JOM 23137

Atropisomerism in (±)-7-methyl- and -phenyl-substituted dinaphtho[2,1-*b*;1′,2′-*d*]phospholes and dinaphth[2,1-*b*;1′,2′-*d*]arsoles

Andrew A. Watson, Anthony C. Willis and S. Bruce Wild

Research School of Chemistry, Australian National University, Canberra, A.C.T. 2601 (Australia)

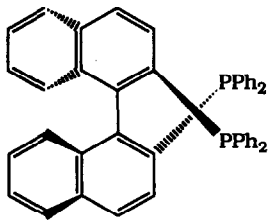
(Received July 23, 1992)

Abstract

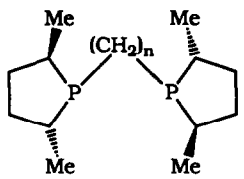
The reaction of 2,2′-dilithio-1,1′-binaphthyl with $RECl_2$ (E = P or As; R = Me or Ph) affords the corresponding (±)-7-substituted dinaphtho[2,1-*b*;1′,2′-*d*]phospholes and dinaphth[2,1-*b*:1′,2′-*d*]arsoles. The molecules are fluxional on the NMR time scale with similar barriers between the conformational isomers (atropisomers) for the four compounds, *viz.* $\Delta G^{\ddagger} = 56 \pm 1$ (243 K, ER = PMe), 56 ± 1 (254 K, ER = PPh), 65 ± 1 (287 K, ER = AsMe), 59 ± 1 (259 K, ER = AsPh) kJ mol^{-1}. An X-ray diffraction study of (*S*)-7-phenyldinaphth[2,1-*b*;1′,2′-*d*]arsole which crystallized out by spontaneous resolution reveals appreciable bending of the distorted naphthyl residues away from each other. The asymmetric unidentates (±)-L coordinate to iron(II) in complexes of the type $[(\eta^5\text{-}C_5H_5)[1,2\text{-}C_6H_4(PMePh)_2]FeL]PF_6$ with a small degree of enantioselection of one atropisomer of (±)-L. The complexes of the arsines are stable on the NMR time scale in CD_2Cl_2 at 20°C, but the corresponding phosphine complexes require cooling for observation of diastereomerism. The 7-methyl substituted arsole is demethylated by bromine giving the corresponding 7-bromo compound, which, in turn, is converted by additional bromine into configurationally stable (±)-[2-(2′-bromo-1,1′-binaphthyl)]dibromoarsine.

1. Introduction

Dissymmetric ligands of C_2 symmetry appear to be superior to asymmetric or C_1 ligands for enantioselective synthesis [1]. For example, homochiral C_2-bis(tertiary phosphines) [2] and arsines [3] have been employed with remarkable success as co-catalysts in a variety of organic reactions. Notable amongst the molecules of this type is the electron-poor ligand BINAP **1**, which contains an axially dissymmetric 1,1′-binaphthyl C_2-linkage between the phosphorus atoms [4]. A recent development in this field has been the synthesis of the optically active electron-rich C_2-bidentates **2** from the corresponding homochiral C_2 phosphide ions and the appropriate alkyl halide [5]. In our view, however, there is a niche in synthesis for a chiral equivalent of electron-poor triphenylphosphine, which is the standard co-catalyst for a number of industrially important organic syntheses, including the OXO process [6], and of Wittig reagents [7]. Accordingly, we have synthesised the electron-poor C_1-unidentates (±)-**3** (R = Me or Ph) and (±)-**4** (R = Me or Ph) [8*] and investigated their suitability for optical resolution. In related work, the nitrogen analogue of **3** or **4** (R = Ph) has been prepared by the oxidative dimerization of *N*-phenyl-2-naphthylamine by neutral potassium permanganate [9] and there is a recent report of the synthesis of analogous sulfur, selenium, and tellurium compounds [10].



(*R*) - **1**



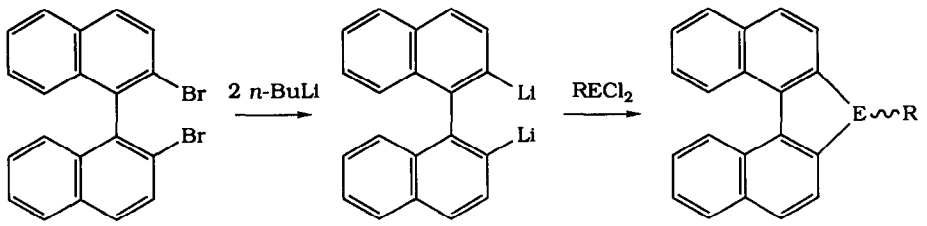
(*R*) - **2** (n = 2 or 3)

2. Results and discussion

The compounds (±)-**3** (R = Me or Ph) and (±)-**4** (R = Me or Ph) were prepared as shown in Scheme 1. The arsine (±)-**4** (R = Ph) crystallized from hot

Correspondence to: Dr. S. B. Wild.

0022-328X/93/$6.00

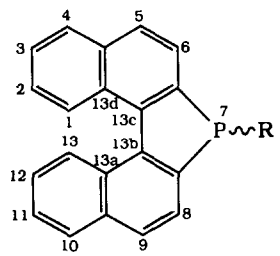


(±)-**3** (E = P; R = Me or Ph)

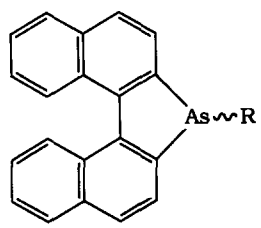
(±)-**4** (E = As; R = Me or Ph)

Scheme 1.

methanol as pale yellow plates, m.p. 139–140°C, which were suitable for X-ray crystallography.



(±)-**3** (R = Me or Ph)



(±)-**4** (R = Me or Ph)

2.1. Crystal structure of (S)-7-phenyldinaphth[2,1-b;1',2'-d]arsole

Compound (±)-**4** (R = Ph) crystallizes in the enantiomorphous monoclinic space group $P2_1$. Crystal data for the compound are given in Table 1. Table 2 gives the positional parameters or for non-hydrogen atoms and Table 3 lists selected bond distances and angles in the molecule. All protons were located in a difference map and included in the refinement with isotropic thermal displacement factors. Refinement of a model as the opposite absolute structure led to a significantly higher R factor (0.025).

The geometry of the molecule is illustrated in Fig. 2. The compound crystallizes as a conglomerate from hot methanol [11]; the crystal chosen for the crystallographic analysis contained molecules of S absolute configuration [12]. The 5-membered ring of the molecule is almost planar [maximum deviation from mean plane of 0.12 Å at (C(10)] with overall dimensions similar to those of corresponding ring in 9-arsafluorene [13]. The arsenic stereocentre in the ring is pyramidal with the naphthyl rings splayed away from each other and showing significant deviation from planarity. The maximum deviations from the mean plane of the rings are 0.09 Å at C(10), −0.04 Å at C(14), −0.07 Å at C(20), and 0.05 Å at C(24). Moreover, within each naphthyl group the fused aromatic rings are bent about the C(14)–C(19) and C(24)–C(29) bonds with angles between the mean planes of the fused rings of 9.9° and 11.5°, respectively. As a consequence of these distortions, there is a dihedral angle of 20.4° between mean planes of the inner pair of rings and one of 39.3° between the mean planes of the outer rings. The contact distance between H(18) and H(28) is 2.31 Å. It is noteworthy that the distortions observed in the structure of (±)-**4** (R = Ph) are similar to those calcu-

TABLE 1. Crystal parameters and experimental data for (±)-4 (R = Ph)

Formula	$C_{26}H_{17}As$
F.W.	404.34
Lattice type	Monoclinic
Space group	$P2_1$
Crystal dimensions (mm)	0.20×0.32×0.06
Cell dimensions	
a (Å)	10.845(1)
b (Å)	8.070(1)
c (Å)	10.916(1)
β (°)	93.91(1)
V (Å^3)	953.1(2)
Z	2
$\rho_{calc.}$ (g cm^{-3})	1.409
Data collection instrument	Philips PW 1100/20
Radiation (graphite monochromator)	Cu Kα
μ (Cu Kα) (cm^{-1})	24.36
λ (Cu Kα) (Å)	1.54056
Temperature (°C)	20(1)
Scan method	θ–2θ
Scan range (2θ) (°)	4–128
No. unique data	1719
No. data used ($I > 3\sigma(I)$)	1644
No. parameters refined	312
R [a]	0.023
R_w [b]	0.035
S [c]	1.56
Largest shift/e.s.d. final cycle	0.01
Largest peak (e Å^{-3})	0.23

[a] $R = \Sigma \| F_o | - | F_c \| / | F_o |$. [b] $R_w = [\Sigma w(| F_o | - | F_c |)^2 / \Sigma w | F_o |^2]^{1/2}$. [c] $S = [\Sigma w(| F_o | - | F_c |)^2 / (N_{observns} - N_{params})]^{1/2}$.

* Reference with asterisk indicates a note in the list of references.

TABLE 2. Atomic coordinates and equivalent isotropic displacement parameters for (±)-4 (R = Ph)

Atom	x	y	z	U_{eq} (Å^2) [a]
As	0.84137(3)	0.50000	0.18348(3)	0.0444(1)
C(10)	0.7716(3)	0.4824(6)	0.4231(3)	0.035(1)
C(11)	0.8677(3)	0.5415(4)	0.3583(3)	0.040(1)
C(12)	0.9780(3)	0.6013(6)	0.4174(4)	0.047(1)
C(13)	0.9936(4)	0.5997(6)	0.5414(4)	0.049(1)
C(14)	0.9059(3)	0.5207(6)	0.6122(3)	0.042(1)
C(15)	0.9287(4)	0.495(1)	0.7409(3)	0.055(1)
C(16)	0.8513(5)	0.4036(8)	0.8055(4)	0.061(2)
C(17)	0.7473(4)	0.3283(6)	0.7467(4)	0.053(1)
C(18)	0.7206(4)	0.3519(5)	0.6231(4)	0.042(1)
C(19)	0.7951(3)	0.4535(4)	0.5536(3)	0.036(1)
C(20)	0.6571(3)	0.4443(5)	0.3448(3)	0.036(1)
C(21)	0.6757(4)	0.4344(5)	0.2201(3)	0.040(1)
C(22)	0.5820(4)	0.3871(6)	0.1325(4)	0.049(1)
C(23)	0.4683(4)	0.3461(6)	0.1689(4)	0.052(1)
C(24)	0.4395(3)	0.3712(5)	0.2934(4)	0.045(1)
C(25)	0.3184(4)	0.3441(6)	0.3296(5)	0.054(1)
C(26)	0.2860(4)	0.3906(6)	0.4428(5)	0.057(2)
C(27)	0.3734(4)	0.4704(6)	0.5243(4)	0.054(2)
C(28)	0.4929(3)	0.4905(8)	0.4946(4)	0.043(1)
C(29)	0.5320(3)	0.4324(5)	0.3812(3)	0.038(1)
C(31)	0.8019(4)	0.7236(6)	0.1221(3)	0.045(1)
C(32)	0.7187(5)	0.8228(7)	0.1758(4)	0.060(2)
C(33)	0.6980(6)	0.984(1)	0.1344(4)	0.070(2)
C(34)	0.7614(5)	1.0427(6)	0.0378(4)	0.058(2)
C(35)	0.8438(4)	0.9428(7)	−0.0175(4)	0.055(1)
C(36)	0.8639(4)	0.7839(6)	0.0253(3)	0.046(1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter where U_{eq} is one-third of the trace of the orthogonalised U tensor.

lated for the transition state geometry of 1,1'-binaphthyls during racemisation [14]. The compound 3,4-benzophenanthrene ([4]-helicene) spontaneously resolves by slow cooling of a solution in ethanol [15]. A striking feature of the structure of this compound is the non-planarity of the "benzene" rings, which are folded in symmetry-related pairs to relieve overcrowding.

TABLE 3. Selected bond distances and bond angles for (±)-4 (R = Ph)

Bond	Distance (Å)	Bond	Angle (°)
As–C(11)	1.939(4)	C(11)–As–C(21)	85.4(2)
As–C(21)	1.941(4)	C(11)–As–C(31)	101.0(2)
As–C(31)	1.962(4)	C(21)–As–C(31)	97.9(2)
C(11)–C(10)	1.384(5)	As–C(11)–C(10)	112.2(2)
C(10)–C(20)	1.491(5)	As–C(21)–C(20)	112.6(3)
C(20)–C(21)	1.391(5)	C(11)–C(10)–C(20)	113.8(3)
		C(21)–C(20)–C(10)	113.7(3)

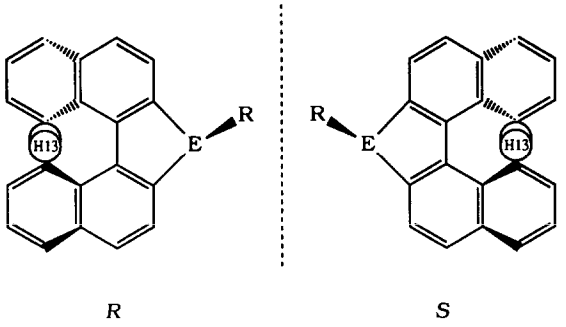


Fig. 1. Enantiomorphic atropisomers of (±)-3 (R = Me or Ph) and (±)-4 (R = Me or Ph).

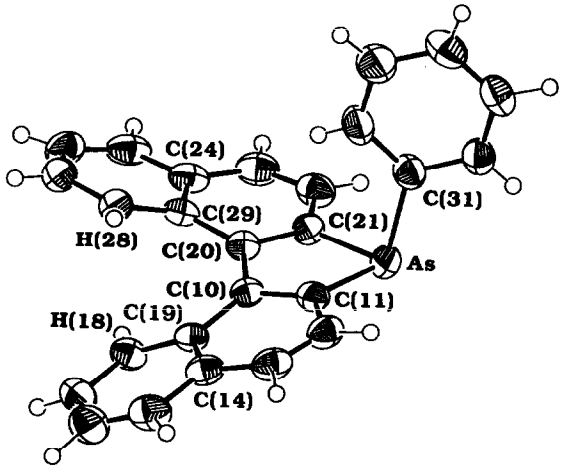


Fig. 2. Molecular structure of (*S*)-4 (R = Ph) showing the atom-numbering scheme adopted for crystallographic purposes. Thermal ellipsoids enclose 50% probability levels.

2.2. *Atropisomerism in (±)-3 (R = Me or Ph) and (±)-4 (R = Me or Ph)*

The atropisomers of (±)-3 and (±)-4 are enantiomorphic and devoid of symmetry. Interconversion of the atropisomers is rendered difficult by the necessity of forcing the diastereotropic proton H_1 and H_{13} past

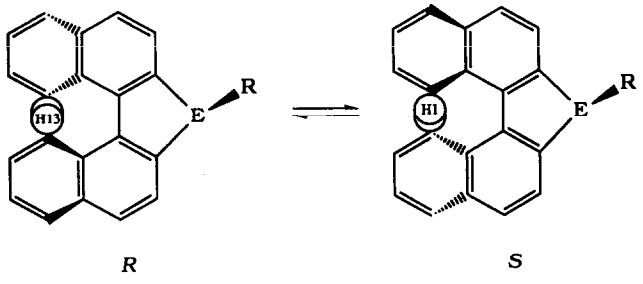


Fig. 3. Interconversion of *R* and *S* atropisomers of (±)-3 (E = P; R = Me or Ph) and (±)-4 (E = As; R = Me or Ph).

TABLE 4. ^{1}H NMR data and free energies of activation ($\Delta G^{\ddagger}$) obtained by the coalescence method for the exchange of H_1 and H_{13} in (±)-3 (R = Me or Ph) and (±)-4 (R = Me or Ph)

Compound	$\Delta\delta$ (Hz)	k_c (s^{-1})	T_c (K)	$\Delta G_c^{\ddagger}$ (kJ mol^{-1})
(±)-3 (R = Me)	2.4	5.3	243	56±1
(±)-3 (R = Ph)	8.3	18.3	254	56±1
(±)-4 (R = Me)	4.2	9.3	287	65±1
(±)-4 (R = Ph)	2.9	6.3	259	59±1

one another in the transition state (Fig. 3). (Inversion of a trivalent phosphorus or arsenic pyramid is a relatively high energy process, *viz.* $\Delta G^{\ddagger}$ 120–140 kJ mol^{-1} for tertiary phosphines and $\Delta G^{\ddagger} > 160$ kJ mol^{-1} for tertiary arsines [16].) In order to isolate an isomer, a half-life of *ca.* 1000 s at 300 K (say) is required; this corresponds to $\Delta G^{\ddagger} > 95$ kJ mol^{-1} at 300 K between isomers [17]. Approximate $\Delta G^{\ddagger}$ values for atropisomerism in (±)-3 and (±)-4 are given in Table 4. The variable temperature ^{1}H NMR data for H_1 and H_{13} of (±)-3 (R = Me) are given in Fig. 4. The activation energies were calculated from the variable temperature ^{1}H NMR data by the coalescence temperature method with use of the expression $\Delta G_c^{\ddagger} = 19.14T_c\ (10.32 + \log T_c/k_c)$ J mol^{-1}, where $k_c = 2.22\ \Delta\nu\ s^{-1}$ is the rate of site exchange calculated from the chemical shift difference in Hz ($\Delta\nu$) for the diastereotopic protons H_1 and H_{13} at the slow exchange limit and T_c is the coalescence temperature [17,18]. From the data presented in Table 4, it is evident that the barrier to atropisomerism in (±)-3 and (±)-4 is rather similar for the various derivatives with the arsine (±)-4 (R = Me) being the most stable of the group. Nevertheless, it is clear from the data that none of the compounds is suitable for resolution under ambient conditions.

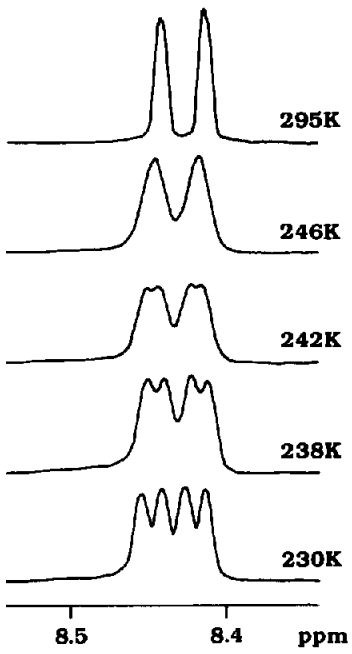
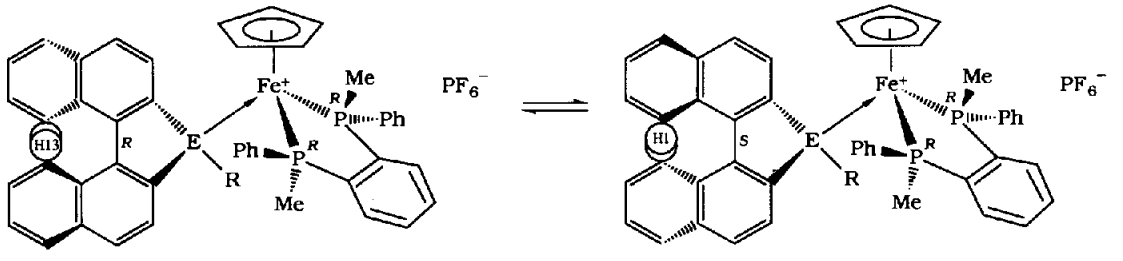


Fig. 4. Variable temperature ^{1}H NMR data for H_1 and H_{13} of (±)-3 (R = Me) in dichloromethane-d_2.

2.3. Attempted diastereoselective synthesis of a resolved 7-substituted dinaphtho[2,1-b;1',2'-d]-phosphole or -arsole complex

The complex [*R*-(*R**,*R**)]-(+)-[(η^5-C_5H_5){1,2-C_6H_4(PMePh)$_2$}Fe(CH_3CN)]PF_6 [19*], [*R*-(*R**,*R**)]-**5**, is a readily prepared chiral auxiliary that can be obtained in homochiral form with use of the appropriate enantiomer of the bis(tertiary phosphine) [20]. Upon being treated with (±)-**3** (R = Me or Ph) or (±)-**4** (R = Me or Ph), the iron complex was expected to give, by displacement of the acetonitrile [18], the pairs of iron(II) derivatives [*R*-(*R**/*S**),(*R**,*R**)]-**6** (E = P or As; R = Me or Ph), epimeric at the introduced chiral phosphorus or arsenic stereocentres. Interconversion between the homochiral forms of the (*R**),(*R**,*R**) and (*S**),(*R**,*R**) diastereomers of the complexes, themselves atropisomers, will again require the forcing of protons H_1 and H_{13} past one another in the respective transition states (Fig. 5). Because of the rapid atropisomerism of the free ligands under the reaction conditions employed, it was anticipated that a stereoselectivity of coordination of the atropisomers would be ob-

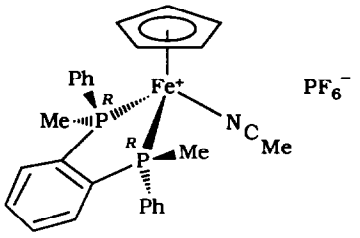


[*R*-(*R**),(*R**,*R**)] - **6** [*R*-(*S**),(*R**,*R**)] - **6**

Fig. 5. Interconversion of diastereomers [(*R**),(*R**,*R**)]-**6** and [(*S**), (*R**, *R**)]-**6**.

served if the 1,1'-binaphthyl rings were conformationally stable in the complexes, reflecting the preference of the auxiliary for a particular enantiomer of the ligand. The reaction of (±)-**3** (R = Me) with [*R*-(*R**, *R**)]-**5** in boiling methanol yielded [*R*-[(*R**/*S**), (*R**, *R**)]]-**6** (E = P, R = Me), which was isolated and recrystallized from a dichloromethane/tetrahydrofuran/diethyl ether mixture. Both the ^1H and ^{31}P NMR spectra of the complex in dichloromethane-d_2 contained broad peaks for the respective nuclei. At 257 K, however, both spectra were resolved; the ^1H NMR spectrum contained two η-C_5H_5 resonances in the ratio 1:1.3; the ^{31}P NMR spectrum consisted of a pair of overlapping ABX systems in similar proportions. Thus, it appears that the diastereomers of the complex, *viz.* atropisomers [*R*-[(*R**),(*R**,*R**)]]- and [*R*-[(*S**),(*R**, *R**)]]-**6** (E = P; R = Me), are conformationally labile in solution above *ca.* 257 K. The complex **6** (E = P; R = Ph) behaved similarly, displaying a singlet for the cyclopentadienyl protons in the ^1H NMR spectrum at 293 K that resolved into two sharp resonances in the ratio 1:2 at 246 K and three broad resonances for the phosphorus nuclei at 293 K that resolved into overlapping 1:2 ABX systems at a similar temperature.

The corresponding iron complexes of the arsines (±)-**4** (R = Me or Ph) were isolated as crystalline solids by a similar procedure. The AsMe complex crystallized from dichloromethane/diethyl ether/tetrahydrofuran mixture as a 0.5-tetrahydrofuran solvate. Both complexes contained configurationally stable phosphorus or arsenic stereocentres on the NMR time scale at 295 K, although it was not found possible to separate the diastereomers of either complex by fractional crystallization. The ratio of diastereomers in each case was *ca.* 1:1.2, even when the solutions were prepared and spectra were recorded at −60°C in dichloromethane-d_2.



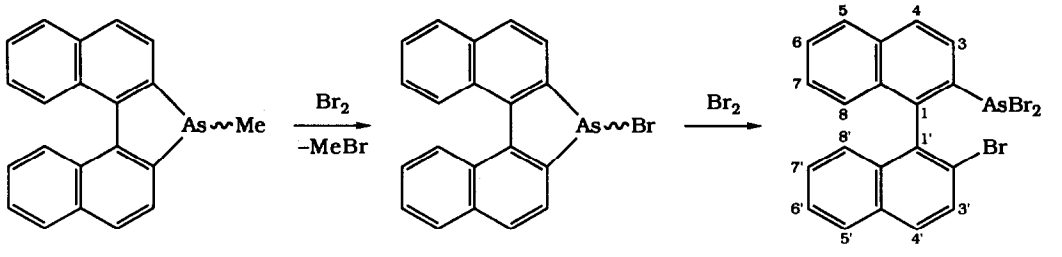
[*R*-(*R**,*R**)] - **5**

2.4. Bromination of (±)-4 (R = Me)

The compound (±)-**4** (R = Br), a potential precursor of the chiral dinaphth[2,1-*b*;1',2'-*d*]arsenide ion, was obtained by treating (±)-**4** (R = Me) with 1 equivalent of Br_2 in chloroform at 0°C and warming the reaction mixture to room temperature (Scheme 2). The ^1H NMR spectrum of the crystalline compound (±)-**4** (R = Br) in dichloromethane-d_2 at 20°C indicated rapid interconversion of atropisomers. Additional bromine cleaves an aryl–arsenic bond in the compound giving (±)-[2-(2'-bromo-1,1'-binaphthyl)]dibromoarsine, (±)-**7**, m.p. 207–208°C (Scheme 2). The complete assignment of the ^1H NMR spectrum of (±)-**7** was achieved with use of a COSY technique. All 12 protons of the compound were discernible in the 300 MHz spectrum. The shielding of protons H_8 and $H_{8'}$ is consistent with an orthogonal arrangement of the binaphthyl rings in the molecule. Dibromoarsine (±)-**7** is a potentially useful intermediate for the synthesis of C_1-unidentate and -bidentate arsines containing the 1,1'-binaphthyl backbone.

3. Conclusion

The C_1-unidentates (±)-**3** (R = Me or Ph) and (±)-**4** (R = Me or Ph) are unsuitable for optical resolution under ambient conditions because of rapid interconversion between the atropisomers of the compounds.



(±)-**4** (R = Me) (±)-**4** (R = Br) (±)-**7**

Scheme 2.

4. Experimental details

Reactions were performed under argon by Schlenk techniques. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded in chloroform-d_1, unless otherwise stated, on Varian Gemini 300 and VXR 300 s spectrometers at the temperatures specified. ^{1}H and ^{13}C chemical shifts are reported as δ values relative to internal Me_4Si; $^{31}P\{^{1}H\}$ chemical shifts are reported as δ values relative to external 85% H_3PO_4. Optical rotations were measured with a Perkin–Elmer Model 241 polarimeter in a 1 dm cell at 294 K. Elemental analyses were performed by staff within the Research School of Chemistry.

4.1. (±)-7-Methyldinaphtho[2,1-b;1',2'-d]phosphole ((±)-3 (R = Me))

A solution of 2,2'-dibromo-1,1'binaphthyl [20] (3.5 g, 8.5 mmol) in tetrahydrofuran (50 ml) at −45°C was treated with ^{n}BuLi (12.5 ml of 1.5 M n-hexane solution, 18.8 mmol) over 10 min [21]. The mixture was maintained at this temperature for 30 min, during which time a pale yellow precipitate formed. The mixture was then cooled to −78°C and a solution of methyldichlorophosphine (1.1 g, 9.0 mmol) was added over 10 min with vigorous stirring. After the addition of the chlorophosphine, the cooling bath was removed and stirring was continued for a further 6 h, giving an almost clear yellow solution. The solvent was removed from this solution, the pale yellow residue was dissolved in dichloromethane (5 ml), and the solution passed through a short column of silica gel with use of n-hexane/diethyl ether (15:1) as eluent. The eluate, after evaporation, afforded the pure phosphine as a pale yellow glass: 1.9 g (75%). Anal. Found: C, 83.8; H, 5.4. $C_{21}H_{15}P$ calc.: C, 84.6; H, 5.1%. ^{1}H NMR (295 K): δ 1.54 (d, 3H, $^{2}J(PH) = 1.7$ Hz, PMe), 7.44–7.56 (m, 4H, H_2, H_3, H_{11}, H_{12}), 7.83–7.93 (m, 4H, H_5, H_6, H_8, H_9), 7.96 (d, 2H, H_4, H_{10}), 8.43 (d, 2H, H_1, H_{13}); (225 K): 8.43 (d, 1H, $^{3}J(HH) = 8.1$ Hz, H_1 or H_{13}), 8.45 (d, 1H, $^{3}J(HH) = 7.8$ Hz, H_1 or H_{13}). ^{31}P NMR (295 K): −19.7 (s). ^{13}C NMR (295 K): 12.4 (d, $^{1}J(CP) = 22.5$ Hz, PMe).

The following compounds were prepared similarly.

4.1.1. (±)-7-Phenyldinaphtho[2,1-b;1',2'-d]phosphole ((±)-3 (R = Ph))

Cream powder; 78% yield. Anal. Found: C, 85.4; H, 4.9. $C_{26}H_{17}P$ calc.: C, 86.7; H, 4.8%. ^{1}H NMR (295 K): δ 7.16–7.34 (m, 5H, C_6H_5), 7.46–7.57 (m, 4H, H_2, H_3, H_{11}, H_{12}), 7.76–7.88 (m, 4H, H_5, H_6, H_8, H_9), 7.95 (d, 2H, H_4, H_{10}), 8.47 (d, 2H, $^{3}J(HH) = 8.2$ Hz, H_1, H_{13}); (236 K): 8.48 (br t, 2H, H_1, H_{13}).

4.1.2. (±)-7-Methyldinaphth[2,1-b;1',2'-d]arsole ((±)-4 (R = Me))

Pale yellow crystals from hot methanol; m.p. 55–57°C; 57% yield. Anal. Found: C, 73.7; H, 4.7. $C_{21}H_{15}As$ calc.: C, 73.7; H, 4.4% ^{1}H NMR (295 K): δ 1.36 (s, 3H, $AsCH_3$), 7.42 (m, 2H, H_2, H_{12}), 7.52 (m, 2H, H_3 H_{11}), 7.87 (br m, 4H, H_5, H_6, H_8, H_9), 7.96 (d, 2H, $^{3}J(HH) = 8.0$ Hz, H_4, H_{10}), 8.24 (d, 2H, $^{3}J(HH) = 8.3$ Hz, H_1, H_{13}); (257 K): 8.24 (d, 1H, $^{3}J(HH) = 8.7$ Hz, H_1 or H_{13}), 8.23 (d 1H, $^{3}J(HH) = 8.7$ Hz, H_1 or H_{13}). ^{13}C NMR (295 K): 12.0 (s, $AsCH_3$).

4.1.3. (±)-7-Phenyldinaphth[2,1-b;1',2'-d]arsole ((±)-4 (R = Ph))

Pale yellow plates from hot methanol; m.p. 139–140°C; 60% yield. Anal. Found: C, 77.1; H, 4.5. $C_{26}H_{17}As$ calc.: C, 77.2; H, 4.2%. ^{1}H NMR (295 K): 7.11–7.27 (m, 5H, C_6H_5), 7.45 (m, 2H, H_2, H_{12}), 7.53 (br m, 2H, H_3, H_{11}), 7.78–7.88 (m, 4H, H_5, H_6, H_8, H_9), 7.95 (br m, 2H, H_4, H_{10}), 8.27 (d, 2H, $^{2}J(HH) = 8.2$ Hz, H_1, H_{13}); (246 K): 8.27 (d, 1H, $^{3}J(HH) = 8.1$ Hz, H_1 or H_{13}), 8.26 (d, 1H, $^{3}J(HH) = 8.4$ Hz, H_1 or H_{13}).

4.2. (±)-7-Bromodinaphth[2,1-b;1',2'-d]arsole ((±)-4 (R = Br))

A solution of (±)-4 (R = Me) (0.4 g, 1.17 mmol) in chloroform (20 ml) at 0°C was treated with a solution of bromine (0.19 g, 1.18 mmol) in the same solvent (2.5 ml). After the addition, the mixture was warmed to room temperature and petroleum ether (b.p. 60–80°C) was added. The product separated as orange crystals, which were filtered off and washed with petroleum ether: m.p. 210–211°C; 0.37 g (78%). Anal. Found: C, 59.0; H, 3.0. $C_{20}H_{12}AsBr$ calc.: C, 59.0; H, 3.0%. ^{1}H NMR (295 K): δ 7.42 (m, 2H, H_2, H_{12}), 7.55 (m, 2H, H_3, H_{11}), 7.95 (m, 6H, H_4, H_5, H_6, H_8, H_9, H_{10}), 8.08 (d, 2H, $^{3}J(HH) = 8.4$ Hz, H_1, H_{13}).

4.3. (±)-[2-(2'-Bromo-1,1'-binaphthyl)]dibromoarsine ((±)-7)

A solution of bromine (0.095 g, 0.59 mmol) in chloroform (2 ml) was added to a solution of (±)-4 (R = Br) (0.2 g, 0.49 mmol) in chloroform (25 ml) at room temperature. After ca. 30 min, the clear yellow mixture was concentrated to half volume under reduced pressure and *n*-hexane (5 ml) was added. The product separated as pale yellow plates: m.p. 207–208°C; 0.2 g (72%). Anal. Found: C, 42.3; H, 2.2; Br, 42.6. $C_{20}H_{12}AsBr_3$ calc.: C, 42.4; H, 2.1; Br, 42.3%. ^{1}H NMR (295 K): δ 7.07 (d, 1H, $^{3}J(HH) = 8.8$ Hz, H_8 or H'_8), 7.13 (d, 1H, $^{3}J(HH) = 8.3$ Hz, H_8 or H'_8), 7.33 (m, 1H, H_7 or H'_7), 7.37 (m, 1H, H_7 or H'_7), 7.54 (m, 1H,

H_6 or H_6'), 7.58 (m, 1H, H_6 or H_6'), 7.82, 7.94 (AB q, 2H, ^3J(HH) = 8.8 Hz, H_3', H_4'), 7.95 (d, 1H, ^3J(HH) = 8.3 Hz, H_5 or H_5'), 8.00 (d, 1H, ^3J(HH) = 8.3 Hz, H_5 or H_5'), 8.17, 8.47 (AB q, 2H, ^3J(HH) = 8.8 Hz, H_3, H_4).

4.4. [R-[(R / S*),(R*,R*)]]-(+)$_{589}$-(η^5-Cyclopentadienyl){7-methyldinaptho[2,1-b;1',2'-d]phosphole}[1,2-phenylenebis(methylphenylphosphine]iron(II) hexafluorophosphate ([R-[(R* / S*),(R*,R*)]]-**6** (E = P, R = Me))*

A mixture of [*R*-(*R**,*R**)]]-**5** (0.28 g, 0.45 mmol) and (±)-**3** (R = Me) (0.16 g, 0.55 mmol) in methanol (30 ml) was heated under reflux for 3 h. The orange solution that resulted was evaporated to dryness to give an orange powder, which was shown by NMR spectroscopy to be *ca.* 90% pure. Recrystallization of the crude product from a dichloromethane/methanol/tetrahydrofuran mixture afforded the pure product as orange prisms: m.p. 210°C (decomp.); 0.29 g (74%); $[\alpha]_D$ + 132° (*c* 0.25, CH_2Cl_2). Anal. Found: C, 62.0; H, 4.9. $C_{46}H_{40}F_6FeP_4$ calc.: C, 62.3; H, 4.6%. ^{1}H NMR (295 K): δ 1.0–2.3 (br m's, 9H, PMe), 4.3 (br s, 5H, C_5H_5), 6.5–8.2 (br m, 26H, aromatics); (CD_2Cl_2, 256 K): δ 1.02 (d, 3H, ^2J(PH) = 8.1 Hz, 7-PMe (minor)), 1.43 (d, 3H, ^2J(PH) = 8.1 Hz, 7-PMe (major), 1.94 (d, 3H, ^2J(PH) = 8.1 Hz, PMe-diphos (major)), 2.12 (d, 3H, ^2J(PH) = 7.2 Hz, PMe–diphos (minor)), 2.3 (br m, 6H, PMe–diphos (major/minor)), 4.15 (s, 5H, C_5H_5 (minor)), 4.35 (s, 5H, C_5H_5 (major)), 6.2–8.2 (br m, 52H, aromatics (major/minor)); major/minor = 1.3:1.0. ^{31}P NMR (CD_2Cl_2, 295 K) 55.0 (br m, 1P), 76.1 (m, 1P), 77.9 (br m, 1P); (CD_2Cl_2, 256 K): δ 55.0 (t, 1P (major)), 56.0 (t, 1P (minor)), 75.8–78.7 (m's, 4P (major/minor)).

The following compounds were prepared similarly.

4.4.1. [R-[(R / S*), (R*,R*)]]-(+)$_{589}$-(η^5-Cyclopentadienyl){7-phenyldinaphtho[2,1-b;1',2'-d]phosphole}{1,2-phenylenebis(methylphenylphosphine)}iron(II) hexafluorophosphate ([R-[(R* / S*),(R*,R*)]]-**6** (E = P, R = Ph))*

Orange prisms from dichloromethane/methanol; m.p. 210°C (decomp.); 78% yield; $[\alpha]_D$ + 55° (*c* 0.26, CH_2Cl_2). Anal. Found: C, 64.3; H, 4.5. $C_{51}H_{42}F_6FeP_4$ calc.: C, 64.6; H, 4.5%. ^{1}H NMR (CD_2Cl_2, 295 K): δ 1.91 (br s, 6H, PMe, 4.61 (s, 5H, C_5H_5), 6.3–8.1 (br m, 31H, aromatics; (CD_2Cl_2, 246 K) 1.7–2.2 (br s, 12H, PMe (major/minor)), 4.59 (s, 5H, C_5H_5 (major)), 4.52 (s, 5H, C_5H_5 (minor)), 6.0–8.2 (br m, 62H, aromatics); major/minor = 2:1. ^{31}P NMR (CD_2Cl_2, 295 K): δ 63.8, 73.3, 76.1 (br m's, 3P); (246 K): 64.6–66.8 (br m (major/minor)), 75.5 (br t), 76.8 (t (minor)), 77.4–79.0 (br m).

4.4.2. [R-[(R / S*), (R*,R*)]]-(+)$_{589}$-(η^5-Cyclopentadienyl){7-methyldinaphth[2,1-b;1',2'-d]arsole}{1,2-phenylenebis(methylphenylphosphine)}iron(II) hexafluorophosphate–0.5-tetrahydrofuran ([R-[(R* / S*), (R*,R*)]]-**6** (E = As, R = Me) · 0.5C_4H_8O)*

Orange crystals from dichloromethane/diethyl ether/tetrahydrofuran mixture; m.p. 200°C (decomp.); 85% yield; $[\alpha]_D$ +193° (*c* 0.31, CH_2Cl_2). Anal. Found: C, 59.7; H, 4.7. $C_{46}H_{40}AsF_6FeP_3 \cdot 0.5C_4H_8O$ calc: C, 59.6; H, 4.6%. ^{1}H NMR (CD_2Cl_2, 295 K): δ 1.07 (s, 3H, AsMe (major)), 1.18 (s, 3H, $AsCH_3$ (minor)), 2.09 (d, 3H, ^2J(PH) = 8.3 Hz, PMe (major)), 2.12 (d, 3H, ^2J(PH = 7.8 Hz), PMe (minor)), 2.22 (d, 3H, ^2J(PH) = 8.7 Hz, PMe (major)), 2.41 (d, 3H, ^2J(PH) = 7.7 Hz, PMe (minor)), 4.22 (s, 5H, C_5H_5 (minor)), 4.32 (s, 5H, C_5H_5 (major)), 6.17 (d, 1H, ^3J(PH) = 8.1 Hz, aromatic-H (minor)), 6.28 (d, 1H, ^3J(PH) = 8.1 Hz, aromatic-H (major)), 7.0–8.0 (br m, 50H, aromatics (major/minor)); major/minor = 1.2:1.0.

4.4.3. [R-[(R / S*),(R*,R*)]]-(+)$_{589}$-(η^5-Cyclopentadienyl){1-phenyldinaphth[2,1-b;1',2'-d]arsole}{1,2-phenylenebis(methylphenylphosphine)}iron(II) hexafluorophosphate ([R-[(R* / S*),(R*,R*)]]-**6** (E = As, R = Ph))*

Orange plates from dichloromethane/methanol; m.p. 225°C (decomp.); 50% yield; $[\alpha]_D$ + 282° (*c* 0.28, CH_2Cl_2). Anal. Found: C, 61.8; H, 4.4. $C_{51}H_{42}AsF_6FeP_3$ calc.: C, 61.7; H, 4.3%. ^{1}H NMR (CD_2Cl_2, 295 K): δ 1.8–2.2 (br m, 12H, PMe (major/minor)), 4.48 (s, 5H, C_5H_5 (minor)), 4.61 (s, 5H, C_5H_5 (major)), 6.4–8.1 (br m, 62H, aromatics (major/minor)); major/minor = 1.3:1.0.

References and notes

1 J. K. Whitesell, *Chem. Rev., 89* (1989) 1581.
2 H. B. Kagan and M. Sasaki, in F. R. Hartley (ed.), *The Chemistry of Organophosphorus Compounds*, Vol. 1, Wiley, Chichester, UK, 1990, pp. 51–102.
3 D. G. Allen and S. B. Wild, *Organometallics, 2* (1983) 394; D. G. Allen, S. B. Wild and D. L. Wood, *Organometallics, 5* (1986) 1009.
4 R. Noyori, *Chem. Soc. Rev., 18* (1989) 187.
5 M. J. Burk, J. E. Feaster and R. L. Harlow, *Organometallics, 9* (1990) 2653; M. J. Burk, *J. Am. Chem. Soc., 113* (1991) 8518.
6 P. Kalck, Y. Peres and J. Jenk, *Adv. Organomet. Chem., 32* (1991) 121.
7 B. E. Maryanoff and A. B. Reitz, *Chem. Rev., 89* (1989) 863.
8 For atom-numbering scheme see: Chemical Abstracts, Ring Systems Handbook Supplement to Vol. 1988, Cumulative Supplement 6, RFS 8446, 1991.
9 R. F. Bridger, D. A. Law, D. F. Bowman, B. S. Middleton and K. U. Ingold, *J. Org. Chem., 33* (1968) 4329; R. F. Bridger, *J. Org. Chem., 35* (1970) 1746.
10 S. Murata, T. Suzuki, A. Yanagisawa and S. Suga, *J. Heterocycl. Chem., 28* (1991) 433.

11 Further crystallographic details (complete bond lengths, angles, thermal parameters, torsion angles, H atom coordinates and structure factors) have been deposited with the Cambridge Crystallographic Data Centre.
12 J. Jacques, A. Collet and S. H. Wilen, *Enantiomers, Racemates, and Resolutions*, Wiley, New York, 1981.
13 D. Satain and M. R. Truter, *J. Chem. Soc.*, (1963) 4414.
14 R. E. Carter and T. Liljefors, *Tetrahedron, 32* (1976) 2915; T. Liljefors and R. E. Carter, *Tetrahedron, 34* (1978) 1611.
15 F. H. Herbstein and G. M. J. Schmidt, *J. Chem. Soc.*, (1954) 3302.
16 K. Mislow, *Trans. N.Y. Acad. Sci., 35* (1973) 227.
17 D. M. Hall, *Prog. Stereochem., 4* (1963) 1; M. Ōbi, *Top. Stereochem., 5* (1970) 31; 14 (1983) 1.
18 G. Binsch and H. Kesler, *Angew. Chem., Int. Ed. Engl., 19* (1980) 411; H. Shanan-Atidi and K. H. Bar-Eli, *J. Phys. Chem., 74* (1970) 961.
19 G. T. Crisp, G. Salem, S. B. Wild and F. S. Stephens, *Organometallics, 8* (1989) 2360. The stereochemical nomenclature adopted here is consistent with recent chemical Abstracts Service indexing practice.
20 N. K. Roberts and S. B. Wild, *J. Am. Chem. Soc., 101* (1979) 6254.
21 A. Miyashita, H. Takaya, T. Souchi and R. Noyori, *Tetrahedron, 40* (1984) 1245.
22 R. Krishnamurti, H. G. Kuivila, N. S. Shaik and J. Zubieta, *Organometallics, 10* (1991) 423.