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New chiral *N*,*P*-oxazolines, and their Ir complexes in asymmetric hydrogenation of an imine

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Dedicated to Professor Josef J. Ziolkowski on the occasion of his 70th birthday, and to acknowledge his contributions to coordination and organometallic chemistry.

Abstract

(+) (1*S*,2*S*)-2-Amino-1-phenyl-1,3-propanediol reacts with ortho-esters to form 4-hydroxymethyl-5-phenyl-1,3-oxazolines. Subsequent reaction of their toluenesulfonyl derivatives with diphenylphosphinolithium yields the *N*,*P*-ligands, (4*S*,5*S*)-2-R-4-diphenylphosphinomethyl-5-phenyl-1,3-oxazoline (R = Me, Et, Ph). X-ray analyses of (4*S*,5*S*)-2-methyl-4-toluenesulfonylmethyl-5-phenyl-1,3-oxazoline and (4*S*,5*S*)-2,5-diphenyl-4-diphenylphosphinomethyl-1,3-oxazoline reveal retention of absolute configuration throughout the synthesis. The [Ir(COD)(*N*,*P*-oxazoline)]PF_6 systems in CH_2Cl_2 effect catalytic hydrogenation of *N*-(1-phenylethylidene)benzylamine, $PhCH_2N = C(Me)Ph$, to the corresponding amine with upto 63% e.e. with the R = Et ligand.

Keywords: Oxazolines; Ligands; Asymmetric hydrogenation; Imines; Ir complexes; X-ray analysis

1. Introduction

Oxazolines have been widely employed in many homogeneous catalytic processes, most commonly as bi- or multidentate ligands [1–5]. Most such ligands (that coordinate, for example, via *N*,*N*- [6–9], *N*,*O*- [10,11], *N*,*P*- [2,3,11–30], *N*,*S*- [7,27,31–33], *N*,*C*- [34,35], *N*,*N*,*N*- [2,9,36], *N*,*O*,*N*- [36–38], *N*,*P*,*N*- [2], *N*,*S*,*N*- [37,39], *N*,*N*,*O*,*N*,*N*- [37,38], *N*,*N*,*N*,*N*- [37,38], and *N*,*N*,*N*,*N*,*N*,*N*-bonding modes [37,38]) have their second (and other) heteroatom tethered to the oxazoline ring through the 2-position (see Fig. 1).

Our studies reported here stem from the use of nitrogen-phosphorus (*N*,*P*) donor oxazoline ligands in asymmetric hydrogenation of imines [2,15,40,41], a long time interest of this group [42]. Considerable success in the application of such *N*,*P*-ligands in such asymmetric catalysis prompted us to initiate this study [43]. Fig. 1 shows some *N*,*P*-oxazolines, and their associated research groups and year of publication; *N*,*P*-oxazoline ligands derived from having phosphine-substituted ferrocenyl moieties at the 2-position are also known [44], but are not shown in Fig. 1.

Although the reported *N*,*P*-oxazolines include structures where the P-atom is attached to the ring through C-atoms 2 or 4, and 5- or 6-membered rings can be formed on coordination to a metal (Fig. 1), there is still need for simple preparative methods of such ligands that allow for minor modification of a synthetic reagent to give a set of closely related ligands for the fine tuning of catalysts.

We present here a synthetic pathway to the chiral (4*S*,5*S*)-2-R-4-diphenylphosphino(methyl)-5-phenyl-1,3-oxazolines (R = Me, Et, Ph), where the P-atom is tethered to the oxazoline ring at C-4 (see Scheme 1), and application of such ligands within Ir species for catalyzed asymmetric hydrogenation of the selected imine, *N*-(1-phenylethylidene)benzylamine, $PhCH_2N = C(Me)Ph$.

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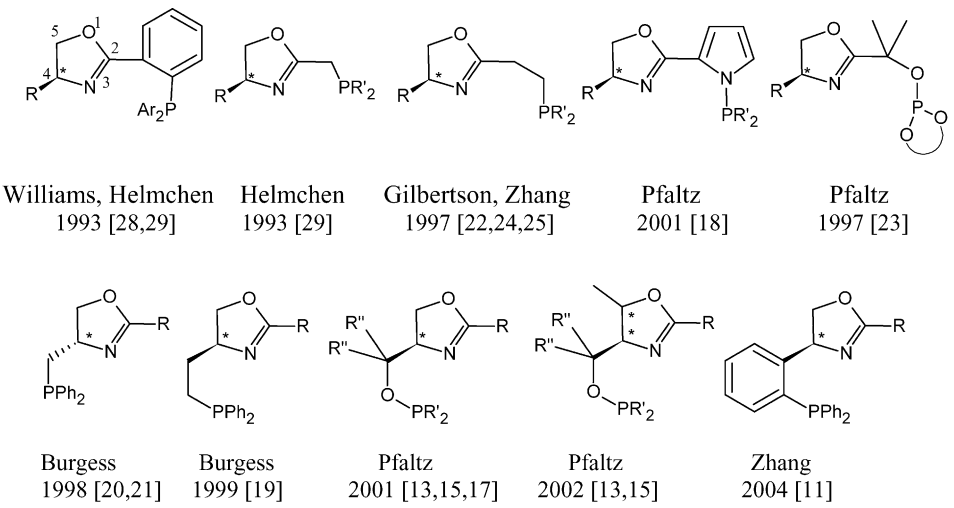


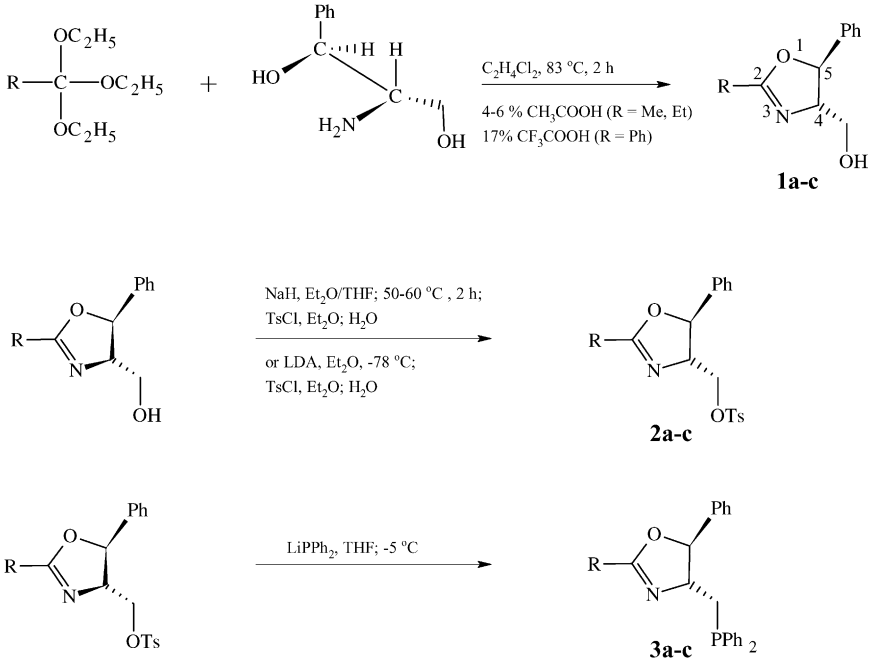
Fig. 1. Some *N,P*-oxazoline ligands (R is typically an alkyl or aryl group); examples with the P-containing moiety attached via C-atom 2 (top row) or C-atom 4 (bottom row).

2. Experimental section

2.1. General techniques, and reagents

Syntheses of oxazolines, and manipulations with Ir complexes, were done under Ar using standard Schlenk and/or glove-box techniques. All non-deuterated solvents (reagent grade) were dried over CaH_2 or Na, distilled under N_2, stored over sodium/benzophenone ketyl in vacuum, and vacuum distilled directly in to a reaction vessel. Deuterated solvents were dried according to standard procedures [45], and stored under Ar or under vacuum.

Triethylortho-acetate, -propionate, -benzoate and (1*S*,2*S*)-(+)-2-amino-1-phenyl-1,3-propanediol were purchased from Aldrich; prior to use, the ortho-esters were distilled, and the diol recrystallized from MeOH/$MeCO_2Et$ [46]. Toluenesulfonylchloride, trifluoroacetic anhydride and acid, NaH, LDA (2.0 M in a heptane/THF/PhC_2H_5 solution), *sec*-BuLi, (*R*) and (*S*)-*N*-(1-phenylethyl)benzylamine, and (*R*)-mandelic acid (Aldrich products), and Ph_2PH (Strem), were used as received, while $LiPPh_2$ was made by a literature procedure [47]. *N*-(1-Phenylethylidene)benzylamine was made as the *E*-isomer following a literature procedure [41]. H_2 (Praxair, Extra Dry) was purified by passage through an Engle-



Scheme 1. Preparation of *N,P*-oxazolines: (**a**) R = Me; (**b**) R = Et; (**c**) R = Ph.

hard "Deoxo" catalyst. $[Ir(COD)Cl]_2$ was made via a literature procedure [48] from $IrCl_3{\cdot}3H_2O$ obtained from Colonial Metals Inc.

NMR spectra were recorded at room temperature (r.t., ~20 °C) in $CDCl_3$ or C_6D_6 on Bruker AC200 or VARIAN XL300 spectrometers, with residual protons of deuterated solvents (^1H, relative to external $SiMe_4$), solvent carbon (^{13}C, relative to external $SiMe_4$), and external $P(OMe)_3$ ($^{31}P\{^1H\}$, $\delta_P = 141.00$ versus 85% aq. H_3PO_4) being used as references; all J values are reported in Hz. The chiral column, Chiraldex β-DM, was obtained from Advanced Separation Technologies Inc. Low-resolution mass spectra were measured on a Kratos Concept IIHQ LSIMS instrument (using thioglycerol or 3-nitro-benzyl alcohol as matrix), and are given as *m/z* with relative % intensities. Microanalyses were performed by Mr. P. Borda in this department.

2.2. Oxazolines (see Scheme 1)

(4*S*,5*S*)-2-R-4-Hydroxymethyl-5-phenyl-1,3-oxazolines (**1**). These compounds were made according to literature methods [46,49] from an ortho-ester and (1*S*,2*S*)-2-amino-1-phenyl-1,3-propanediol in DMF or preferably $ClCH_2CH_2Cl$ solution using catalytic amounts of acetic or trifluoroacetic acid. **1a** (R = Me, yield 85%), **1b** (R = Et, 91%) and **1c** (R = Ph, 93%) were isolated as white solids, their NMR data agreeing with those in the literature [46,50].

(4*S*,5*S*)-2-R-4-toluenesulfonylmethyl-5-phenyl-1,3-oxazolines (2) (see Scheme 1). The toluene-sulfonyl derivatives of **1** were made using modified methods of Meyers et al. [46].

2.2.1. ***2a*** *(R = Me)*

Method 1: 4.8 mL of the 2.0 M solution (9.60 mmol) of LDA were added dropwise to 1.5 g (7.84 mmol) of **1a** in 50 mL of dry Et_2O at −78 °C, and the reaction mixture was allowed to warm slowly to −10 °C. Then 1.49 g (7.82 mmol) of TsCl in 20 mL of Et_2O was added dropwise, the mixture stirred at r.t. for 2 h, and then poured into ice-water (~80 mL). The Et_2O layer was separated and the aqueous layer was then shaken with further Et_2O (3 × 50 mL). The combined ether fractions were then dried over $MgSO_4$; this was filtered off, and the Et_2O removed from the filtrate under vacuum to leave a white crystalline solid that was washed with cooled Et_2O (20 mL) and dried under vacuum. Yield 70%.

Method 2: 1.64 g (8.37 mmol) of **1a** in 70 mL of Et_2O and 15 mL of THF were added dropwise to a suspension of 280 mg (11.70 mmol) of NaH in 10 mL of THF at r.t., the mixture was heated at 60 °C for 30 min and then cooled to r.t., when 1.62 g (8.50 mmol) of TsCl in 10 mL of THF was added slowly. The mixture was then stirred for 1.5 h and poured into the ice-water (~80 mL). Subsequent work up was identical to that described above. Yield 73%.

^1H NMR ($CDCl_3$, 200 MHz), δ: 2.04 (s, 3H, =*C*–C*H*$_3$), 2.43 (s, 3H, Ts–C*H*$_3$), 4.15 (m, 3H, N–C*H*–C*H*$_2$), 5.35 (d, 1H, O–C*H*, $J_{HH} = 6.2$), 7.15–7.40 (m, 7H, phenyl–*H*), 7.77 (d, 2H, phenyl-*H*, $J_{HH} = 10.0$). $^{13}C\{^1H\}$ ($CDCl_3$, 75 MHz), δ singlets: 13.99 (1C, =*C*–CH$_3$), 21.59 (1C, Ts–*C*H$_3$), 70.21 (1C, N–*C*H), 73.17 (1C, O–*C*H), 83.03 (1C, *C*H$_2$), 125.39 (2C, C_{Ar}), 127.93 (2C, C_{Ar}), 128.44 (1C, C_{Ar}), 128.82 (2C, C_{Ar}), 129.88 (2C, C_{Ar}), 132.49 (1C, C_{Ar}), 139.64 (1C, C_{Ar}), 145.05 (1C, C_{Ar}), 166.59 (1C, *C*=N). m.p. 72–74 °C. MS, *m/z*: 346 ($[M]^+$, 100%), 174 ($[M\text{-}MeC_6H_4SO_3]^+$, 40%); 132 (100%). Anal. found: C 62.7; H 5.5 N 4.05; S 9.1%. Calc. for $C_{18}H_{19}O_4NS$: C 62.59; H 5.54; N 4.06; S 9.28%.

2.2.2. ***2b*** *(R = Et) and* ***2c*** *(R = Ph) were prepared using Method 2*

(4*S*, 5*S*)-2- Ethyl- 4-toluenesulfonylmethyl-5-phenyl-1,3-oxazoline (**2b**) was isolated as a colourless, viscous liquid. Yield: 78%, ^1H ($CDCl_3$, 200 MHz), δ: 1.20 (t, 3H, CH$_2$–C*H*$_3$, $J = 10.0$), 2.36 (q, 2H, C*H*$_2$–CH$_3$, $J = 10.0$), 2.43 (s, 3H, Ts–C*H*$_3$), 4.15 (m, 3H, N–C*H*–C*H*$_2$), 5.26 (d, 1H, C*H*–Ph, $J_{HH} = 6.0$), 7.22–7.40 and 7.75–7.80 (m, 9H, phenyl–*H*). $^{13}C\{^1H\}$ ($CDCl_3$, 75 MHz), δ singlets: 9.91 (1C, CH$_2$–*C*H$_3$), 14.92 (1C, *C*H$_2$–CH$_3$), 21.20 (1C, Ts–*C*H$_3$), 70.10 (1C, *C*H$_2$), 72.76 (1C, N–*C*H), 82.41 (1C, O–*C*H), 124.99 (2C, C_{Ar}), 127.56 (2C, C_{Ar}), 128.05 (1C, C_{Ar}), 128.49 (2C, C_{Ar}), 129.58 (2C, C_{Ar}), 132.30 (1C), 139.64 (1C, C_{Ar}), 144.73 (1C, C_{Ar}), 170.30 (1C, *C*=N). MS, *m/z*: 360 ($[M]^+$, 100%), 188 ($[M\text{-}Ts]^+$, 20%), 132 (65%). Anal. found: C 62.9; H 5.9; N 3.8%. Calc. for $C_{19}H_{21}O_{14}NS$: C 63.49; H 5.89; N 3.90%.

(4*S*, 5*S*)-2,5-Diphenyl- 4-toluenesulfonylmethyl-1,3-oxazoline (**2c**) was isolated as a white solid. Yield: 87%, ^1H ($CDCl_3$, 200 MHz), δ: 2.42 (s, 3H, C*H*$_3$), 4.27 (m, 3H, N–C*H*–C*H*$_2$); 5.49 (d, 1H, C*H*–Ph, $J_{HH} = 6.2$), 7.22–7.97 (m, 14H, phenyl–*H*). $^{13}C\{^1H\}$ (CDCl3, 75 MHz), δ singlets: 21.65 (1C, *C*H$_3$), 70.45 (1C, *C*H$_2$), 73.70 (1C, N–C*H*), 83.15 (1C, O–C*H*), 125.53 (2C, C_{Ar}), 127.03 (1C, C_{Ar}), 128.5 (2C, C_{Ar}), 128.59 (2C, C_{Ar}), 128.96 (2C, C_{Ar}), 129.96 (2C, C_{Ar}), 131.97 (2C, C_{Ar}), 132,7 (2C, C_{Ar}), 139.90 (1C, C_{Ar}), 145.08 (2C, C_{Ar}), 165.21 (1C, –*C*=N). m.p. 77–80 °C. MS, *m/z*: 408 ($[M]^+$, 100%), 105 (85%). Anal. found: C 68.1; H 5.2; N 3.5; S 7.7%. Calc. for $C_{23}H_{21}O_4NS$: C 67.79; H 5.19; N 3.44; S 7.87%.

The more complex, uncoupled ^{13}C NMR spectra were also measured for **2a**–**c**, and revealed $^1J_{CH}$ and $^3J_{CH}$ values in the ranges 92–158 and 1–8 Hz, respectively.

(4*S*,5*S*)-2-R-4-Diphenylphosphinomethyl-5-phenyl-1,3-oxazolines (**3**) (see Scheme 1). These were made following literature procedures for incorporation of a PPh_2 moiety [39,51,52]. Typically, a THF solution of **2** (with amounts varying from 0.30–2.0 g) was slowly added to a THF solution of $LiPPh_2$ ($LiPPh_2$/**2** ~ 2) at −5 °C, and the mixture was stirred for 3 h. Some orange polymeric type solid that precipitated was filtered off, and the filtrate concentrated to give an orange oil; this was washed with Et_2O (4 × 5 mL),

and the ether fractions were combined and concentrated to give a colourless oil. The oils (R = Me, Et, Ph) were obtained in yields of 20–50%, and were analyzed by ^{1}H and ^{31}P{^{1}H} NMR.

(4*S*,5*S*)-2-Methyl-4-diphenylphosphinomethyl-5-phenyl-1,3-oxazoline (**3a**). ^{31}P{^{1}H} (C_6D_6, 81 MHz), δ: −25.8 (s). ^{1}H (C_6D_6, 200 MHz), δ: 2.05 (s, 3H, C*H*$_3$), 2.29 (ddd, 1H, C*H*$_2$, J_{HH} = 9.3, 13.55, $^2J_{PH}$ = 2.2), 2.66 (ddd, 1H, C*H*$_2$, J_{HH} = 5.2, 13.45, $^2J_{PH}$ = 1.4), 3.98 (ddd, seen as m, 1H, N–C*H*), 5.30 (d, 1H, Ph–C*H*, J_{HH} = 6.4), 7.2–7.5 (m, 15H, phenyl–*H*).

(4*S*,5*S*)-2-Ethyl-4-diphenylphosphinomethyl-5-phenyl-1,3-oxazoline (**3b**). ^{31}P{^{1}H} (C_6D_6, 81 MHz), δ: −25.07 (*s*). ^{1}H (C_6D_6, 200 MHz), δ: 1.14 (t, 3H, CH$_2$–C*H*$_3$, J_{HH} = 10.0), 2.25 (q & ddd 3H, C*H*$_2$–CH$_3$ & CH–C*H*$_2$, J_{HH} = 10.0), 2.69 (ddd, 1H, C*H*$_2$, J_{HH} = 4.2, 14.1, $^2J_{PH}$ = 2.0), 4.25 (m, 3H, N–C*H*–CH$_2$), 5.32 (d, 1H, C*H*–Ph, J_{HH} = 6.2), 7.22–74 and 7.75–7.6 (m, 15H, phenyl–*H*). ^{13}C{^{1}H} ($CDCl_3$, 75 MHz), δ singlets: 9.53 (1C, *C*H$_3$), 20.66 (1C, CH$_3$–*C*H$_2$), 35.25 (1C, P–*C*H$_2$), 71.61 (1C, N–*C*H), 85.38 (1C, O–*C*H), 125.06 (1C, C_{Ar}), 127.56 (2C, C_{Ar}), 127.65 (2C, C_{Ar}), 127.86 (1C, C_{Ar})], 131.52 (4C, C_{Ar}), 132.18 (4C, C_{Ar}), 136.75 (1C, C_{Ar}), 137.56 (1C, C_{Ar}), 139.89 (1C, C_{Ar}), 167.02 (1C, *C*=N). [Uncoupled ^{13}C NMR spectra were also measured for **3b**, and revealed $^1J_{CH}$, $^3J_{CH}$ and $^1J_{CP}$ values in the ranges 127–150, 4–13, and 15 Hz, respectively]. MS, *m/z*: 390 ([M + O]$^+$, 55%), 374 ([M]$^+$, 65%), 334 (35%), 301 (40%), 285 (45%), 199 (95%), 185 (65%), 131 (100%), 117 (55%).

(4*S*,5*S*)-2-Phenyl-4-diphenylphosphinomethyl-5-phenyl-1,3-oxazoline (**3c**). ^{31}P{^{1}H} (C_6D_6, 81 MHz), δ: −24.83 (s). ^{1}H (C_6D_6, 200 MHz), δ: 2.23 (ddd, 1H, C*H*$_2$, J_{HH} = 8.8, 13.75, $^2J_{PH}$ = 2.4), 2.76 (ddd, 1H, C*H*$_2$, J_{HH} = 5.4, 13.75, $^2J_{PH}$ = 2.0), 4.4 (ddd, seen as m, 1H, N–C*H*), 5.44 (d, 1H, C*H*–Ph, J_{HH} = 6.6), 7.2–7.5 and 8.25 (m, 20H, phenyl–*H*) (see Scheme 2).

2.3. *[Ir(COD)(3)]PF$_6$ (4)*

Typically, ∼100 mg (0.15 mmol) of [Ir(COD)Cl]$_2$ and an equimolar amount of **3** were left to react in CH_2Cl_2 (10 mL) at r.t. for 30 min, when $AgPF_6$ (76 mg, 0.30 mmol) was added to the solution. After 4 h, a dark orange filtrate was decanted from the grey precipitate of AgCl, and was concentrated to ∼2 mL, when ∼10 mL of Et_2O was added to precipitate an oily solid; this was dissolved in warm C_6H_6 (15 mL), and then the solvent was removed under vacuum to leave an orange solid.

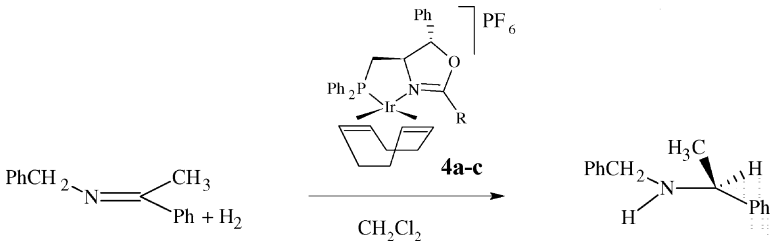
Complex **4a** containing oxazoline **3a**. Yield 75%. ^{31}P{H} NMR ($CDCl_3$, 81 MHz), δ: 30.93 (s), −143.88 (sept, PF_6^-, J_{PF} = 712). ^{1}H NMR ($CDCl_3$, 200 MHz), δ: 2.1 (m, 3H of COD), 2.4 (m, 3H of COD), 2.57 (m, 4H of COD), 2.7 (s, 3H, C*H*$_3$), 2.80 (ddd, sees as td, 1H, C*H*$_2$, J_{HH} = 4.6, 13.5), 3.05 (ddd, seen as td, 1H, C*H*$_2$, J_{HH} = 5.9, 13.2), 3.55 (m, 1H of COD), 4.33 (ddd, seen as m, 1H, N–C*H*, J_{HH} = 1.0, 2.3), 5.35 (m, 1H of COD), 6.03 (d, 1H, Ph–C*H*, J_{HH} = 4.0), 7.20–8.20 (m, 15H, phenyl–*H*). MS, *m/z*: 659 ([M-PF_6]$^+$, 20%), 580 (100%), 552([M-PF_6-COD)]$^+$, 30%). Anal. found: C 48.3, H 4.6, N 1.6%. Calc. for $C_{31}H_{34}NOP_2F_6Ir{\cdot}0.5\ C_6H_6$: C 48.40, H 4.42, N 1.66%.

Complex **4b** containing oxazoline **3b**. Yield, 72%. ^{31}P{^{1}H} NMR ($CDCl_3$, 81 MHz), δ: 28.73 (s), −142.75 (sept, PF_6^-, J_{PF} = 714). ^{1}H ($CDCl_3$, 200 MHz), δ: 1.30 (t, 3H, C*H*$_3$–CH$_2$, J_{HH} = 7.5), 1.70 (m, 3H of COD), 2.19 (m, 3H of COD), 2.40 (m, 1H of COD), 2.6 (q, 2H, CH$_3$–C*H*$_2$, J_{HH} = 7.5), 2.70 (ddd, seen as m, 1H, C*H*$_2$), 3.15 (ddd, 1H, C*H*$_2$, J_{HH} = 8.0, 12.0, $^2J_{PH}$ = 2.0), 3.33 (m, 2H of COD), 4.00 (m, 1H of COD), 4.07 (ddd, seen as m, 1H, N–C*H*), 4.22 (m, 1H of COD), 5.30 (m, 1H of COD), 5.69 (d, 1H, Ph–C*H*, J_{HH} = 10.0), 7.2–7.5 (m, 15H, phenyl–*H*). MS, *m/z*: 672 ([M-PF_6]$^+$, 14%), 594 (100%), 562 ([M-PF_6-COD)]$^+$, 29%). Anal. found: C 46.8, H 4.4, N 1.6%. Calc. for $C_{32}H_{36}NOP_2F_6Ir$: C 46.94, H 4.43, N 1.71%.

Complex **4c** containing oxazoline **3c**. Yield 69%. ^{31}P{^{1}H} NMR ($CDCl_3$, 81 MHz), δ: 21.4 (s), −143.75 (septet, PF_6^-, J_{PF} = 714.0). ^{1}H ($CDCl_3$, 200 MHz), δ: 1.70 (m, 4H of COD), 1.94 (m, 2H of COD), 2.16 (m, 1H of COD), 2.39 (m, 1H of COD), 2.70 (ddd, 1H, C*H*$_2$, J_{HH} = 12.1, 15.0, $^2J_{PH}$ = 8.0), 3.15 (ddd, 1H, C*H*$_2$, J_{HH} = 12.0, 18.0, $^2J_{PH}$ = 4.0), 3.31 (m, 1H of COD), 4.00 (m, 1H of COD), 4.22 (m, 1H of COD), 4.7 (ddd, seen as m, 1H, N–C*H*, J_{HH} = 1.0, 2.3), 5.20 (m, 1H of COD), 6.05 (d, 1H, Ph–C*H*, J_{HH} = 6.0), 7.20–7.50 (m, 18H, phenyl–*H*), 8.25 (m, 2H, phenyl–*H*). MS, *m/z*: 722 ([M-PF_6]$^+$, 4%), 281 (5%), 77 (100%). Anal. found: C 49.8, H 4.0, N 1.4%. Calc. for $C_{36}H_{36}NOP_2F_6Ir$: C 49.88, H 4.19, N 1.62%.

2.4. *X-ray diffraction study*

Crystals of **1c** and **2a**, suitable for X-ray analysis, were grown slowly at r.t. from CH_2Cl_2, and Et_2O solutions, re-



Scheme 2. The asymmetric hydrogenation reaction, and the Ir precursor catalyst complexes **4** ((**a**) R = Me; (**b**) R = Et; (**c**) R = Ph).

Table 1
Crystallographic data for **2a** and **3c**

	2a	**3c**
Formula	$C_{18}H_{19}NO_4S$	$C_{28}H_{24}NOP$
Fw	345.41	421.45
Crystal size (mm^3)	$0.50 \times 0.35 \times 0.20$	$0.42 \times 0.32 \times 0.05$
Colour, habit	Colourless, block	Colourless, plate
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$ (#19)	$P2_12_12_1$
a (Å)	5.5954(2)	5.5095(7)
b (Å)	13.9241(9)	9.399(1)
c (Å)	22.034(6)	44.526(6)
$\alpha = \beta = \gamma$ (°)	90	90
V ($Å^3$)	1716.7(3)	2305.8(5)
Z	4	4
ρ ($g\,cm^{-3}$)	1.336	1.214
Temperature (K)	223(1)	173(2)
Total no. of reflns	8767	11327
No. of unique reflns	2896	4077
R_{int}	0.029	0.0249
R_1, wR_2 (F^2, all data)	0.052; 0.097	0.0374; 0.0839

spectively, of the compounds. Crystals of **3c** formed from the oily product that was left standing for weeks at r.t. under Ar. Structures of all three were determined but, during the course of our studies, that of **1c** was reported by Gzella and Rozwadowska [53]; our data agree very well with those reported, and so the structural determination of **1c** is not detailed here.

X-ray diffraction data for **2a** and **3c** were collected on a Rigaky/ADSC diffractometer fitted with a CCD detector, and a Bruker SMART system, respectively, using graphite monochromated Mo Kα radiation (λ = 0.71069 Å). The crystallographic data and principle parameters of the refinements are given in Table 1.

The **2a** structure was solved by direct methods [54] and expanded using Fourier techniques [55]. The non-H-atoms were refined anisotropically, while the H-atoms were included in fixed positions. All calculations were performed using the teXsan crystallographic software package from the Molecular Structure Corporation [56].

The structure of **3c** was solved and refined using SHELXS-86 and SHELXL-97 programs [57]. The space group was determined based on systematic absences and intensity statistics [57]. A direct-methods solution was calculated, and this provided most non-H-atoms from the E-map. Full-matrix least squares/difference Fourier cycles were performed, and these located the remaining non-H-atoms. All non-H-atoms were refined with anisotropic displacement parameters, and each H-atom was placed in an ideal position and refined as a riding atom with an isotropic displacement parameter.

Complete crystallographic material for **2a** and **3c** has been deposited with the Cambridge Crystallographic Data Centre; copies of the data (CCDC: 237168 (**2a**), and 237169 (**3c**)) can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: 44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

2.5. Hydrogenation of N-(1-phenylethylidene)-benzylamine, $PhCH_2N{=}C(Me)Ph$

A glass sleeve (20 mL capacity) with a magnetic stirring bar was charged under Ar usually with CH_2Cl_2 (7 mL) containing 66 mg (0.31 mmol) of the imine and 0.1–6.0 mol% of type-**4** catalyst. The sleeve was then placed in a Parr steel autoclave (35 mL) that was charged with H_2 (3–55 bar), and then the mixture was stirred at temperatures between 22 and 80 °C for selected times. After the H_2 pressure was released, the yellow product mixture was analyzed by GC to determine the conversion of imine to $PhCH_2N(H)CH(Me)Ph$ (HP-17 capillary column, 25 m × 0.25 mm (0.26 μm film), 160 °C for 2 min, 20 °C/min^{-1}, 220 °C, He head pressure 15 psi); the retention times for the amine and imine were 5.48 and 7.19 min, respectively. Hydrogenations at 1 atm H_2 were conducted in Schlenk glass-ware.

The e.e. values of the amine were determined by chiral GC analysis of the corresponding trifluoroacetamide derivatives using a reported procedure [58] (Chiraldex β-DM, 10 m × 0.25 mm, 80 °C for 5 min, 0.3 °C/min^{-1}, 95 °C; He head pressure 46 psi); the retention times were 58.03 and 60.13 min, respectively, for the (*S*)- and (*R*)-forms of $PhCH_2N(C(O)CF_3)CH(Me)Ph$. Enantioselectivities of the amines were occasionally determined also from ^1H NMR spectra (in $CDCl_3$) of the diastereomeric salts formed with (*R*)(−)-mandelic acid, $PhC(H)(OH)(CO_2H)$, using the integration ratios of the CH quartet and the combined CH and CH_2 signals. Typically, a mixture of the (+)- and (−)-amines (∼7 mg, 0.033 mmol), isolated from the reaction mixture by vacuum distillation, was dissolved in ∼0.6 mL of $CDCl_3$ and the ^1H NMR spectrum measured after (*R*)(−)-mandelic acid was added in ∼2 mg increments, until the integration of the mandelic acid CH signal (δ 4.88) exceeded that of the CH quartet (δ 3.88) of the *R,S*-amine salt. The NMR e.e. values were usually within 10% of those determined by GC, but were more variable.

3. Results and discussion

*3.1. Type-**3** oxazolines*

As depicted in Scheme 1, the indicated stereoisomer of a hydroxymethyl-oxazoline (**1**) is readily formed in good yield (85–93%) by a known procedure [46,49], from (1*S*,2*S*)-2-amino-1-phenyl-1,3-propanediol and an ortho-ester in refluxing 1,2-dichloroethane in the presence of an organic acid catalyst. The oxazolines **1a–c** have been prepared also via reaction of the propanediol with the corresponding imino ether hydrochloride [32,46,50]. The $–CH_2(OH)$ was then converted to the tosylate (**2a**–**c**) by reaction with NaH or LDA, and then TsCl in a Et_2O or THF [46]. The Et_2O washing procedure proved optimum for purification of the tosylates, as use of column chromatography or recrystallization led to their decomposition. The tosylates were well characterized by elemental

analysis, ^{1}H and ^{13}C{^{1}H} NMR, and MS, while the structure of **2a** was also determined crystallographically (see below). Nucleophilic substitution of tosyl group by $LiPPh_2$ at −5 °C in THF generated the *N*,*P*-oxazolines (**3a**–**c**), with chiral centres at both C-4 and C-5; these oxazolines were well characterized spectroscopically, but the elemental analyses of the oily materials obtained were not satisfactory (typically 1–2% low in C); fortunately, a crystal of **3c** eventually formed and its structure was confirmed crystallographically (see below).

The ^{1}H NMR data for **2a**–**c** and **3a**–**c** are as expected, and signals for the R substituent, the tosyl-Me, the single proton at C-5 (a doublet because of coupling to the C-4 proton), the single proton at C-4 (coupled to the C-5 proton and the diastereotopic CH_2 protons) and the CH_2 protons themselves, are readily assigned; in **2a**–**c**, the N=CH–CH_2 protons appear as a combined multiplet, but in **3a**–**c**, these CH and CH_2 proton signals are distinguished. $^{2}J_{PH}$ values for **3a**–**c** are in the range 1.4–8.0 Hz, consistent with literature data [59], while the δ_P singlet is found at ∼−25.

The oxazolines **3a**–**c** were first made by our group in 1999 [60], prior to the related chiral C-4/C-5 phosphite, *N*,*P*-systems reported by Pfalz's group in 2002 (see Fig. 1 [13,15]). Also related to **3a**–**c** is the *N*,*P*-type from Burgess's group (see Fig. 1) that has just one chiral group at C-4 [19–21,61]. Our synthetic route, involving just 3 steps from commercially available materials (fewer steps than reported for the *N*,*P*-types mentioned above), appears attractive, and readily adaptable to changing the substituent at C-5, and incorporating other heteroatoms such as N, S, and O, in place of P.

3.2. *X-ray structures of **1c**, **2a** and **3c***

The structure of **1c**, the hydroxymethyl oxazoline, as determined by ourselves and Gzella and Rozwadowska [53], reveals the *S*-configuration at both C-4 and −5, as in the reactant propanediol; **2a** and **3c** also maintain the same configuration at these C-atoms (Figs. 2 and 3, respectively), and all 3 structures crystallize in the same orthorhombic space group $P2_12_12_1$. The presence of different substituents at C-4 (CH_2X, where X = OH, OTs, or PPh_2) or C-2 (Ph, Me, or Et) has no significant effect on the bond distances or angles (Table 2) within the oxazoline ring, which is essentially planar in all 3 structures. However, in **1c**, the H-atom of the OH group is involved in intermolecular H-bonding to the N-atom, leading to chains of molecules and a C6-C5-C4-C13 torsion angle (atom numbering as for **2a**, Fig. 2) of −113°, and a so-called anticlinal conformation of the C13 atom of the CH_2OH group with respect to the C6 atom of the Ph ring [53]. This torsion angle increases with increasing size of the C-4 substituent to −128.8° in **2a**, −131.2° in **3c**, and is the range of −100 to −140° found for other 4-hydroxymethyl (or methoxy)-5-phenyl derivatives of oxazolines [62–65]. As a result of the intermolecular H-bonding in **1c**, the hydroxyl O14 atom is synclinal with respect to the N3–C4 bond of the oxazoline ring (N3-C4-C13-O14 = 68.1°), and anticlinal conformation with respect to the C–C bond of the oxazoline ring (torsion angle = −46.5°). Within **2a** and **3c**, the Ts and PPh_2 groups are in anticlinal conformation with the N–C bond of the oxazoline (torsion angles = −176.1° and −179.42°, re-

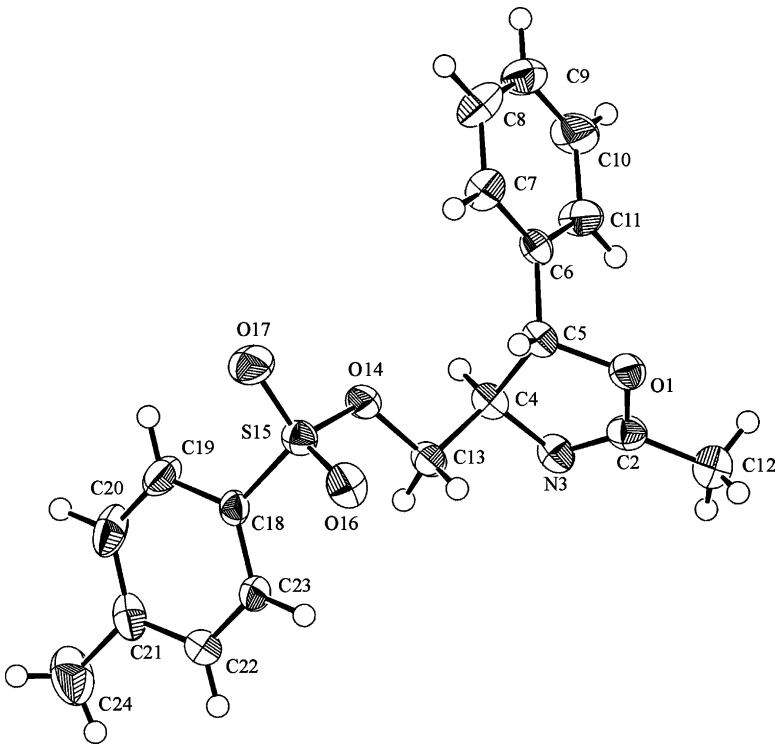


Fig. 2. ORTEP diagram for (4*S*,5*S*)-2-methyl-4-toluenesulfonylmethyl-5-phenyl-1,3-oxazoline (**2a**), with 50% probability ellipsoids.

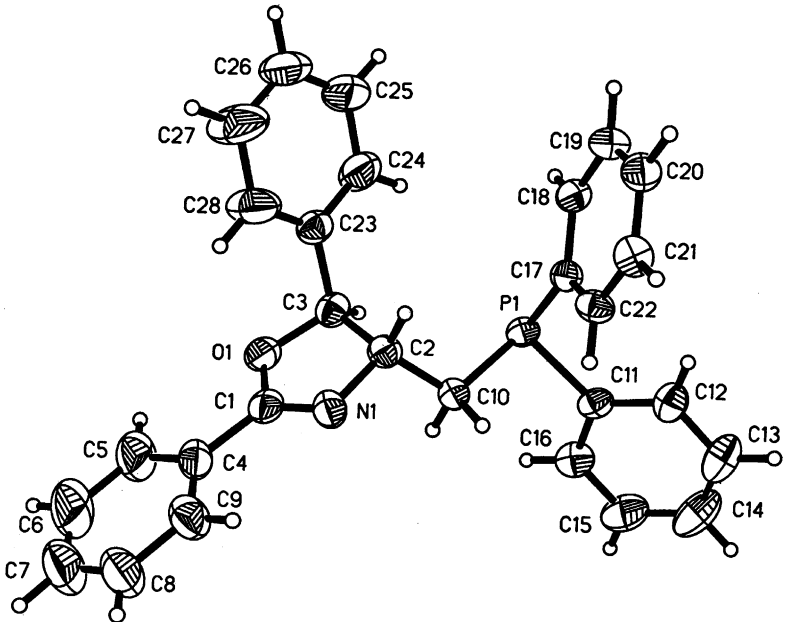


Fig. 3. ORTEP diagram for (4*S*,5*S*)-2,5-diphenyl-4-diphenylphosphinomethyl-1,3-oxazoline (**3c**), with 50% probability ellipsoids.

spectively), and in synclinal conformation with the oxazoline C–C bond (torsion angles = 66.6° and 64.5°, respectively).

3.3. Ir(I) complexes with the N,P-oxazolines

The orange [Ir(COD)(**3**)]PF_6 complexes (**4a**–**c**, Scheme 2) were made by a standard procedure [41] from the $[Ir(COD)Cl]_2$ precursor by reaction with the oxazoline (**3a**–**c**), followed by treatment with $AgPF_6$. NMR and MS data, and elemental analysis are consistent with the formulation, with *N*,*P*-bonding of the oxazoline in a square-planar complex. The complexes exhibit δ_P singlets between 21–30 (45–55 ppm downfield-shifted from those of the free oxazolines), while small downfield coordination shifts (up to 1 ppm) are seen in the ^1H NMR spectra for the CH_2, C-4 and C-5 protons of the oxazoline ring. The CH_2 and CH=CH proton signals of the COD ligand generally appear in the δ 1.7–2.5, and 3.3–5.3 regions, respectively. The NMR data are consistent with data for analogous [Ir(COD)(*N*,*P*-oxazoline)]PF_6 complexes [40,41]. The MS data show a peak for the parent molecular cation.

3.4. Catalytic hydrogenation of N-(1-phenylethylidene)-benzylamine

The catalytic hydrogenation of the imine *N*-(1-phenylethylidene)benzylamine to *N*-(1-phenylethyl)benzylamine was used to screen the activity of the precursor Ir complexes

Table 2
Selected bond distances (Å) and angles (°) for **1c**, **2a** and **3c**

1c[a]		**2a**		**3c**[b]	
C2—O1	1.371(4)	C2—O1	1.363(3)	C1—O1	1.367(3)
N3—C2	1.259(4)	N3—C2	1.265(3)	N1—C1	1.272(3)
N3—C4	1.485(4)	N3—C4	1.467(2)	N1—C2	1.475(3)
C4—C5	1.546(5)	C4—C5	1.546(2)	C2—C3	1.559(3)
C5—O1	1.469(4)	C5—O1	1.458(2)	C3—O1	1.453(2)
C4—C13	1.510(5)	C4—C13	1.514(2)	C2—C10	1.524(3)
O14—C13	1.402(5)	O14—C13	1.457(3)	P1—C10	1.860(2)
				P1—C17	1.832(2)
				P1—C11	1.846(2)
O1—C2—N3	118.0(3)	O1—C2—N3	118.5(2)	O1—C1—N1	118.5(2)
N3—C4—C5	104.0(3)	N3—C4—C5	105.4(1)	N1—C2—C3	104.1(2)
N3—C4—C13	110.3(3)	N3—C4—C13	109.2(2)	N1—C2—C10	109.4(2)
C10—C2—C3—C11	−113.1(4)	C6—C5—C4—C13	−128.8(2)	C10—C2—C3—C23	−131.2(2)
N3—C4—C13—O14	68.1(4)	N3—C4—C13—O14	−176.1(1)	N1—C2—C10—P1	−179.42(13)
C5—C4—C13—O14	−47.5(4)	C5—C4—C13—O14	66.6(2)	C3—C2—C10—P1	64.5(2)

[a] The values, taken from our structural determination, are in excellent agreement with those given in ref. 53; the atom-labelling is that used for **2a**.
[b] The atom-labelling for **3c** (Fig. 3) is different to that used for **1c** and **2a** (Fig. 2).

Table 3
Imine hydrogenation catalyzed by type-**4** precursor complexes[a]

Entry	Catalyst/mol.%	H_2 (atm)	T (°C)	Time (h)	Conversion of imine (%)	Formation of amine (%)[b]	e.e. (*S*) (%)
1	No catalyst	55	80	72	64	0[c]	0
2	**4a**/0.1	48	80	108	83	26[c]	10
3	**4a**/1.0	55	80	45	99	50[c]	19
4	**4a**/4.0	55	80	5	100	96	33
5	**4b**/0.1	55	80	72	89	41[c]	35
6	**4b**/1.0	55	80	16	100	87[c]	55
7	**4b**/4.0	55	80	5	100	95	58
8	**4b**/4.0	55	80	3	100	97	63
9	**4b**/6.0	3	22	2	100	100	60
10	**4b**/4.0	3	22	24	100	95	63
11	**4b**/4.0	3	22	2.5	100	86	51
12	**4b**/3.0	3	22	92	50	18	14
13	**4b**/2.0	3	22	92	30	25	14
14	**4b**/4.0	1	22	22	66	61	59
15	**4b**/4.0[d]	3	22	3	92	92	∼1.5
16	**4b**/4.0[e]	3	22	23	78	84	∼1
17	**4c**/0.1	48	80	185	85	41[c]	3
18	**4c**/0.1	1	40	72	28	∼1[c]	[f]
19	**4c**/0.1	1	22	64	3	3[c]	[f]
20	**4c**/1.0	55	80	15	60	11[c]	2.5
21	**4c**/4.0	55	80	5	100	93	7

[a] In CH_2Cl_2, unless stated otherwise.
[b] Percentage of the amine hydrogenation product in the total products.
[c] White polymeric and imine hydrolysis products seen (see text).
[d] In MeOH solution.
[e] In THF solution.
[f] Values of e.e. not determined because of low conversion to amine.

4a–c. The results are compiled in Table 3. In the absence of catalyst (entry 1), imine is converted to "by-products" comprising acetophenone and benzylamine (hydrolysis products of the imine), and an unidentified white product that is insoluble in halogenated and aromatic solvents. The water required for the hydrolysis likely comes from removal of O_2 from the H_2 using the "Deoxo" catalyst, where the O_2 is converted to H_2O. The white product could derive from imine polymerization of the imine [66]. At low (0.1–1.0 mol.%) catalyst (entries 2,3,5,6,17–20), there is also significant formation of by-products but, with **4b** as precursor (entry 6), high conversion of imine to give the *S*-amine in 55% e.e. can be realized. The imine conversion and enantioselectivity increase significantly at 4 mol.% catalyst with 55 atm H_2 (entries 4,7,8): at essentially complete conversion of the imine over a few hours at 55 atm H_2 and 80 °C, a modest 33% e.e. is attained with **4a** (entry 4), and a good 63% e.e. is reached with **4b** (entry 8), while **4c** gives only 7% e.e (entry 21). The catalyst precursor **4b** at 4 mol.% is clearly the most effective, and could be used under mild conditions (r.t. and 1–3 atm H_2) to give high conversions to amine, again with up to 63% e.e. (entries 10,11,14). High conversions of the imine to amine were catalyzed by **4b** in MeOH and in THF under mild conditions, but with practically no enantioselectivity (entries 15,16).

N-(1-Phenylethylidene)benzylamine was also used as the imine substrate by Pfaltz's group [41] for evaluation of catalytic activity of analogous Ir complexes of the *N*,*P*-oxazolines shown in the first entry of Fig. 1, with various R groups at C-4; a maximum 76% e.e. was attained using 4% mol catalyst (with R = ^{i}Pr) in CH_2Cl_2 at r.t., but at 100 atm H_2. It is evident that steric factors at positions adjacent to the coordinated *N*-atom (i.e. at the 2- or 4-position) play a key role in determining the enantioselectivity, but a more detailed understanding must await future spectroscopic, kinetic and mechanistic studies, and detection of intermediate Ir-hydride and -imine intermediates.

4. Conclusions

Chiral (4*S*,5*S*)-2-R-4-diphenylphosphinomethyl-5-phenyl-1,3-oxazolines (R = Me, Et, Ph) can be prepared in good yield from commercially available reagents in three steps. The oxazolines readily form [Ir(COD)(*N*,*P*-oxazoline)]PF_6 complexes that are active precursors for asymmetric hydrogenation of *N*-(1-phenylethylidene)benzylamine; essentially complete hydrogenation to the amine product with a maximum 63% e.e. was attained using the R = Et oxazoline system at r.t. under 3 atm H_2.

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