



Chiral palladacycle promoted asymmetric synthesis of functionalized bis-phosphine monoxide ligand

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ABSTRACT

An organopalladium complex containing orthometalated (*R*)-(1-(dimethylamino)ethyl)naphthalene as the chiral auxiliary has been used to promote the asymmetric hydroalkoxylation reactions between weak nucleophile methanol and 1,1-bis(diphenylphosphino)ethylene or 1,1-bis(diphenylphosphino)ethylene monoxide in good regio- and stereo-selectivities in the presence of an external base. The major addition product obtained from methanol and 1,1-bis(diphenylphosphino)ethylene monoxide was subsequently isolated in a quantitative yield in its configurationally pure form and characterized by means of two-dimensional rotating-frame nuclear Overhauser enhancement (ROESY) NMR spectroscopy as well as single crystal X-ray diffraction analysis. The enantiomerically pure bis-phosphine monoxide ligand was subsequently liberated in high yield.

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1. Introduction

Bis-phosphine monoxides (BPMOs) have proven to be successful hemilabile ligands for hydroformylation [1–5], carbonylation [6] and other reactions [7–12]. Recent reports have also highlighted their use in phosphine-copper-catalyzed addition reactions [13–15]. Due to the presence of both the soft (P) and hard (O) nucleophilic centers on one heterobidentate ligand, bis-phosphine monoxides show unique coordination, stabilization and chelating properties which make them quite useful in organometallic synthesis and catalysis [16]. However, optically pure bis-phosphine monoxides are relatively rare and most of them are obtained from existing chiral bis-phosphines *via* selective oxidation reactions thus limiting the available derivatives [17,18]. The synthesis of functionalized chiral bis-phosphine monoxide ligands *via* addition reactions from easily accessible non-chiral bis-phosphines is much less developed.

Over the past few years, our group has reported the use of chiral cyclometalated-amine complexes as efficient promoters for asymmetric synthesis of chiral phosphines by means of Diels–Alder reactions [19–22], hydroamination reactions [23], hydrophosphination reactions [24–28] and hydroarsination reactions [29]. Asymmetric oxidation of polyphosphines has also been studied [30]. In this paper, we present two synthetic pathways towards a chiral bis-phosphine monoxide *via* hydroalkoxylation reactions and selective oxidation reactions.

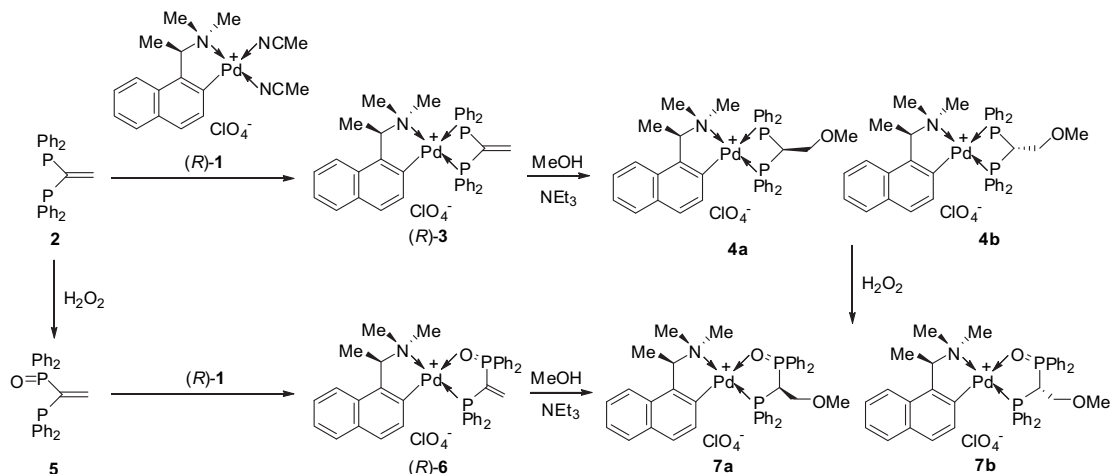
2. Results and discussion

Hydroalkoxylation of the achiral bis-phosphine monoxide. It is well known that the vinylidene double bond of 1,1-bis(diphenylphosphino)ethylene **2** is activated towards a series of addition reactions when the bis-phosphine is coordinated to transition metals [30]. However, their addition products are not chiral upon liberation from metal templates due to the existence of two symmetric phosphorus atoms. It is expected therefore that selective oxidation of one of the two phosphorus atoms can make the 1,1-bis(diphenylphosphino)ethylene a prochiral molecule and consequently render the addition products optically active. Hence 1,1-bis(diphenylphosphino)ethylene monoxide **5** was prepared *via* direct oxidation. A solution of 1,1-bis(diphenylphosphino)ethylene and one equivalent of hydrogen peroxide were stirred in dichloromethane for 2 h followed by column chromatography. The reaction mixture was composed of unreacted 1,1-bis(diphenylphosphino)ethylene, its monoxide **5**, and its dioxide. 1,1-bis(diphenylphosphino)ethylene monoxide **5** was isolated as yellowish solid in 52% yield and 1,1-bis(diphenylphosphino)ethylene was recycled in 15% yield. The ³¹P NMR spectrum of **5** in CDCl₃ exhibited a pair of doublet resonance signals at δ –12.2 and 29.0 (J_{PP} = 83.5 Hz). It is noteworthy that addition of more or less amount of hydrogen peroxide will result in lower yield of 1,1-bis(diphenylphosphino)ethylene monoxide.

As illustrated in Scheme 1, the 1,1-bis(diphenylphosphino)ethylene monoxide **5** was coordinated to (*R*)-**1** regioselectively to form the neutral complex (*R*)-**6** in 99% yield. The ³¹P NMR spectrum of the crude product in CDCl₃ exhibited only one pair of doublets

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Scheme 1. Chiral palladacycle promoted asymmetric hydroalkoxylation reaction of bis-phosphine **2** and bis-phosphine monoxide **5**.

resonance signals at δ 35.7 and 49.3 ($J_{\text{PP}} = 64.4$ Hz). Complex (R)-**6** was crystallized from dichloromethane–diethyl ether in quantitative yield and analyzed by X-ray crystallography (Fig. 1), as well as optical rotation measurement $[\alpha]_{\text{D}} +22$ (c 0.5, CH_2Cl_2). Selected bond lengths and angles are given in Table 1. Crystal data and a summary of the crystallographic analyses are given in Table 2. The structural analysis affirmed that the newly formed five-membered chelate ring has the asymmetric skew conformation of λ helicity, and the soft donor P atom takes up the expected coordination position *trans* to the NMe_2 moiety while the hard donor O atom is *trans* to the naphthalene carbon.

The coordination product (R)-**6** was subsequently treated with methanol in benzene. In the absence of any external base, methanol shows no reactivity with (R)-**6** under ambient conditions. However, upon addition of one equivalent of triethylamine, the hydroalkoxylation reaction proceeds smoothly at room temperature. The reaction was monitored by the ^{31}P NMR spectroscopy and was found

to be complete in 6 h to give a 4:1 mixture of diastereomers **7a** and **7b** in 95% conversion yield. (Scheme 1) The ^{31}P NMR spectrum of the crude product exhibited two pairs of doublets resonance signals at δ 43.8, 58.6 ($J_{\text{PP}} = 30.0$ Hz) (**7a**) and 42.9, 58.0 ($J_{\text{PP}} = 25.1$ Hz) (**7b**). Although the stereoselectivity of the hydroalkoxylation reaction is not affected by the amount of triethylamine when this mild base is more than one equivalent, it is influenced by solvent effects. When the reaction is performed in various solvents such as ethyl acetate, dichloromethane, acetone, tetrahydrofuran, acetonitrile and methanol, it gave lower conversion yields and the ratio of **7a** to **7b** were 4.3:1, 2.8:1, 2.8:1, 2.8:1, 2.5:1 and 3:1 respectively. It is noteworthy that the adducts **7a** and **7b** were interconvertible. However, this process took quite a long time and only occurred in solution in the presence of external base and is attributed to the abstraction of H atom at the chiral center by the base. The major isomer **7a** was obtained from dichloromethane and diethyl ether as colorless crystals, 0.623 g (60% yield): $[\alpha]_{\text{D}} +14$ (c 0.5, CH_2Cl_2). Unfortunately,

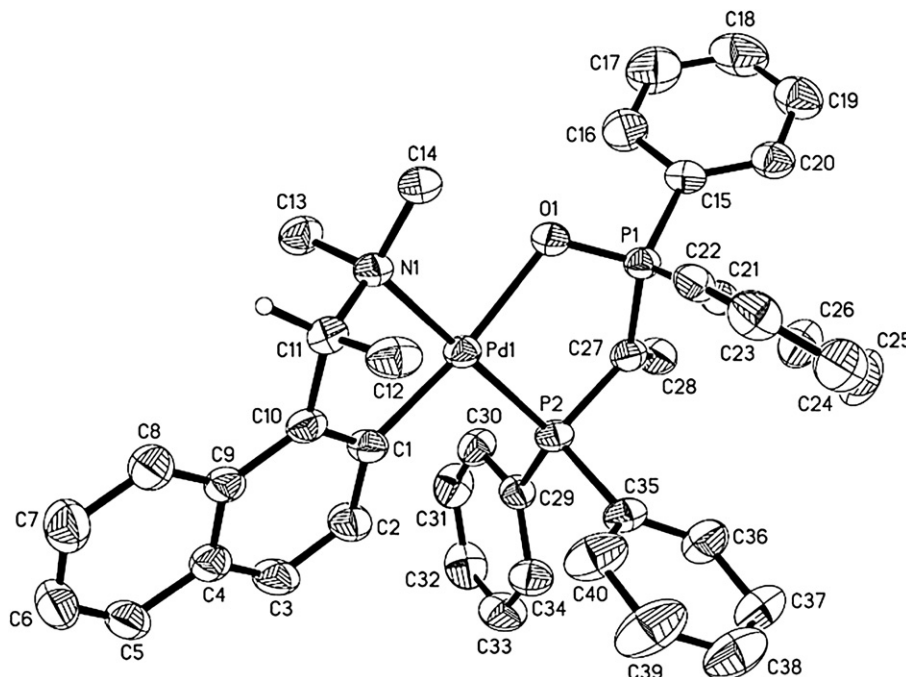


Fig. 1. Molecular structure and absolute stereochemistry of complex (R)-**6**.

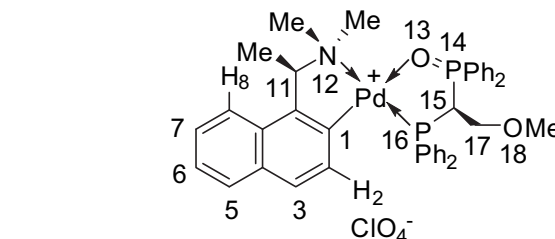
Table 1
Selected Bond Lengths (Å) and Angles (deg) for (R)-**6**.

| | | | |
|-----------------|-----------|------------------|------------|
| Pd(1)–C(1) | 1.984(3) | C(1)–Pd(1)–O(1) | 172.28(11) |
| Pd(1)–N(1) | 2.106(2) | P(2)–Pd(1)–O(1) | 89.31(6) |
| Pd(1)–O(1) | 2.152(2) | N(1)–Pd(1)–O(1) | 90.87(9) |
| Pd(1)–P(2) | 2.2523(8) | C(1)–Pd(1)–P(2) | 98.37(9) |
| O(1)–P(1) | 1.507(2) | Pd(1)–P(2)–C(27) | 102.79(10) |
| P(1)–C(27) | 1.802(3) | Pd(1)–O(1)–P(1) | 115.55(11) |
| P(2)–C(27) | 1.838(3) | O(1)–P(1)–C(27) | 107.54(13) |
| C(1)–Pd(1)–N(1) | 81.50(12) | P(2)–C(27)–P(1) | 108.79(15) |
| P(2)–Pd(1)–N(1) | 177.19(7) | | |

single crystals of the complex **7a** that are suitable for X-ray structural investigation could not be produced. Accordingly, it was necessary to determine the absolute stereochemistry of complex **7a** by the 2D rotating-frame nuclear Overhauser enhancement (ROESY) ^1H NMR technique. We have previously applied this reliable 2D NMR technique for the assignments of the absolute stereochemistry in a series of coordinated chiral phosphines containing orthometalated naphthylamine auxiliary [31].

Assignment of absolute stereochemistry of addition product. Fig. 2 shows the numbering scheme of the complex **7a** used in the 2D ROESY NMR analysis. In this NMR analysis, the well-established stereochemical features of the orthometalated (R)-naphthylamine unit incorporated within the complex **7a** are used as the internal stereochemical references. Due to the repulsive interaction between Me(11) and the proximal H(8) naphthylene proton, Me(11) invariably takes up the axial disposition in the stable five-membered organopalladium ring which adopts the static δ absolute conformation. On the other hand, the prochiral NMe groups attached to the organopalladium ring are locked by the rigid δ ring conformation into the nonequivalent axial and equatorial positions. The axial NMe group projects perpendicularly below the palladium-centered square plane, while the equatorial NMe group protrudes somewhat above the plane and towards the adjacent oxygen donor in the O-P ring. With reference to the unique structural feature of the auxiliary, appropriate interchelate NOE interactions between the naphthylamine auxiliary and the bis-phosphine monoxide chelate would allow the assignment of the absolute stereochemistry of complex **7a**.

Selected $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR data of complex **7a** are given in Table 3. These NMR assignments are based on a series of $^{31}\text{P}\{^1\text{H}\}$ and ^1H and 2D ^1H ROESY NMR studies of complex **7a**. Fig. 3 shows

**Fig. 2.** Numbering scheme of complex **7a** for the ROESY NMR studies.

the 2D ^1H – ^1H ROESY NMR spectra of the major addition product **7a**. In this spectrum, the characteristic NOE patterns within the orthometalated (R)-naphthylamine ring are clearly recorded. For example, the driving forces for Me(11) to assume the axial position, i.e., the H(8)–Me(11) (A) and H(8)–H(11) (M) repulsive interactions, are clearly reflected in the spectrum. Strong NOE signals (B), (G), (H) are observed for the expected proximities between H(11) and three methyl groups Me(11), NMe(ax), NMe(eq) respectively. Signal (C) represent the NOE interaction between Me(11) and NMe(eq) while no interaction between Me(11) and NMe(ax) is observed.

In Fig. 3, the 2D ROESY NMR spectrum of **7a** shows long-range interchelate NOE interactions between Me(18) and Me(11) (signal D), Me(18) and NMe(eq) (signal E). Furthermore, NOE signal (I) is observed between H(15) and NMe(eq). No interaction between NMe(ax) and H(15), or NMe(ax) and Me(18) is observed. These NOE signals thus indicate that Me(18) is located on the same side above the coordination square plane with Me(11) and NMe(eq). Accordingly, the absolute configuration at the new-formed carbon center is *R*.

Selective oxidation of co-ordinated bis-phosphines. Another synthetic pathway towards **7a** and **7b** is the selective oxidation of coordinated bis-phosphines in the hydro-alkoxylation products **4a** and **4b**. As shown in Scheme 1, the bis-phosphine 1,1-bis(diphenylphosphino)-ethane **2** was co-ordinated to chiral palladium template (R)-**1** to form the neutral complex (R)-**3**. The ^{31}P NMR spectrum of the crude product in CDCl_3 exhibited a pair of doublet resonance signals at δ –4.4 and 13.6 (J_{PP} = 25.1 Hz). The coordination product (R)-**3** was subsequently treated with methanol and 30% equivalent of triethylamine in dichloromethane at room temperature for 1.5 h, giving the desired hydroalkoxylation products **4a** and **4b** in 96% yield. In the absence of triethylamine, this equilibrium reaction only has 82% conversion yield with more reaction time required. The ^{31}P NMR spectrum of the crude products exhibited two pairs of doublet resonance signals at δ –17.5, 8.4 (J_{PP} = 47.6 Hz) and –20.5, 7.9 (J_{PP} = 49.4 Hz) with the ratio 1.5:1. The cationic diastereomers **4a** and **4b** could not be separated efficiently by chromatography or fractional crystallization. The diastereomeric mixture in dichloromethane was subsequently treated with hydrogen peroxide. The stereoselectivity of the oxidation reaction is affected by external base. Two equivalents of hydrogen peroxide were used in all the conditions described below. Without NEt_3 , only 5% of **4a**, **4b** were transformed into **7a**, **7b** in dichloromethane or methanol at room temperature in 24 h. The ^{31}P NMR spectroscopy was used to monitor the reaction and it exhibited two new pairs of doublet resonance signals at δ 43.8, 58.6 (J_{PP} = 30.0 Hz) (**7a**) and

Table 2
X-ray Crystallographic Data of (R)-**6**.

| | |
|------------------------------------|--|
| formula | (R)- 6 |
| fw | $\text{C}_{40}\text{H}_{38}\text{ClNO}_5\text{P}_2\text{Pd}$ |
| space group | 816.50 |
| cryst syst | $\text{P2}_1(1)2_1(1)$ |
| $a/\text{\AA}$ | orthorhombic |
| $b/\text{\AA}$ | 11.1540(4) |
| $c/\text{\AA}$ | 16.6940(7) |
| α/deg | 21.0834(7) |
| β/deg | 90° |
| γ/deg | 90° |
| $V/\text{\AA}^3$ | 90° |
| Z | 3925.8(3) |
| T/K | 4 |
| $D_{\text{calc}}/\text{g cm}^{-3}$ | 173(2) |
| μ/mm^{-1} | 1.381 |
| $\lambda/\text{\AA}$ | 0.665 |
| Flack parameters | 0.71073 |
| $R1$ (obsd data) ^a | –0.02(2) |
| $wR2$ (obsd data) ^b | 0.0274 |
| | 0.0356 |

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.^b $wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$, $w^{-1} = \sigma^2(F_o)^2 + (aP)^2 + bP$.**Table 3**
Selected ^1H NMR Spectra Chemical Shift Values of **7a** in CDCl_3 .

| | | | |
|-------------------------|------|-------------------------|------|
| CHMe | 2.12 | CH_2OMe | 3.40 |
| CH_2OMe | 2.79 | CHMe | 4.58 |
| NMe(ax) | 3.06 | PCHCH ₂ | 4.70 |
| NMe(eq) | 3.16 | | |

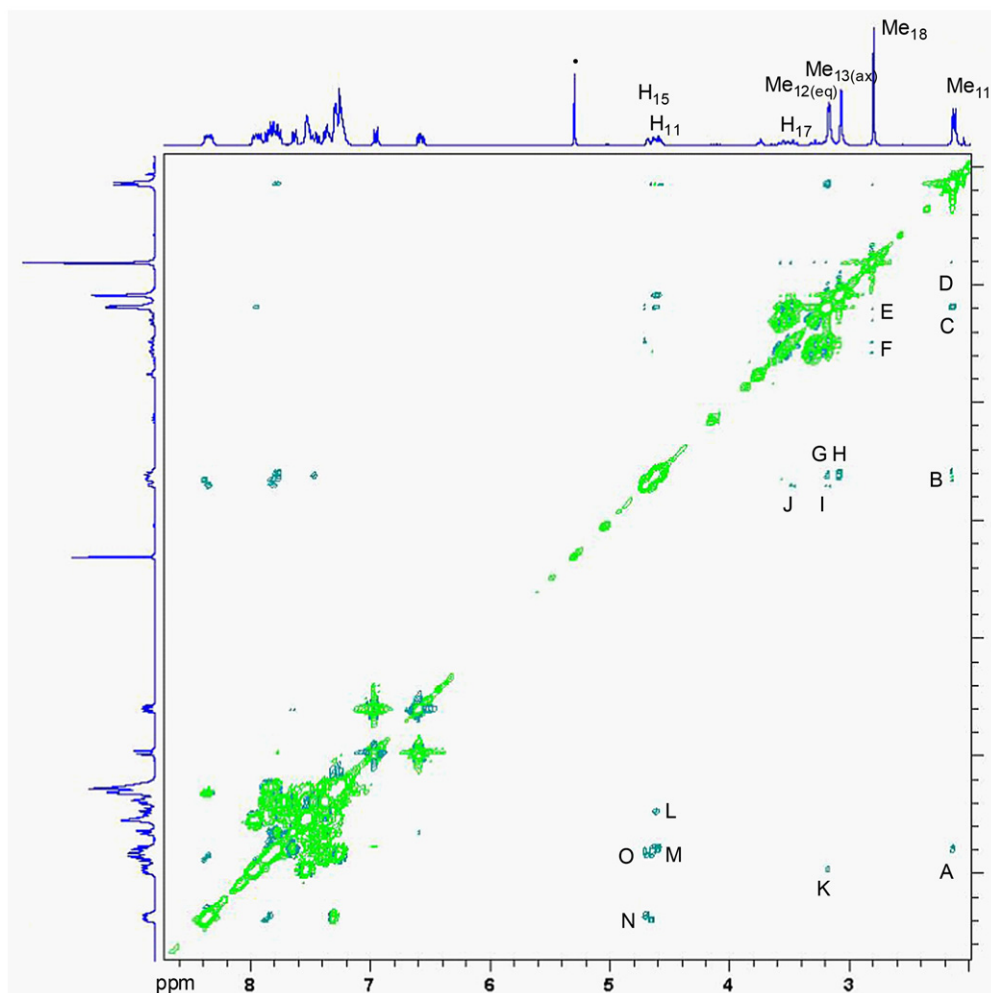


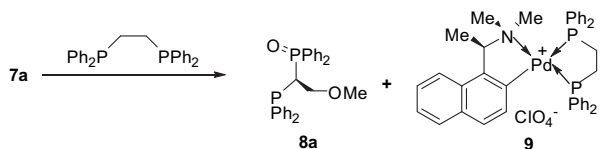
Fig. 3. Two-dimensional ^1H ROESY NMR spectrum of complex **7a** in CDCl_3 . All off-diagonal peaks are of negative intensity. Selected NOE contacts: A, H8-Me11; B, H11-Me11; C, Me11-Me12(eq); D, Me11-Me18; E, Me12(eq)-Me18; F, H17-Me18; G, H11-Me12(eq); H, H11-Me12(ax); I, H15-Me12(eq); J, H15-H17; K, H17-Ph; L, H11-Ph; M, H11-Ph'; N, H15-Ph; O, H15-Ph'.

42.9, 58.0 ($J_{\text{PP}} = 25.1$ Hz) (**7b**) with the ratio 1:1.2. In this process, no other products were formed and the oxidation reaction only occurred at the phosphorus center which is *trans* to the naphthalene carbon. When the reaction was performed at 40 °C under the same conditions, around 50–60% of **4a, b** were converted into **7a, b** in the same ratio together with coordination product (*R*)-**6** and few minor un-identified impurities. Treatment of (*R*)-**3** with hydrogen peroxide in a similar manner could not yield (*R*)-**6** as the product. Some unidentified chemicals were found in reaction mixture. Also, in the absence of external base, (*R*)-**6** could not be obtained from **7a, b** by the reverse reaction. From the discussion above, (*R*)-**6** was possibly obtained from oxidation intermediates of **4a, b** with hydrogen peroxide.

With 120% equivalent of NEt_3 , 60% of **4a, b** were converted into **7a, b** in dichloromethane or methanol respectively at room temperature in 24 h. The ^{31}P NMR spectrum found two new pairs of doublet resonance signals at δ 43.8, 58.6 ($J_{\text{PP}} = 30.0$ Hz) (**7a**) and 42.9, 58.0 ($J_{\text{PP}} = 25.1$ Hz) (**7b**) with the ratio 3:1. The difference of these two solvent systems is that, when the reaction was performed in dichloromethane solution, (*R*)-**6** was obtained while none of it was yielded in methanol solution. In addition, the ratio of **7a** to **7b** in this reaction is consistent with that of the direct hydroalkoxylation reaction of (*R*)-**6** with methanol (when it was performed in methanol solution). From the discussion above, we believe that with triethylamine as external base, the reaction rate of

4a, b to (*R*)-**6** is faster than the rate of **4a, b** to **7a, b** when treated **4a, b** with hydrogen peroxide. However, once (*R*)-**6** was formed in solution, it would subsequently undergo hydroalkoxylation reaction with methanol and was converted into **7a, b**.

Free ligand liberation. The bis-phosphine monoxide ligand in **7a** could be rapidly displaced from the chiral palladium template by the strong chelating agent diphenylphosphino ethane (dppe) as shown in Scheme 2. The corresponding optically active ligand **8a** was liberated with formation of complex **9** [32]. The reaction mixture was passed through a column of Florisil using dichloromethane as eluent to yield a colorless solution. Removal of solvent under reduced pressure gave **8a** as white solid in 75% yield, $[\alpha]_{\text{D}} +56.7$ (c 0.5, CH_2Cl_2). The ^{31}P NMR spectrum of bis-phosphine monoxide **8a** exhibited a pair of doublet resonance signals at δ -15.2, 33.7 ($J_{\text{PP}} = 67.0$ Hz). As illustrated in Scheme 3, the optical purity of **8a** was confirmed by the quantitative reparation of **7a** from the liberated ligand and (*R*)-**1**. The ^{31}P NMR spectrum of the crude product in CDCl_3 exhibited only a pair of doublet signals at δ 43.8, 58.6 ($J_{\text{PP}} = 30.0$ Hz). These signals are identical to those recorded for the major diastereomer **7a** generated directly from original ligand. As a further test of the optical purity of the liberated ligand and to confirm the identity of the minor product, **8a** was re-coordinated to the equally accessible (*S*)-**1**. The ^{31}P NMR spectrum of the crude recomplexation product in CDCl_3 exhibited only a pair of doublet signals at δ 42.9, 58.0 ($J_{\text{PP}} = 25.1$ Hz). These



Scheme 2. Liberation of optically active bisphosphine monoxide ligand **8a**.

signals were identical with those observed for the minor product **7b**. Hence, it could be confirmed that **7b** was indeed the minor product of the original asymmetric synthesis and the liberated bisphosphine monoxide **8a** is indeed optically pure.

In conclusion, two converging synthetic pathways sharing a common metal template promoted asymmetric hydroalkoxylation and oxidation process have been illustrated for the synthesis of chiral bis-phosphine monoxide ligands. These ligands are currently being evaluated for catalytic potential in various organic synthetic scenarios.

3. Experimental

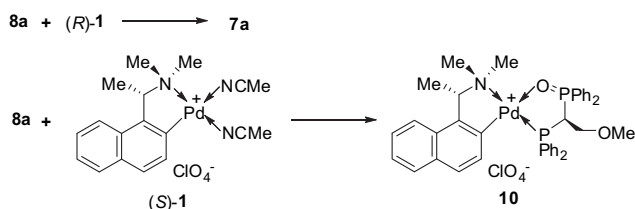
Reactions involving air-sensitive compounds were performed under an inert atmosphere of argon using standard Schlenk techniques. Solvents were dried and freshly distilled according to standard procedures and degassed prior to use when necessary. The ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra recorded at 25 °C on Bruker ACF 300 and 500 MHz spectrometers. Optical rotations were measured on the specified solution in a 0.1 dm cell at 20 °C with a Perkin–Elmer model 341 polarimeter. Elemental analyses were performed by the staff in the Elemental Analysis Laboratory of the Division of Chemical and Biological Chemistry of Nanyang Technological University. Melting points were measured using the SRS Optimelt Automated Melting Point System, SRS MPA100.

The chiral palladium complexes bis(acetonitrile) [(*S*)-1-[1-(dimethylamino)ethyl]-2-phenyl-C, *N*]-palladium(II) perchlorate ((*R*)-**1**) [32] were prepared according to literature methods.

Caution! All perchlorate salts should be handled as potentially explosive compounds.

3.1. Synthesis of 1,1-bis(diphenylphosphino)-ethylene monoxide, **5**

A mixture of 1,1-bis(diphenylphosphino)ethylene (1.982 g, 5.000 mmol) and hydrogen peroxide (0.170 g, 5.000 mmol) in dichloromethane (80 mL) was stirred at room temperature for 2 h. The solvent was removed under reduced pressure. This material was chromatographed on a silica gel column with ethyl acetate–dichloromethane (1:3 v/v) as the eluent, giving the bis-phosphine monoxide **5** as yellowish solid: 1.072 g (52% yield). Mp 112–113 °C. Anal. Calcd. for $\text{C}_{26}\text{H}_{22}\text{P}_2\text{O}$: C, 75.7; H, 5.4. Found: C, 75.3; H, 5.6. ^{31}P NMR (CDCl_3) δ -12.2, 29.0 (J_{PP} = 83.5 Hz); ^1H NMR (CDCl_3) δ 6.06 (ddd, 1H, CHH' , $^2J_{\text{HH}'} = 1.3$ Hz, $J_{\text{PH}} = 39.6$ Hz, $J_{\text{PH}'} = 8.0$ Hz), 6.96 (ddd, 1H, CHH' , $^2J_{\text{HH}'} = 1.3$ Hz, $J_{\text{PH}'} = 22.3$ Hz, $J_{\text{PH}} = 11.6$ Hz), 7.19–7.76 (m, 20H, aromatics).



Scheme 3. Re-complexation studies for confirmation of optical purity.

3.2. Synthesis of [(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthyl-C, *N*]-1,1-bis(diphenylphosphino)-ethylene monoxide-*P*, *O*]-palladium(II) perchlorate, (*R*)-**6**

A mixture of 1-bis(diphenylphosphino)ethane monoxide **5** (0.843 g, 2.044 mmol) and (*R*)-**1** (0.994 g, 2.045 mmol) in dichloromethane (60 mL) was stirred at room temperature for 2 h. After removal of the organic solvent, the complex (*R*)-**6** was isolated as yellow solid, 1.837 g (99% yield). $[\alpha]_{\text{D}}^{20} +22$ (c 0.5, CH_2Cl_2); Mp 158 °C (dec.). Anal. Calcd. for $\text{C}_{40}\text{H}_{38}\text{ClNO}_5\text{P}_2\text{Pd}$: C, 58.8; H, 4.7; N, 1.7. Found: C, 58.3; H, 4.7; N, 1.4. ^{31}P NMR (CDCl_3) δ 35.7, 49.3 (J_{PP} = 64.4 Hz); ^1H NMR (CDCl_3) δ 1.88 (d, 3H, CHMe , $^3J_{\text{HH}} = 6.2$ Hz), 2.94 (s, 6H, NMe_2), 4.48 (qn, 1H, $^3J_{\text{HH}} = ^4J_{\text{PH}} = 6.2$ Hz, CHMe), 6.28–6.44 (m, 2H, CCH_2), 6.89–7.78 (m, 26H, aromatics).

3.3. Hydroalkoxylation reaction. Isolation of complex **7a**

A mixture of (*R*)-**6** (1.000 g, 1.225 mmol), triethylamine (0.124 g, 1.225 mmol) and methanol (2 mL) was stirred in benzene (50 mL) at room temperature for 6 h. The solvent was removed and complex **7a** was obtained from dichloromethane and diethyl ether as colorless crystals, 0.623 g (60% yield). $[\alpha]_{\text{D}}^{20} +14$ (c 0.5, CH_2Cl_2); Mp 195 °C (dec.). Anal. Calcd. for $\text{C}_{41}\text{H}_{42}\text{ClNO}_6\text{P}_2\text{Pd}$: C, 58.0; H, 5.0; N, 1.7. Found: C, 57.4; H, 5.1; N, 1.6. ^{31}P NMR (CDCl_3) δ 43.8, 58.6 (J_{PP} = 30 Hz); ^1H NMR (CDCl_3) δ 2.12 (d, 3H, CHMe , $^3J_{\text{HH}} = 6.2$ Hz), 2.79 (s, 3H, OMe), 3.06 (s, 3H, NMeax), 3.16 (d, 3H, $J_{\text{PH}} = 3.2$ Hz, NMeeq), 3.40 (m, 2H, CH_2OMe), 4.58 (qn, 1H, $^3J_{\text{HH}} = ^4J_{\text{PH}} = 6.2$ Hz, CHMe), 4.70 (m, 1H, CHCH_2OMe), 6.57–8.39 (m, 26H, aromatics).

3.4. Liberation of bis-phosphine monoxide **8a**

A mixture of **7a** (0.103 g, 0.121 mmol) and diphenylphosphino ethane (0.048 g, 0.120 mmol) was stirred in dichloromethane at room temperature for 15 min. The resulting yellowish mixture was passed through a silica gel chromatographic column using dichloromethane–acetone as eluent. Removal of solvent under reduced pressure gave **8a** as air-sensitive yellowish solid, 0.040 g (75% yield), $[\alpha]_{\text{D}}^{20} +40.9$ (c 0.1, CH_2Cl_2). ^{31}P NMR (CDCl_3) δ -15.2, 33.7 (J_{PP} = 67.0 Hz); ^1H NMR (CDCl_3) δ 2.69 (s, 3H, OMe), 3.36–3.47 (m, 2H, CH_2OMe), 5.30–5.32 (m, 1H, CHCH_2OMe), 7.29–7.80 (m, 20H, aromatics).

3.5. X-ray crystal structure determinations of complexes (*R*)-**6**

Crystal data and a summary of the crystallographic analyses are given in Table 2. Diffraction data were collected at the Nanyang Technological University using a Bruker X8 Apex diffractometer with Mo $\text{K}\alpha$ radiation (graphite monochromator). All non-H atoms were refined anisotropically, while Hydrogen atoms were introduced at a fixed distance from the carbon atoms and were assigned fixed thermal parameters. The absolute configurations of the chiral complexes were determined unambiguously using the Flack parameter [33].

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Appendix A. Supplementary material

CCDC 779850 contains the supplementary crystallographic data for complex (*R*)-**6**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk/deposit>.

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