Dinaphtho[2,1-*b*; 1′,2′-*d*]phospholes: a New Class of Atropisomeric Phosphorus Ligands†

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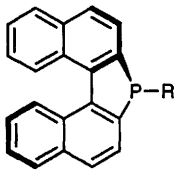
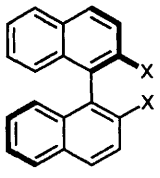
The parent and some alkyl and aryl substituted dinaphtho[2,1-*b*; 1′,2′-*d*]phospholes **1** have been synthesized and shown to be atropisomerically stable below room temperature.

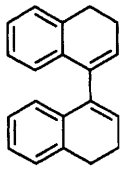
Chiral phosphorus compounds are of interest because they are effective ligands in transition metal catalysed asymmetric reactions.[1] Of particular relevance are those compounds possessing C_2 or higher symmetries and whose chirality originates from the geometry of the whole molecule, rather than from the presence of stereogenic carbon centres.[2,3] BINAP **2a** is the most popular phosphorus derivative of this kind and is the ligand of choice in several enantioselective catalytic reactions.[4] The related cyclic derivatives, *i.e.* the phospholes **1**, are still unknown despite the fact that phospholes[5] have been shown to possess complimentary qualities with respect to open phosphines.[6] Here we report on the synthesis of the parent compound and of a representative set of *P*-alkyl and aryl-substituted dinaphtho[2,1-*b*; 1′,2′-*d*]phospholes **1**.



1a; R = H
b; R = Ph
c; R = Me
d; R = Et
e; R = CH_2Ph
f; R = $CH_2CH(Me)Et$
g; R = neomenthyl



2a; X = PPh_2
b; X = Br
c; X = Li



3

Originally compound **1b** was prepared *via* the McCormack reaction[7] from bis-dialine **3** and dichlorophenylphosphine. The reaction, performed at 220 °C with neat reagents in the air, afforded directly the aromatic product **1b** in 20–25% yield. Much better results were obtained from the reaction at room temperature of dichlorophenylphosphine with 2,2′-dilithiobinaphthyl **2c**, prepared from racemic 2,2′-dibromobinaphthyl **2b** and butyllithium in tetrahydrofuran at −60 °C. Compound **1b**, purified by flash chromatography (hexane–methylene dichloride, 9 : 1), was isolated in 80–84% yield. According to the same procedure, *P*-alkyl-substituted phospholes **1c** and **1d**‡ could be readily obtained in high yield by reaction with the appropriate phosphorated reagent.

Treatment of **1b** with lithium promotes the cleavage of the phenyl carbon–phosphorus bond affording the corresponding phospholyl anion. This is smoothly converted into the *P*-alkyl substituted phospholes **1c–g** by reaction at room temperature with the corresponding alkyl halide. This procedure is complimentary to the direct preparation described above and can be used whenever the alkylphosphine dichloride is not available or difficultly accessible.

Protonation of phospholyl anion affords the unsubstituted parent phosphole **1a**, isolated as a crystalline powder after flash chromatography (45% yield). Unlike simple 1*H*-phospholes, which dimerize rapidly at room temperature,[8] this

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‡ *Selected data for*: **1b**; m.p. 157–158 °C; ^{1}H NMR ($CDCl_3$) δ 7.18–7.35 (series of m, Ar, 5H), 7.45–7.60 (series of m, Ar, 4H), 7.75–7.90 (series of m, Ar, 4H), 7.96 (dd, *J* 1.5, 7.8 Hz, Ar, 2H), 8.47 (d, *J* 8.1 Hz, Ar, 2H); ^{31}P NMR ($CDCl_3$) δ −4.69 (s); *m/z* 360.3 (M^+, 100%), 328.2 (20), 281.1 (80) and 140.8 (18). **1c** (80% yield); m.p. 102–105 °C; ^{1}H NMR ($CDCl_3$) δ 1.61 (d, $^2J_{HP}$ 1.5 Hz, CH_3), 7.52–7.63 (series of m, Ar, 4H), 7.91–8.02 (series of m, Ar, 4H), 8.03 (dd, *J* 1.2, 7.8 Hz, 2H) and 8.53 (d, *J* 9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) (aliphatic C only) δ 12 (d, $^1J_{CP}$ 15.3 Hz, CH_3); *m/z* 298.3 (M^+, 85%), 281.3 (95), 252.3 (10) and 140.8 (70%). **1d** (82% yield); m.p. 122–124 °C; ^{1}H NMR ($CDCl_3$) δ 0.90 (dd, $^3J_{HH}$ 7.5, $^3J_{PH}$ 12.9 Hz, CH_3), 2.05 (dd, $^3J_{HH}$ 7.5, $^2J_{PH}$ 3.0 Hz, CH_2), 7.49–7.62 (series of m, Ar, 4H), 7.88–8.03 (series of m, Ar, 4H), 8.02 (dd, *J* 1.2, 8.1 Hz, 2H) and 8.52 (d, *J* 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) (aliphatic only) δ 9.45 (d, $^2J_{CP}$ 5 Hz, CH_3), 21.19 (d, $^1J_{CP}$ 19.63 Hz, CH_2); *m/z* 312.4 (M^+, 50%), 281.3 (96), 252.4 (10) and 140.8 (15%).

compound is substantially stable even in solution. Its ^{1}H NMR spectrum is characterized by the doublet P–H resonance at δ 5.55 ($^1J_{P-H}$ 195 Hz).

Phospholes **1** are atropisomerically chiral molecules which may experience two different fluxional processes: pyramidal inversion at phosphorus or flipping of the naphthyl rings. The first is a chirality-invariant high energy process, for which an energy barrier of about 130 kJ mol^{-1} can be expected,[9] while the second results in net inversion of configuration.

Optically active phospholes **1f** and **1g**§ were prepared from menthyl chloride and 2-methylbutyl iodide, respectively. Both these products showed, in ^{31}P NMR at low temperature, two separate resonances which coalesced at *ca.* 10 °C into a single unresolved peak. As the optical activity of **1f** and **1g** was unchanged even after prolonged heating in solution, the conclusion is that in these substrates interconversion of the atropisomeric naphthyl array is a fast process at room temperature, with an approximate $\Delta G^{\ddagger}$ value of 50–60 kJ mol^{-1} estimated from NMR spectra. A similar behaviour is envisaged for the other phospholes and this should be the basic reason why our attempts to achieve antipode separation were frustrated.

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§ *Selected data for*: **1f** (45% yield); m.p. 142–148 °C; $[\alpha]_D^{25}$ −112.2 (*c* 0.3, $CDCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.89 (t, $^3J_{HH}$ 9.0 Hz, CH_3), 1.13 (d, $^3J_{HH}$ 5.4 Hz, CH_3), 1.20–1.90 (series of m, 5H), 7.48 (dd, *J* 1.5, 6.6 Hz, Ar, 2H), 7.55 (dd, *J* 1.5, 8.1 Hz, Ar, 2H), 7.83–8.02 (series of m, Ar, 4H), 8.00 (d, *J* 7.8 Hz, 2H) and 8.45 (d, *J* 8.7 Hz, 2H); ^{31}P NMR ($CDCl_3$) δ −11.20 (bs). **1g** (60% yield); m.p. 117–120 °C; ^{1}H NMR ($CDCl_3$) δ 0.37 (d, $^3J_{HH}$ 6.6 Hz, CH_3), 1.10 (d, $^3J_{HH}$ 6.9 Hz, CH_3), 1.15 (d, $^3J_{HH}$ 6.9 Hz, CH_3), 0.4–1.9 (series of m, 7H), 2.22 (m, 1H), 3.10 (m, CH P), 7.47 (dd, *J* 1.5, 6.9 Hz, Ar, 2H), 7.54 (dd, *J* 1.2, 8.1 Hz, Ar, 2H), 7.75–8.95 (series of m, Ar, 4H), 7.99 (d, *J* 8.5 Hz, 2H) and 8.46 (dd, *J* 3.0, 8.7 Hz, 2H); ^{31}P NMR ($CDCl_3$) δ −0.87 (bs); *m/z* 422.3 (M^+, 25%), 284.3 (100), 252.3 (40) and 140.8 (7).

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