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Synthesis, characterization and the crystal structures of novel achiral and chiral α -ferrocenyl α -aminophosphine oxides

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Abstract

Novel achiral α -ferrocenyl α -aminophosphine oxides (2a–2e) have been prepared by the reaction of ferrocenylaldimines (1a–1e) with Ph₂PLi at room temperature in 63–92% yield. Similarly, starting from L-phenylalaninol derived ferrocenylaldimine (3), the corresponding (*S*,*S*)-phosphine oxide (4) and its (*R*,*S*)-diastereomer (5) were isolated by fractional crystallization in 41% and 16% yield, respectively. All the achiral and chiral α -aminophosphine oxides were air-stable and easily accessible. They were fully characterized by elemental analysis, ¹H NMR, ³¹P NMR and IR spectra. In addition, structures of 2e and 4 have been determined by X-ray single-crystal analysis. © 2006 Elsevier B.V. All rights reserved.

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Ligands which contain multiple mixed donors, such as hard and soft donors (often called hybrid ligands) find increasing use in chemistry due to the new properties and reactivities introduced in the hybrid ligand-metal interactions. Aminophosphine oxides are a class of hybrid ligand possessing two potential donor atoms - the amino group nitrogen and the oxygen from the phosphine oxide group. Studies on this type of ligand are relatively small. Dodoff et al. reported that certain Pt(II) and Pd(II) complexes with aminophosphine oxides were important biologically active compounds [1]. Starting from α -aminoacids, some α -aminophosphine oxides were also synthesized as potential HIV-Protease Inhibitors [2]. Recently, Balakrishna et al. found that reactions of Ph₂PN(H)Ph with paraformaldehyde or aromatic aldehydes led to the insertion of 'RCH' into the P(III)–N bond to give α -aminophosphine oxides $Ph_2P(O)CH(R)N(H)Ph$ (R=H, Ar) and they studied the coordination properties of Ph₂P(O)CH₂N(H)Ph with

Zn, Cd, Hg and U [3–5]. In addition, aminophosphine oxides are found to be useful ligands in some catalytic reactions. For example, in the hydroformylation of olefins, some aminophosphine oxides were reported to be remarkably more active than their corresponding aminophosphines in combination with rhodium [6-8]. The mixed donor aminophosphine oxide ligands also gave good results in the ruthenium-catalyzed asymmetric transfer hydrogenation reactions (up to 93% ee) [9,10]. We are interested in the design and synthesis of new hybrid ligands and their applications. In this aspect, the ferrocenecontaining ligands are especially attractive because of the specific and unique geometries as well as electronic properties that the ferrocene provides [11–16]. In this communication, we present the synthesis, characterization and the crystal structures of novel achiral and chiral α -ferrocenyl α -aminophosphine oxides obtained from the reaction of ferrocenvlaldimines with Ph₂PLi.

The ferrocenylaldimines (1a-1e) were readily prepared by condensation of formylferrocene with arylamines according to the published procedure [17]. Reaction of ferrocenylaldimines (1) with Ph₂PLi was carried out in THF at room temperature for 10 h. After hydrolysis and

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purification, the products 2 were obtained in 63-92% yield. It was found that the isolated products 2 were α -aminophosphine oxides instead of the corresponding α -aminophosphines. The results showed that an oxidation process took place during the work up (Scheme 1). These new achiral α -ferrocenyl α -aminophosphine oxides were characterized by elemental analysis, ¹H NMR, ³¹P NMR and IR spectra [18]. The IR spectra show the $v_{\rm NH}$ of 2e at 3321 cm^{-1} and that of the others in the range of $3399-3443 \text{ cm}^{-1}$. The strong absorption around 1175-1188 cm⁻¹ is assigned to $v_{P=0}$. In addition, absorptions at approximately 1000 and 1100 cm^{-1} indicate the existence of an unsubstituted Cp ring [19]. The ³¹P NMR spectra of 2a and 2c show single resonances at 29.7 and 29.8 ppm, respectively. The ¹H NMR spectra of 2 show an irregular triplet at 4.92–5.02 ppm for the CH protons. For 2a and 2c the signals of NH appear at 4.26 and 4.40 ppm, respectively as an irregular doublet, while for 2b, 2d and 2e the corresponding signals shift to upfield and overlap with the signals of the substituted Cp ring. The molecular structure of 2e has been determined by single-crystal X-ray analysis [20]. Fig. 1 shows that compound 2e exists as a dimer in the crystal due to intermolecular N-H...O=P hydrogen bonds between H (from NH) of one molecule and O (from P=O) of an adjacent molecule $(d_{(N...O)} = 3.171(3) \text{ Å}, \quad d_{(H...O)} = 2.39(3) \text{ Å}, \quad N-H...O$ bond angle is 168(3)°). In **2e**, the P–O bond distance is 1.486(2) Å and the P-C bond distances are in the range of 1.796(3)-1.849(3) Å. The data are comparable to those found in the literature [3,5]. The geometry around the nitrogen is nearly planar and the sum of the angles is 355°.

Based on the above results, we used an optically active ferrocenylaldimine (3) obtained from the reaction of formylferrocene with L-phenylalaninol. We hope to be able to induce chirality at the C atom of imino group and get a single diastereomer or two diastereomers that can be easily separated. As expected, the reaction of 3 with Ph_2PLi pro-





Fig. 1. Dimer of 2e showing intermolecular N-H...O=P H-bonding. Selected bond lengths (Å) and bond angles (°): P(1)-O(1) 1.486(2), P(1)-C(11) 1.849(3), P(1)-C(20) 1.796(3), P(1)-C(26) 1.812(3), N(1)-C(11) = 1.459(3). N(1)-C(12)1.391(4), N(1)—H(1E) 0.79(3); O(1) - P(1) - C(11)111.54(13), O(1) - P(1) - C(20)113.24(13), O(1) - P(1) - C(26)C(20) - P(1) - C(26)111.93(14), 105.13(14), C(20) - P(1) - C(11)108.17(14), C(26) - P(1) - C(11)106.38(14), N(1)-C(11)-P(1)106.0(2).C(12)-N(1)-C(11)123.9(2). C(12)-N(1)-H(1E) 115(2), C(11)-N(1)-H(1E) 116(2).

ceeded smoothly and the corresponding phosphine oxides were obtained as a mixture of diastereomers after preparative TLC on silica gel plates eluting with CH_2Cl_2 :acetone (10:1) (Scheme 2). The two diastereomers were separated successfully by fractional crystallization from dichloromethane-petroleum ether at r.t., giving 4 in 41% yield and its diastereomer 5 in 16% yield [18].

The (*S*,*S*) configuration of the chiral carbon atoms in **4** is confirmed by X-ray structural analysis [20]. Fig. 2 shows that in the lattice of **4** there also exist intermolecular hydrogen bonds. However, this time the hydrogen bonds between H (from OH not NH) in one molecule and O (from P=O) in an adjacent molecule ($d_{(O...O)} = 2.708(3)$ Å, $d_{(H...O)} = 1.80(4)$ Å, O–H...O bond angle is $168(4)^\circ$) form a one dimensional chain structure of **4**. In **4**, the P–O bond distance is 1.493(2) Å and the P–C bond distances are in the range of 1.807(3)–1.862(3) Å, which resemble the values found in **2e**. Unlike **2e**, the geometry around the nitrogen is trigonal pyramidal with an angle sum of 335° .





Fig. 2. 1D chain structure of **4** showing intermolecular O-H...O=P H-bonding. Selected bond lengths (Å) and bond angles (°): P(1)-O(1) 1.493(2), P(1)-C(11) 1.862(3), P(1)-C(12) 1.817(3), P(1)-C(18) 1.807(3), N(1)-C(11) 1.475(3), N(1)-C(24) 1.475(4), N(1)-H(1E) 0.84(3); O(1)-P(1)-C(11) 110.24(13), O(1)-P(1)-C(12) 110.58(14), O(1)-P(1)-C(18) 110.78(14), C(12)-P(1)-C(11) 109.05(14), C(18)-P(1)-C(11) 107.31(12), C(18)-P(1)-C(12) 108.80(15), N(1)-C(11)-P(1) 104.96(18), C(24)-N(1)-C(11) 115.6(2), C(24)-N(1)-H(1E) 109.2(19), C(11)-N(1)-H(1E) 110(2).

In conclusion, the new achiral α -ferrocenyl α -aminophosphine oxides were prepared in good to excellent yields in one simple synthetic step from the reaction of ferrocenylaldimines with Ph₂PLi. Furthermore, starting from L-phenylalaninol derived ferrocenylaldimine, the corresponding (*S*,*S*)-phosphine oxide and its (*R*,*S*)-diastereomer were obtained by a similar procedure. Since amino alcohols are inexpensive and easily available, structural variations will be convenient to introduce. Applications of these novel ferrocene-containing α -aminophosphine oxides in catalysis and asymmetric synthesis are currently under investigation in our laboratory. The results will be reported in due course.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche. 2006.02.027.

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- [18] Synthesis of compound 2e: Small lithium sticks (0.023 g, 3.3 mmol) were added quickly to a stirred solution of triphenylphosphine (0.395 g, 1.5 mmol) in 10 mL THF at room temperature under nitrogen and stirred for 5 h. Then the reaction mixture was transferred to a Schlenk flask by syringe and *tert*-butyl chloride (0.16 mL, 1.5 mmol) was added at 0 °C. After stirring at room temperature for 1 h to get rid of PhLi, 1e (0.25 g, 0.75 mmol) was added and stirred for 10 h. The reaction mixture was quenched with water and extracted with dichloromethane. The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure.

The residue was purified by preparative TLC on silica gel plates using CH₂Cl₂-acetone (10:1) as eluent, to produce 0.253 g (63%) of 2e as vellow solids. m.p. 199-200 °C. IR (KBr Pellet): 3321, 1609, 1514, 1436, 1220, 1182, 1116, 1002, 831, 727, 696, 496 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): *b* 7.75 (m, 4H, Ph-H), 7.46 (m, 2H, Ph-H), 7.37 (m, 4H, Ph-H), 6.76 (d, J = 8.8 Hz, 2H, Ar-H), 6.65 (d, J = 8.8 Hz, 2H, Ar-H), 4.92 (m, 1H, CH), 4.10 (s, 1H, C₅H₄), 4.07 (s, 1H, C₅H₄), 4.02 $(s, 1H, C_5H_4), 3.94 (m, 4H, C_5H_4 + NH + CH_2), 3.86 (s, 5H, C_5H_5),$ 1.36 (t, J = 7.0 Hz, 3H, CH₃). Anal. Calc. for C₃₁H₃₀FeNO₂P: C, 69.54; H, 5.65; N, 2.62. Found: C, 69.12; H, 5.62; N, 2.61%. Compounds 2a-2d were prepared by a similar procedure. 2a: 92%, Anal. Calc. for C₂₉H₂₆FeNOP: C, 70.89; H, 5.33; N, 2.85. Found: C, 70.46; H, 5.32; N, 2.89%. 2b: 68%, Anal. Calc. for C₃₀H₂₈FeNOP: C, 71.30; H, 5.58; N, 2.77. Found: C, 71.15; H, 5.66; N, 2.71%. 2c: 78%, Anal. Calc. for C₂₉H₂₅ClFeNOP: C, 66.25; H, 4.79; N, 2.66. Found: C. 66.11; H, 4.78; N, 2.61%. 2d: 65%, Anal. Calc. for C₃₀H₂₈FeNO₂P: C, 69.11; H, 5.41; N, 2.69. Found: C, 69.08; H, 5.45; N, 2.57%. The chiral compound 4 and 5 were prepared by a similar procedure. 4: 41%, $[\alpha]_{D}^{20} = -106 (c = 0.095, CH_2Cl_2).$ m.p. 165 °C. IR (KBr Pellet): 3341, 3250, 3057, 1596, 1562, 1436 1114, 1003, 839, 741, 698, 492 cm⁻¹. ¹H NMR (400 MHz, DMSO): δ 7.74 (m, 4H, Ph-H), 7.56 (m, 2H, Ph-H), 7.47 (m, 4H, Ph-H), 7.20 (m, 3H, Ph-H), 7.14 (d, J = 7.0 Hz, 2H, Ph-H), 4.74 (d, J = 9.4 Hz, 1H, CH), 4.11 (s, 5H, C₅H₅), 3.98 (s, 1H, C₅H₄), 3.92 (s, 1H, C₅H₄), 3.88 (s, 1H, C₅H₄), 3.41 (s, 1H, C₅H₄), 3.29 $(dd, J = 10.6, 3.8 Hz, 1H, CH_2OH), 3.20 (dd, J = 10.6, 4.6 Hz, 1H,$ CH₂OH), 3.12 (m, 1H, NHCH), 2.80 (dd, J = 12.8, 6.8 Hz, 1H, CH_2Ph), 2.70 (dd, J = 12.8, 6.6 Hz, 1H, CH_2Ph). ³¹P{¹H}NMR (162 MHz, DMSO): δ 29.5. Anal. Calc. for C₃₂H₃₂FeNO₂P: C, 69.95; H, 5.87; N, 2.55. Found: C, 69.48; H, 5.83; N, 2.56%. 5: 16%, Anal. Calc. for C₃₂H₃₂FeNO₂P: C, 69.95; H, 5.87; N, 2.55. Found: C, 69.56; H, 5.84; N, 2.54%.

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- [20] Crystals of 2e and 4 were obtained by recrystallization from dichloromethane- petroleum ether at r.t.. A single crystal of 2e or 4 suitable for X-ray analysis was mounted on a glass fiber. All measurements were made on a Rigaku-IV imaging plate area detector with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The data were corrected for Lorentz and polarization factors. The structures were solved by direct methods [21] and expanded using Fourier techniques and refined by full-matrix least-squares methods. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included but not refined. All calculations were performed using the teXsan [22] crystallographic software package of Molecular Structure corporation. Crystal data for 2e: M = 535.38, Orthorhombic, space group Pbca, a = 12.346(3) Å, b = 20.343(4) Å, c = 21.411(4) Å, $\alpha = 90^{\circ}$, $\beta = 90^{\circ}$, $\gamma = 90^{\circ}$, V = 5377.9(19) Å³, Z = 8, $\mu = 0.649 \text{ mm}^{-1}, D_c = 1.322 \text{ Mg/m}^3, F(000) = 2240, \theta 2.15-25.00^\circ,$ 14,094 reflections collected, 4346 reflections unique ($R_{(int)} = 0.0398$), The final *R* indices $[I \ge 2\sigma(I)]$: $R_1 = 0.0493$, $wR_2 = 0.1054$, *R* indices (all data): $R_1 = 0.0823$, $wR_2 = 0.1154$. CCDC No. 287661. Crystal data for 4: M = 549.41, Orthorhombic, space group P2(1)2(1)2(1), a = 8.8686(18) Å, b = 12.526(3) Å, c = 24.481(4) Å, $\alpha = 90^{\circ}$, $\beta = 90^{\circ}$, $\gamma = 90^{\circ}$, $V = 2719.6(9) \text{ Å}^3$, Z = 4, $\mu = 0.643 \text{ mm}^{-1}$, $D_c = 1.342 \text{ Mg/}$ m^3 , F(000) = 1152, θ 1.66–25.50°, 9079 reflections collected, 4952 reflections unique ($R_{(int)} = 0.0329$), The final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0381$, $wR_2 = 0.0918$, R indices (all data): $R_1 = 0.0434$, $wR_2 = 0.0936$. CCDC No. 287660. Copies of the data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033, e-mail:deposit@ccdc.cam.ac.uk or on the web www: http://www.ccdc.cam.ac.uk).
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