SHORT PAPER

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An interesting dihedral angle expansion in a series of monophosphoramides of (*R*)-(+)-1,1′-binaphthyl-2-2′-diamine†

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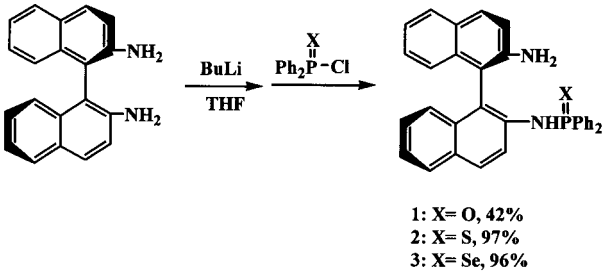
The dihedral angle of the two naphthyl rings in the chiral ligands monodiphenylphosphoramide **1**, monodiphenylthiophosphoramide **2** and monodiphenylselenophosphoramide **3** of (*R*)-(+)-1,1′-binaphthyl-2-2′-diamine increased by 10° for each step along the series: O, S, Se as demonstrated by X-ray crystal analysis

Keywords: chiral diphenylphosphoramide, chiral diphenylthiophosphoramide, chiral diphenylselenophosphoramide, (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine

In the course of exploring new chiral ligands, we found that the chiral monodiphenylphosphoramide **1**, monodiphenylthiophosphoramide **2** and monodiphenylselenophosphoramide **3** of (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine are efficient ligands in the asymmetric addition reaction of diethylzinc to aldehydes in the presence of titanium(IV) isopropoxide to give the corresponding *sec*-alcohols in high ee (Scheme 1).[1] In fact, Noyori has concluded that the dihedral angle of two naphthyl rings in his famous chiral ligands such as BINAP or BINOL play a very important role in chiral inductions.[2] Thus we tried to determine the structures of these chiral ligands by X-ray analysis and to determine the dihedral angle of two naphthyl rings in ligands **1**, **2**, and **3** (Figs. 1, 2 and 3). Their bond lengths were elucidated in Tables 1–3, respectively. We surprisingly found a very interesting phenomenon in these chiral ligands. As shown in Fig. 4, the dihedral angle of two naphthyl rings expanded in 10° for each step along the series of O, S, Se (Fig. 4). The Van der Waals radius of heteroatoms (0:1.52 Å, S:1 80 Å, Se 1 90 Å) on the phosphorus is obviously the key factor for this expansion. We believe that the repulsion between the nitrogen atom and the heteroatom on phosphorus caused this interesting dihedral angle expansion of two naphthyl rings. Concerning the chiral induction abilities of these chiral ligands in the asymmetric addition reaction of diethylzinc to arylaldehydes, we re-examined the previously reported ee in the asymmetric addition reaction of diethylzinc to aldehydes in the presence of titanium(IV) isopropoxide by these chiral ligands under the same reaction conditions.[1] We found that, in our chiral ligand series **1–3**, when



Scheme 1

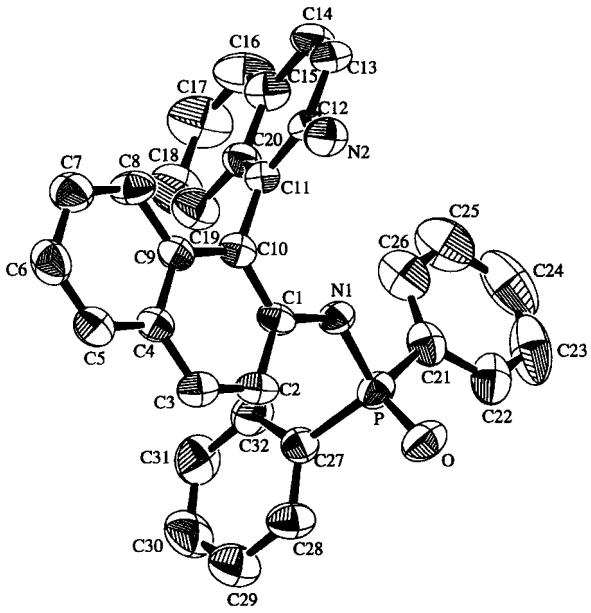


Fig. 1 The crystal structure of **1**.

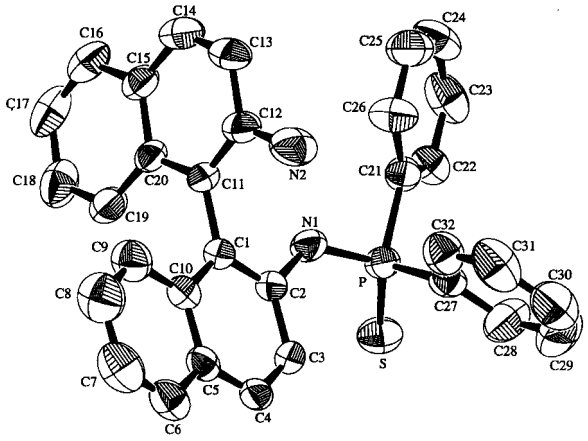


Fig. 2 The crystal structure of **2**.

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† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

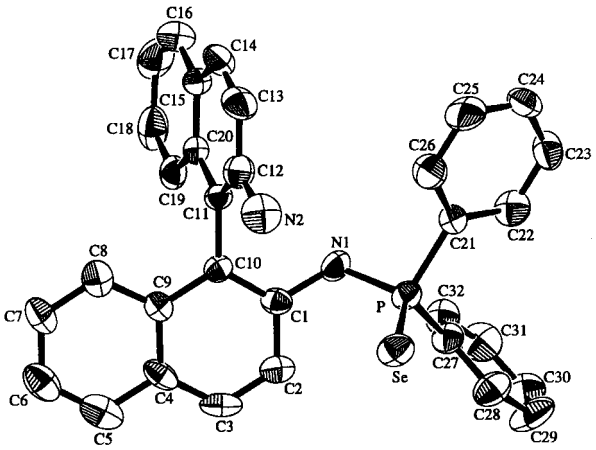


Fig. 3 The crystal structure of **3**.

Table 1 The bond lengths of **1**

Atom	Atom	Distance/Å	Atom	Atom	Distance/Å
C(1)	C(33)	1.70(1)	Cl(2)	C (33)	1.68(1)
P	O	1.475(5)	P	N(1)	1.659(6)
P	C(21)	1.785(8)	P	C(27)	1.819(8)
N(1)	C(1)	1.416(9)	N(2)	C(12)	1.372(9)
C(1)	C(2)	1.423(10)	C(1)	C(10)	1.401(10)
C(2)	C(3)	1.355(10)	C(3)	C(4)	1.393(10)
C(4)	C(5)	1.401(10)	C(4)	C(9)	1.429(10)
C(S)	C(6)	1.37(1)	C(6)	C(7)	1.41(1)
C(7)	C(8)	1.35(1)	C(8)	C(9)	1.412(10)
C(9)	C(10)	1.416(10)	C(10)	C(11)	1.487(10)
C(11)	C(12)	1.395(9)	C(11)	C(20)	1.433(9)
C (12)	C(13)	1.424(10)	C(13)	C(14)	1.35(1)
C(14)	C(15)	1.43(1)	C(15)	C(16)	1.43(1)
C(15)	C(20)	1.42(1)	C(16)	C(17)	1.34(1)
C(17)	C(18)	1.38(1)	C(18)	C(19)	1.36(1)
C(19)	C(20)	1.397(10)	C(21)	C(22)	1.39(1)
C(21)	C(26)	1.39(1)	C(22)	C(23)	1.34(1)
C(23)	C(24)	1.36(2)	C(24)	C(25)	1.41(2)
C(25)	C(26)	1.37(1)	C(27)	C(28)	1.38(1)
C(27)	C(32)	1.406(10)	C(28)	C(29)	1.40(1)
C(29)	C(30)	1.38(1)	C(30)	C(31)	1.35(1)
C(31)	C(32)	1.37(1)			

Table 2 The bond lengths of **2**

Atom	Atom	Distance/Å	Atom	Atom	Distance/Å
S	P	1.948(2)	P	N (1)	1.662(4)
P	C(21)	1.825(4)	P	C(27)	1.817(5)
N(1)	C(2)	1.412(5)	N(2)	C(12)	1.393(6)
C(1)	C(2)	1.369(6)	C(1)	C(10)	1.431(6)
C(1)	C(11)	1.506(6)	C(2)	C(3)	1.424(5)
C(3)	C(4)	1.371(6)	C(4)	C(5)	1.403(6)
C(5)	C(6)	1.421(6)	C(5)	C(10)	1.422(6)
C(6)	C(7)	1.344(7)	C(7)	C(8)	1.398(8)
C(8)	C(9)	1.360(7)	C(9)	C(10)	1.411(6)
C(I1)	C(12)	1.375(7)	C(11)	C(20)	1.436(6)
C(12)	C(13)	1.418(7)	C(13)	C(14)	1.345(8)
C(14)	C(15)	1.406(8)	C(15)	C(16)	1.421(7)
C(15)	C(20)	1.424(6)	C(16)	C(17)	1.348(8)
C(17)	C(18)	1.396(8)	C(18)	C(19)	1.369(8)
C(19)	C(20)	1.408(6)	C(21)	C(22)	1.375(6)
C(21)	C(26)	1.389(6)	C(22)	C(23)	1.390(7)
C(23)	C(24)	1.367(9)	C(24)	C(25)	1.360(8)
C(25)	C(26)	1.382(7)	C(27)	C(28)	1.385(7)
C(27)	C(32)	1.370(7)	C(28)	C(29)	1.375(9)
C(29)	C(30)	1.356(9)	C(30)	C(31)	1.375(10)
C(31)	C(32)	1.374(8)			

Table 3 The bond lengths of **3**

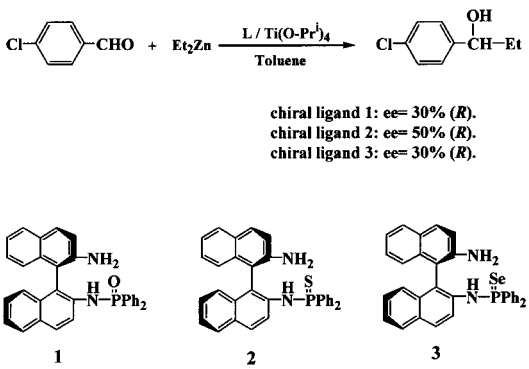
Atom	Atom	Distance/Å	Atom	Atom	Distance/Å
Se	P	2.096(3)	Cl(1)	C(33)	1.46(3)
C(2)	C(33)	1.63(3)	P	N(1)	1.701(9)
P	C(21)	1.811(9)	P	C(27)	1.805(10)
N(1)	C(1)	1.40(1)	N(2)	C(12)	1.38(1)
C(1)	C(2)	1.42(1)	C(1)	C(10)	1.39(1)
C(2)	C(3)	1.36(1)	C(3)	C(4)	1.41(1)
C(4)	C(5)	1.41(1)	C(4)	C(9)	1.41(1)
C(5)	C(6)	1.38(2)	C(6)	C(7)	1.38(2)
C(7)	C(8)	1.36(1)	C(8)	C(9)	1.40(1)
C(9)	C(10)	1.43(1)	C(10)	C(11)	1.47(1)
C(11)	C(12)	1.41(2)	C(11)	C(20)	1:45(1)
C(12)	C(13)	1.40(1)	C(13)	C(14)	1.35(2)
C(14)	C(15)	1.42(2)	C(15)	C(16)	1.40(2)
C(15)	C(20)	1.42(1)	C(16)	C(17)	1.34(2)
C(17)	C(18)	1.44(2)	C(18)	C(19)	1.39(1)
C(19)	C(20)	1.39(1)	C(21)	C(22)	1.39(1)
C(21)	C(26)	1.39(1)	C(22)	C(23)	1.39(2)
C(23)	C(24)	1.38(1)	C(24)	C(25)	1.37(2)
C(25)	C(26)	1.39(2)	C(27)	C(28)	1.40(1)
C(27)	C(32)	1.38(1)	C(28)	C(29)	1.36(2)
C(29)	C(30)	1.39(2)	C(30)	C(31)	1.36(2)
C(31)	C(32)	1.37(1)	C(33)	C(33)	1.52(3)

the dihedral angle was about 90°, the highest ee (50%) could be achieved and when the dihedral angle was < 90° or > 90°, the achieved ee's were lower (Scheme 2). We believe these findings will assist future ligand design and the mechanistic interpretation of similar reactions.

Fig. 4 The dihedral angle of the two naphthyl rings.

Experimental

The chiral ligands **1**, **2**, and **3** were prepared according to the literature.[1] X-ray crystallography was carried out as below. A suitable crystal with $0.32 \times 0.25 \times 0.18$ mm^3 dimensions was mounted on the top of a glass capillary. Data were collected on a Rigak u AFC7R diffractometer with graphite-monochromated MO-K_α radiation $\lambda = 0.71069$ Å using the ω-2θ technique at 20 °C. A total of 4554 unique reflection was collected. The data were collected for Lorentz polarization effects. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotrophically by full-matrix least squares. All hydrogen



Scheme 2

atoms were included in calculated position. All calculations were performed using the TEXSAN crystallographic software package. Final R and R_w values were 0.054 and 0.056 for 1659 observed reflection for **1**, 0.043 and 0.045 for 2045 observed reflection for **2** and 0.050 and 0.052 for 1783 observed reflection for **3**. Their crystal structures have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: CCDC 156634 for **1**, CCDC 156635 for **2** and CCDC 156636 for **3**.

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3 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1985 and 1992.