]	103(2)	103(2)	103(2)
$P_{cacld.}$ [Mgm^{-3}]	1.501	1.528	1.504
λ[Å]	0.71073	0.71073	0.71073
μ[mm^{-1}]	1.457	1.464	1.510
F(000)	1984	5528	1744
Flack parameter	0.032(8)	0.002(4)	0.008(17)
R_1(obsd. Data)[a]	0.0622	0.0740	0.0695
wR_2[b]	0.1234	0.1020	0.1410

[a] $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0||$.
[b] $wR_2 = \sqrt{\{\sum[w(F_0^2 - F_c^2)^2] / \sum[w(F_0^2)^2]\}}$, $w^{-1} = \sigma^2(F_0^2) + (aP)^2 + bP$.

When the hydroarsination reaction was carried out on 3-diphenylphosphanyl-but-3-en-1-ol no elimination product was observed and only the expected hydroarsination product was present. This could be attributed to the longer chain length of CH_2CH_2OH moiety for 3-diphenylphosphanyl-but-3-en-1-ol which renders a weaker Pd–O interaction.

3. Experimental

All air-sensitve manipulations were carried out using Schlenk and cannula techniques under a positive pressure of purified nitrogen. All NMR spectra were recorded at 25 °C on Bruker Avance 300 and 500 spectrometer. Optical rotations were measure on the specified solution in a 0.1 dm cell at 20 °C with a Perkin–Elmer 341 polarimeter. Elemental analysis was performed by the Elemental Analysis Laboratory of the Division of Chemistry and Biological Chemistry at Nanyang Technological University. Melting points were measured the SRS Optimelt Automated Melting Point System, SRS MPA100. The enantiomerically pure of complexes (*Rc*)-**1** [12], 3-diphenylphosphanyl-but3-en-1-ol [9g] and 2-diphenylphosphanyl-prop-2-en-1-ol [9g] were prepared as previously reported.

Caution! *All perchlorate salts should be handled as potentially explosive compounds. Care should be taken in handling highly toxic arsine and cyanide compounds.*

3.1. Hydroarsination reaction. Isolation of (R)-1-[1-(dimethylamino)ethyl]-2napthyl-C,N][(R)-3-(diphenylphosphino)-4-(diphenylarsino)butan-1-ol]palladium(II)] perchlorate (Rc,Rc)-**4a**

A solution of the complex (*Rc*)-**2a** (0.5 g, 0.84 mmols) in dichloromethane was treated with aqueous silver perchlorate (0.4 g, 1.93 mmols) for 2 h. The white precipitate, silver chloride was filtered off using Celite. The solution was subsequently washed with water (3 × 30 ml), and then the organic layer was dried over magnesium sulphate. The solvent was removed and the yellow solid was redissolved in methanol (100 ml). This solution was treated with diphenylarsine (0.19 g, 0.84 mmols) at −78 °C. The reaction mixture was then stirred for 24 h. The crude product was monitored by ^{31}P NMR until no more starting material was present. Removal of solvent under reduced pressure gave the crude products as a yellow solid. The crude product mixture was then purified through a silica gel column with dichloromethane/acetone as the eluent and then crystallised from dichloromethane/hexane to give complex (*Rc,Rc*)-**4a** as white crystals; m.p. 210–211 °C (decomp.), $[\alpha]_D = +92.0$ (c 0.7, CH_2Cl_2); 0.411g (55% yield). $C_{42}H_{44}ClNO_5PAsPd$:calcd. C 56.6, H 4.9, N 1.6. Found: C 56.4, H 4.8, N 1.5. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 77.6. ^{1}H NMR ($CDCl_3$, δ): 1.26 (m, 1H, $Ph_2AsCH'HCH$), 1.47 (m, 1H, $Ph_2AsCH'HCH$), 2.01(1H, m, $PCHCH_2$), 2.19 (d, 3H, $^3J_{HH} = 6.4$ Hz, CH*Me*), 2.54 (s, 3H, N*Me*), 2.86 (m, 2H, CH_2CH_2OH), 2.93 (m, 2H, CH_2CH_2OH) 2.95 (s, 3H, N*Me*), 3.70 (t, 1H, $^3J_{HH} = 6.7$ Hz, OH), 4.62 (qn, 1H, $^3J_{HH} = 6.1$ Hz, C*H*Me), 6.75–8.43 (m, 26H, aromatics).

3.2. Dichloro[(R)-3-(diphenylphosphino)-4-(diphenylarsino)butan-1-ol]palladium(II) (Rc)-**7a**

A solution of the complex (*Rc,Rc*)-**4a** (0.2 g, 0.22 mmols) in dichloromethane was stirred with concentrated hydrochloric acid (5 mL) for 16 h. The excess acid was then removed by washing with water (3 × 20 mL) and the organic layer was dried using magenesium sulphate. Upon removal of the solvent, a pale yellow solid was obtained (0.12 g, 83% yield); m.p. 223–224 °C (decomp.), $[\alpha]_D = -37.9$ (c 0.5, CH_2Cl_2). $C_{28}H_{28}Cl_2OPAsPd$:calcd. C 50.6, H 4.2. Found: 50.4, H 4.0. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 77.5. ^{1}H NMR ($CDCl_3$, δ): 1.21 (m, 1H, $Ph_2AsCH'HCH$), 1.56 (m, 1H, $Ph_2AsCH'HCH$), 1.76 (1H, m, $PCHCH_2$), 3.20 (m, 2H, CH_2CH_2OH), 3.50 (m, 2H, CH_2CH_2OH), 7.28–7.36 (20H, m, aromatics).

3.3. Decomplexation of [(R)-3-(diphenylphosphino)-4-(diphenylarsino)butan-1-ol], (Rc)-**8a**

A solution of the complex (*Rc*)-**7a** (0.10 g, 0.15 mmols) in dichloromethane was stirred vigorously with aqueous potassium cyanide (0.3 g) for 30 min. The resulting colourless organic layer was separated, washed with water and dried ($MgSO_4$). Upon the removal of solvent, a white solid (*Rc*)-**8a** was obtained, $[\alpha]_D = -37.9$ (c 0.5, CH_2Cl_2); 0.065 g (88% yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −1.2. ^{1}H NMR ($CDCl_3$, δ): 1.28 (m, 1H, $Ph_2AsCH'HCH$), 1.88 (m, 1H, $Ph_2AsCH'HCH$), 1.92 (1H, m, PC*H*CH2), 2.57 (m, 2H, CH_2CH_2OH), 3.70 (m, 2H, CH_2CH_2OH), 7.28–7.36 (20H, m, aromatics).

3.4. Hydroarsination reaction isolation of (R)-1-[1-(dimethylamino)ethyl]-2-napthyl-C,N][(R)-3-(diphenylphosphino)-4-(diphenylarsino)propan-1-ol]palladium(II) perchlorate (Rc,Rc)-**4b**

A solution of the complex (*Rc*)-**2b** (0.53 g, 0.92 mmols) in dichloromethane was treated with aqueous silver perchlorate (0.57 g, 2.76 mmols) for 2 h. The white precipitate, silver chloride was filtered off using Celite. The solution was subsequently washed with water (3 × 30 ml), and then the organic layer was dried over magnesium sulphate. The solvent was removed and the yellow solid was redissolved in methanol (100 ml). This solution was treated with diphenylarsine (0.21 g, 0.00092 mols) at −78 °C. The temperature was maintained for 10 h then stirred at room temperature for 24 h. The crude product was monitored by ^{31}P NMR until no more starting material was present. Two new signals were observed at δ 66.3 and 55.6 in the ratio of 2.6 to 1 respectively. Removal of solvent under reduced pressure gave the crude products as a yellow solid. The crude product mixture was then purified through a silica gel column with dichloromethane/acetone as the eluent. The major isomer was then crystallised from acetonitrile- diethyl ether to give complex (*Rc,Rc*)-**4b** as white crystals; (0.18 g, 25% yield); m.p. 203–204 °C (decomp.), $[\alpha]_D = -116$ (c 0.3, CH_2Cl_2). $C_{41}H_{42}ClNO_5PAsPd$:calcd. C 56.2, N 1.6 H 4.8. Found: 56.4, N 1.7, H 4.6. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 66.3. ^{1}H NMR ($CDCl_3$, δ): 2.12 (d, 3H, $^3J_{HH} = 6.2$ Hz, CH*Me*), 2.85 (s, 3H, N*Me*), 2.95 (s, 3H, N*Me*), 3.05 (1H, m, Ph_2PCHCH_2), 3.50 (m, 2H, CH_2OH), 3.69 (m, 1H, $Ph_2AsCH'HCH$), 3.91 (m, 1H, $Ph_2AsCH'HCH$), 4.46 (qn, 1H, $^3J_{HH} = 6.1$ Hz, C*H*Me), 6.72–8.26 (m, 26H, aromatics).

3.5. Dichloro[(R)-3-(diphenylphosphino)-4-(diphenylarsino) propan-1-ol]palladium(II) (Rc)-**7b**

A solution of the complex (*Rc,Rc*)-**4b** (0.1 g, 0.13 mmols) in dichloromethane was stirred with concentrated hydrochloric acid (5 mL) for 16 h. The excess acid was then removed by washing with water (3 × 20 mL) and the organic layer was dried using magenesium sulphate. Upon removal of the solvent, a pale yellow solid was obtained (0.066 g, 79% yield); m.p. 213–214 °C (decomp.), $[\alpha]_D = -120$ (c 0.5, CH_2Cl_2). $C_{27}H_{26}Cl_2OPAsPd$:calcd. C 49.9, H 4.0. Found: 50.3, H 4.2. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 70.0. ^{1}H NMR ($CDCl_3$, δ): 2.40–2.78 (2H, m, Ph_2AsCH_2CH), 3.32 (m, 2H, CH_2OH), 3.63 (m, 1H, Ph_2PCHCH_2), 7.30–7.56 (m, 20H, aromatics).

3.6. Decomplexation of [(R)-3-(diphenylphosphino)-4-(diphenylarsino)propan-1-ol, (Rc)-**8b**

A solution of the complex (*Rc*)-**7b** (0.05 g, 0.077 mmols) in dichloromethane was stirred vigorously with aqueous potassium cyanide (0.3 g) for 30 min. The resulting colourless organic layer was separated, washed with water and dried ($MgSO_4$). Upon the removal of solvent, a white solid (*Rc*)-**8b** was obtained, $[\alpha]_D = +30$ (c 0.3, CH_2Cl_2); 0.033 g (90% yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −9.0 ^{1}H NMR ($CDCl_3$, δ): 2.19 (d, 2H, $^3J_{HH} = 7.7$ Hz, Ph_2AsCH_2CH), 2.61 (1H, m, $PCHCH_2$), 3.72–3.95 (m, 2H, CH_2OH), 7.28–7.38 (m, 20H, aromatics).

3.7. Hydroarsination reaction isolation of (R)-1-[1-(dimethylamino)ethyl]-2-napthyl-C,N][(R)-3-(diphenylphosphino)-4-(diphenylarsino)prop-1-ene]palladium(II) perchlorate (Rc)-**6b**

Purification from silica column chromatography followed by crystallisation from dichloromethane-diethyl ether gave the minor product **(*Rc*)-10** as white crystals; (0.12 g, 15% yield); m.p. 203–204 °C (decomp.), $C_{41}H_{40}ClNO_4PAsPd$:calcd. C 57.3, N 1.6 H 4.7. Found: 57.4, N 1.7, H 4.6. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 55.6. ^{1}H NMR ($CDCl_3$, δ): 1.97 (d, 3H, $^3J_{HH} = 6.1$ Hz, CH*Me*), 2.84 (s, 6H, NMe_2), 3.25 (2H, m, $AsCH_2C$), 4.64 (qn, 1H, $^3J_{HH} = 6.1$ Hz, C*H*Me), 5.07 (d, 1H, $^2J_{HH} = 2.1$ Hz C]C*H'*H), 5.77 (1H, $^2J_{HH} = 2.1$ Hz C]CH'*H*), 6.76–8.05 (m, 26H, aromatics)

3.8. X-ray crystal structure determinations of complexes (Rc,Rc)-**4a**, (Rc,Rc)-**4b** and (Rc)-**6b**

Crystal data and a summary of the crystallographic analyses are given in Table 4. Diffraction data were collected on a Bruker X8 CCD diffractometer with Mo Kα radiation (graphite monochromator). SADABS absorption corrections were applied. All non-hydrogen atoms were refined anisotropically, while 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 [11].

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Appendix A. Supplementary material

CCDC-815920 [for (*Rc,Rc*)-**4a**], –815921 [for (*Rc,Rc*)-**4b**], –815922 [for (*Rc*)-**6**; contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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