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1,8-Bis(phosphino)naphthalenes: Synthesis and Molecular Structures

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ABSTRACT

A series of 1,8-bis(phosphino)naphthalenes **2** *was prepared by treating 1,8-dilithionaphthalene with the appropriate chloro- or bromophosphines RR'PX; R, R' = Me (for* **2a***), iPr (for* **2c***), Cy (for* **2d***), Ph (for* **2f***); R = tBu, R' = Ph (for* **2e***) (X = Cl) and R, R' = Et; X = Br (for* **2b***). The resulting bisphosphines were characterized by NMR spectroscopy, mass spectrometry, and elemental analysis. X-ray crystal structure analyses were performed for 1,8-bis(diisopropylphosphino)-naphthalene (***2c***), 1,8-bis(dicyclohexylphosphino)-naphthalene (***2d***), and rac-1,8-bis(tert-butylphenylphosphino)naphthalene (***2c***). In each case, the proximity of the PR_2 groups leads to distortion,the main feature of which is the out-of-plane displacement of the P atoms. However, the distortions arising from the bulky PCy_2 groups in* **2d** *were remarkably small.* © 1997 John Wiley & Sons, Inc. Heteroatom Chem **8:**539–550, 1997

INTRODUCTION

Peri-substituted naphthalenes are characterized by intramolecular or, more precisely, *transannular* interactions between the substituents in the 1- and 8-positions [1]. These interactions can be repulsive, as in the case of steric effects arising from crowding of substituents, or attractive, caused by weak or strong bonding [2]. Steric strain associated with 1,8-disubstituted naphthalenes has received much attention [3]. Relief of such strain may be accomplished by *in-* and *out-of-plane* deflection of the substituents and distortion or buckling of the aromatic ring system. Moreover, the close proximity of spin-active nuclei has, in many cases, led to unique NMR-spectroscopic effects [4].

We are interested in the structures and properties of 1,8- diorganophosphino-substituted naphthalenes [5], which can be regarded as phosphorus analogues of 1,8-bis(dimethylamino)naphthalene, known as a "proton sponge" [6]. Of these, only 1,8-bis(dimethylphosphino)naphthalene **2a** [4a] and 1,8-bis(diphenylphosphino)naphthalene **2f** [4c,7] have been fully described previously. They are members of a class of bidentate ligands with a rigid C_3-backbone that have potential significance in transition-metal–catalyzed reactions [7]; for instance, the six-membered palladium(II) chelates that they form have been demonstrated to be extremely active catalysts for copolymerization of CO/ethylene [8].

Here we report the synthesis of the 1,8-bis(phosphino)naphthalenes **2b–2e** (where emphasis is on the introduction of bulky alkyl substituents), together with a summary of their NMR data and X-ray crystal structures (**2c–2e**), including also those of the known compounds **2a** and **2f.**

Dedicated to Prof. William E. McEwen on the occasion of his seventy-fifth birthday.

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RESULTS AND DISCUSSION

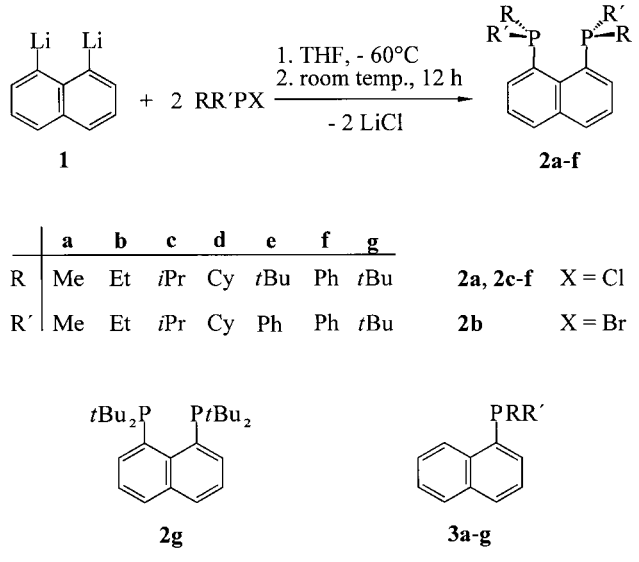
Synthesis and Properties of Ditertiary 1,8-Bis(phosphino)naphthalenes

The synthesis of the ditertiary 1,8-bis(phosphino)-naphthalenes **2a–2f** was straightforward, as shown in Scheme 1. 1,8-Bis(dimethylphosphino)naphthalene **2a** and 1,8-bis(diphenylphosphino)naphthalene **2f** were prepared previously by similar routes [4a,4c,7]. We have reinvestigated **2a** and **2f,** studying their $^{13}C\{^1H\}$ NMR spectra. The formation of 1,8-bis(dicyclohexylphosphino)naphthalene **2c** has been communicated [4c], but neither experimental nor complete spectroscopic data have been reported subsequently.

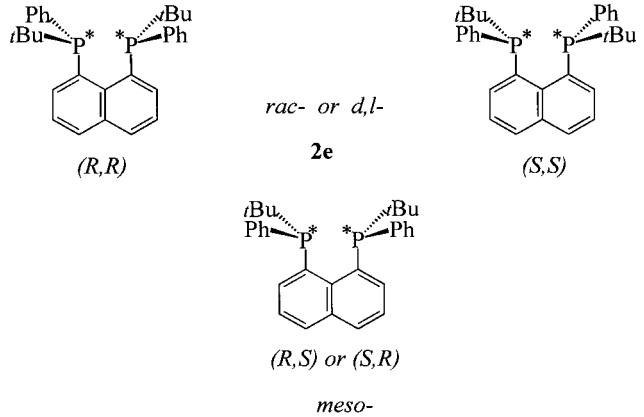
Suspensions of 1,8-dilithionaphthalene **1** in THF, conveniently prepared from 1-bromonaphthalene by twofold lithiation [7,9], were treated with THF solutions of the appropriate chloro- or bromophosphines at −60°C, and the mixtures were stirred at room temperature overnight. The bisphosphines **2a–2f** were isolated by hydrolysis, followed by extraction with dichloromethane and recrystallization. $^{31}P\{^1H\}$ NMR spectroscopic investigations of the reaction mixtures (C_6D_6-capillary) indicated that, apart from the bisphosphines **2a–2f** as main products, the monophosphines **3** and other unidentified phosphorus-containing compounds had been formed. The number and quantity of by-products (determined by the intensity ratios in the ^{31}P NMR spectra) were found to decrease, roughly, with the steric bulk of the phosphino groups that were being introduced. It has been shown that, in reactions of certain dilithio compounds with chlorophosphines, problems may arise from lithium-transfer and phosphorus–carbon bond cleavage reactions. This is the case if the lithio and phosphorus centers come into close proximity in the monolithio–monophosphine, initially formed, as for example in 2-lithio-2′-diphenylphosphinobiphenyl [10]. We expect an analogous situation in a 1-lithio-8-phosphinonaphthalene intermediate.

In the reaction of **1** with racemic chloro-*tert*-butylphenylphosphine, formation of the diasteroisomers *rac*- or *d,l*-**2e** and *meso*-**2e** is possible by virtue of the chirality and high inversion barrier at the phosphorus atoms (Scheme 2).

However, for steric reasons, the *d,l*-diastereoisomer (racemate) was formed in higher yield than the *meso*-analogue in which the bulky *tert*-butyl groups point to the same side of the naphthalene unit. $^{31}P\{^1H\}$ NMR spectroscopy (C_6D_6-capillary) of the crude product in CH_2Cl_2 indicated that *d,l*- and *rac*-**2e** (singlets at δ = 4.86 and δ = 4.61) had been formed in a 4:1 ratio. Such a small ^{31}P chemical shift difference is typical of diastereoisomers of P(III) derivatives [11]. *rac*-**2e** could be isolated and was characterized by X-ray crystal structure analysis, but we did not succeed in separating the *meso*-diastereoisomer from by-products (see above) and remaining *rac*-**2e.** Attempts to prepare the even bulkier 1,8-bis(di-*tert*-butylphosphino)naphthalene **2g** in an analogous fashion, according to Scheme 1, failed. Instead, solely di-*tert*-butyl-1-naphthylphosphine **3g** was obtained in low yield. We assume that the steric bulk of the tBu_2P groups prevents double substitution and thus renders the formation of the monosubstitution product **3g** more favorable.



SCHEME 1 Synthesis of 1,8-bis(diorganophosphino)-naphthalenes **2a–2f.**



SCHEME 2 Diastereoisomers of 1,8-bis(*tert*-butylphenylphosphino)naphthalene (**2e**).

The ditertiary 1,8-bis(phosphino)naphthalenes **2a–2f** were readily soluble in chlorinated organic solvents ($CHCl_3$, CH_2Cl_2) and ethers (THF, Et_2O) and poorly soluble in alcohols (MeOH, EtOH). In contrast to previous reports, in which **2a** and **2f** have been described as air-stable solids [4a,4c], we found that, apart from **2e** (*rac*), the ditertiary 1,8-bis(phosphino)naphthalenes were air-sensitive, even in the solid state. 1,8-Bis(diphenylphosphino)-naphthalene **2f,** for example, was slowly oxidized in air to the bisphosphine dioxide [12]. We ascribe this behavior to a mutual enhancement of basicity of the diphenylphosphino groups caused by their spatial proximity, unlike the situation in the air-stable triphenylphosphine. Chiral bisphosphines [13] such as *rac*-**2e** are the ligands of choice for a wide range of enantioselective transition-metal–catalyzed processes [14]. While chirality may be independently incorporated on either the linking carbon chain or the phosphorus centers of these ligands, only a limited number of P-chiral bisphosphines have been reported.

NMR Spectroscopy and Mass Spectrometry

The 1,8-bis(phosphino)naphthalenes **2** were studied by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy (**2a–2f**), and mass spectrometry (EI) (**2b–2f**). Most instructive were the ^{13}C NMR spectra, followed by the ^{1}H and ^{31}P{^{1}H} NMR spectra. Atom numbering (C,H,P) is explained in Figure 1.

^{13}C NMR Spectra of **2a–2f**

The ^{13}C NMR data of compounds **2a–2f** are summarized in Table 1. The assignment of the signals is based on correlation experiments (HH, CH, and COLOC). For **2a** and **2f,** our assignments differ from previous reports [4a, 7]. The quaternary carbon atoms C-4a, C-8a, and C-1,8 of the naphthalenediyl unit in compounds **2a–2f** gave rise to characteristic signals in the ^{13}C NMR spectra. For C-4a and C-8a, both of which experience equal coupling to both phosphorus nuclei P-1 and P-2 because of their symmetric orientation, virtual triplets (vt) were observed at $\delta \approx 134$ and between $\delta = 140$ and $\delta = 145$, with typical J values of $^2J_{CP} \approx 21$ to 24 Hz and $^3J_{CP} \approx 6$ Hz. *Virtual* triplets of AXX′-spin systems were observed because of the magnetic inequivalence of P-1 (X) and P-2 (X′), as was indicated by a CP-MAS solid-state NMR spectroscopic investigation of **2f** ($J_{PP} > 199$ Hz) [4c]. Despite the dissymmetric location of C-1 and C-8 in the molecule with respect to P-1 and P-2, virtual triplets with $J \approx 11$ to 15 Hz were observed between $\delta = 136$ and $\delta = 141$. As the measurable coupling is composed of $^1J_{CP}$ and $^3J_{CP}$, which are of similar order, no information on trends in steric demands of the phosphino groups and their preferred conformations in solution could be obtained. The NMR data of the secondary phenyl and naphthalenediyl carbon atoms were less informative. Interestingly, a virtual triplet with a small coupling of $J \approx 1.7$ Hz was observed for C-2,7 in **2a.** The aliphatic carbon atoms C-α, C-β, and C-γ, and also C-*i* in **2e** also displayed interesting NMR-spectroscopic features. For C-α in **2a** and **2e,** C-β and C-β' in **2b–2e,** C-γ and C-γ' in **2d,** and C-*i* in **2e,** virtual triplets were observed. This indicates a considerable P–P interaction that can be interpreted as direct coupling (through-space) [4a–c,7]. The δ(C-α) values of the substituents R and R′ on phosphorus increase in the order Me < Et < *i*Pr < *t*Bu/Ph (**2a** < **2b** < **2c** < **2e**) (β-effect); Cy (**2d**) being the only exception. $^1J(C_{alkyl}P)$ values were small (1.6 Hz in **2a** and 3.6 Hz in **2e**) or unresolved. For **2c** and **2d,** *pairs* of virtual triplets were observed for the methyl and methylene carbons of the isopropyl and cyclohexyl groups, indicating that C-β and C-β' in **2c** and **2d,** and C-γ and C-γ' are in **2d** diastereotopic.

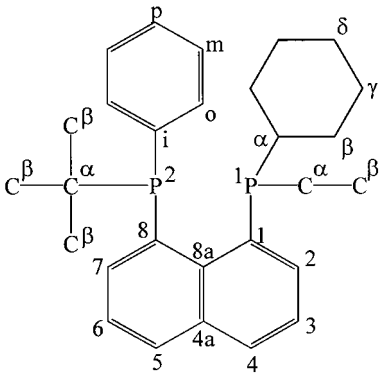


FIGURE 1 Atom numbering (C, H, P) in compounds **2a–2f.**

^{1}H NMR Spectra of **2a–2f**

The ^{1}H NMR spectra of **2a, 2b,** and **2d–2f,** recorded at 400 MHz, showed the expected ABC signal patterns for the aromatic protons of the 1,8-naphthalenediyl units with typical J values (without ^{31}P: [AA′BB′CC′] spin systems [15]). For **2f,** a coupling ^3J(PH) = 4 Hz was reported [7]. However, for the compounds studied here, ^3J(PH) couplings were not observed. Because of the presence of naphthalenediyl *and* phenyl groups, the aromatic region in the ^{1}H NMR spectra of **2e** and **2f** was complex. In the spectra of **2a–2f,** recorded at 200 MHz, the ABC patterns in the aromatic region (7–8 ppm) were not completely resolved. The NMR parameters of the aliphatic protons were more instructive. In the ali-

TABLE 1 $^{31}P\{^{1}H\}$ and ^{13}C NMR data of 1,8-bis(diorganophosphino)naphthalenes **2a–2f**[a] [in $CDCl_3$, rel. H_3PO_4 (ext. = 0) and $CDCl_3$ (int. = 77.05): δ, J_{PC} in Hz and multiplicity[b] in O].

Compound δ_P	*C-1,8*	*C-2,7*	*C-3,6*	*C-4,5*	*C-4a*	*C-8a*	*C-i*	*C-o*	*C-m*	*C-p*	*C-α*	*C-β*
2a	140.98	130.62	125.15	129.99	133.86	139.53	—	—	—	—	17.08	—
	13.8	*1.7*	—	—	*6.1*	23.2					*1.6*	—
−53.77	(t)	(vt)	(s)	(s)	(t)	(t)					(vt)	—
2b	137.69	131.57	124.85	129.94	134.11	141.77	—	—	—	—	22.43	10.34
	14.1	—	—	—	*6.0*	*22.2*					—	*8.3*
−26.37	(vt)	(s, br)	(s)	(s)	(t)	(vt)					(s)	(vt)
2c[c]	137.55	133.26	124.64	129.90	134.11	142.71	—	—	—	—	27.17	21.38,β
	13.9	—	—	—	*6.0*	*20.9*					—	*9.2*
−4.79	(vt)	(s)	(s)	(s)	(vt)	(vt)					(s)	19.80,β′
												9.0
												(t)
2d[d]	136.22	133.57	124.52	129.83	134.36	143.02	38.01	30.88	27.75	26.79	—	—
	14.6	—	—	—	*6.0*	*21.9*	*br*	*8.3*	*5.1*	—		
−15.09	(vt)	(s)	(s)	(s)	(vt)	(vt)	(s)	30.05	27.40	(s)		
								8.2	*4.6*			
								(vt)	(vt)			
2e	136.57	136.24	124.42	130.22	133.95	144.59	139.67	133.21	127.50	126.86	33.30	29.02
	11.2	*br*	—	—	*6.5*	*24.4*	*8.7*	*8.5*	*2.6*	—	*3.6*	*9.0*
+4.88	(vt)	(s)	(s)	(s)	(vt)	(vt)	(vt)	(vt)	(vt)	(s)	(vt)	(vt)
2f	135.85	137.87	125.44	131.03	134.48	140.22	140.12	133.76	128.18	127.81	—	—
	15.2	*br*	—	—	*6.3*	*24.1*	—	*10.6*	*3.3*	—		
−14.06	(vt)	(s)	(s)	(s)	(vt)	(vt)	(s)	(vt)	(vt)	(s)		

[a]Recorded at 50.3 MHz with $CDCl_3$ as solvent and internal standard at 77.05 ppm; assignments are based on CH COSY, COLOC (**2b, 2d–2f**), and DEPT90 measurements (**2b, 2d**) at 100.61 MHz or, in the case of **2a** and **2c**, on comparison with **2b**.
[b]Because of $J_{PP} > 100$ Hz (cf. **2f**: $J_{PP} > 199$ Hz in the solid state [4c, 7]), virtual triplets (vt) were observed.
[c]β and β' denote *gauche*- and *trans*-Me, respectively (assignment by comparison [25]).
[d]C-i, -o, -m, -p denote C-α, -β, -γ and -δ, respectively.

phatic region, the ^{1}H NMR spectra of **2a–2e** were complicated by (1) coupling of protons with P-1 *and* P-2 (X and X′) and (2) diastereotopy of methylene and/or methyl protons in the case of **2b–2e** (cf.^{13}C NMR above). The $[A_6A'_6XX']$ spin system in **2a** has been discussed previously [4a]. As expected, a formally analogous situation was found in **2b–2d** with $[A_6A'_6B_2B'_2C_2C'_2XX']$ (**2b,** Figure 2), $[A_{12}A'_{12}B_2B'_2XX']$ (**2c**), $[A_2A'_2B_4B'_4C_4C'_4D_2D'_2XX']$ (**2d**), and $[A_9A'_9XX']$ spin systems (**2e**) (not taking diastereotopy of protons into account in the case of **2d,** vide infra).

Hence, for the methyl protons in **2b** and **2e** (A-parts) a virtual quintet (**2b,** $A_6A'_6$-part) and a virtual triplet (**2e,** $A_9A'_9$-part) with $J \approx 7.6$ and 6.4 Hz were observed, which were simplified to a virtual triplet (**2b**) and a singlet (**2e**) in the ^{31}P-decoupled spectra. This again illustrates the remarkable through-space interaction and confirms the magnetic equivalence of the methyl groups in **2b** and **2e.** As possible mechanisms, a mutual overlap of the nonbonding electron pairs on phosphorus or an H-contact with the electron pair on the neighboring phosphorus atom by rotation of the R_2P group about the P-C(naphthyl)-axis were proposed [4a]. In this context, it is noteworthy that the diastereotopic methyl groups in **2c**

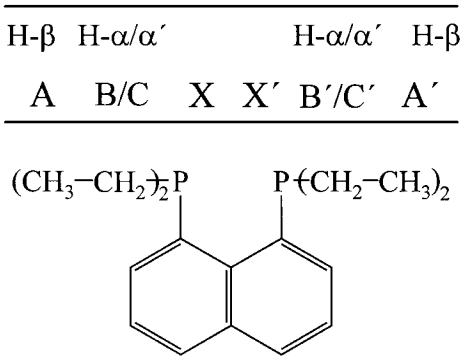


FIGURE 2 $[A_6A'_6B_2B'_2C_2C'_2XX']$ spin system in **2b.**

gave rise to two doublets of doublets only, with typical values of $^{3}J(H_\alpha H_\beta) = 7.1$ and 6.9 Hz, and $^{3}J(H_\beta P) = 13.2$ and 12.6 Hz [16]. Consequently, apart from the indirect $^{3}J(H_\beta P_1)$, no direct $H_\beta P_2$-coupling was observed for **2c.** It is not clear yet how the proposed mechanism can account for this finding.

The methylene and methine protons in **2b, 2c,** and **2d** (B-, C-, and D-parts) gave rise to more complex signals. In the ^{1}H NMR spectrum of **2b,** recorded at 400 MHz, a pair of multiplets, each com-

posed of six lines ($J \approx 7.5$ Hz), was observed for the diastereotopic methylene hydrogens H-α and H-α' ($B_2B'_2C_2C'_2$-part, Figure 2). The methine proton in **2c** was represented by a septet [$^3J(H_\alpha H_\beta) \approx {}^3J(H_\alpha H_{\beta'}) \approx$ 7.0 Hz] in the ^{1}H NMR spectrum. Again, no H,P-coupling (expected <3 Hz) was observed. Finally, the proton NMR spectrum of **2d** displayed very complex, unresolved, broad multiplets between $\delta = 1.11$ and $\delta = 2.06$. Apparently, a thorough ^{1}H NMR-spectroscopic investigation of **2d** is complicated by the diastereotopy of the methylene groups at C-β and C-γ (see ^{13}C NMR above) and line-broadening caused by dynamic processes.

$^{31}P\{^1H\}$ NMR Spectra

The $^{31}P\{^1H\}$ NMR spectra of the bisphosphines **2a–2f** (in $CDCl_3$) showed sharp singlets, indicating that the phosphorus atoms were equivalent in solution. The δ_P-values of **2a–2f** (Table 1) are shifted to high energy in the order [R,R′]: Me,Me (**2a**), Et,Et (**2b**), Cy,Cy (**2d**), Ph,Ph (**2f**), *i*Pr, *i*Pr (**2c**), *t*Bu, Ph (**2e**). Moreover, for the bis(dialkylphosphines) **2a–2c** (R = R′ = Me, Et, *i*Pr) and for the bis(alkylarylphosphine) **2e** (R = *t*Bu, R′ = Ph), this low-field shift occurs almost linearly (cf. β-effect) [17] and reflects the increase in steric demand of the substituents R on phosphorus, which leads to a larger cone angle θ [18]. The δ_P-values of the bis(dicyclohexylphosphine) **2d** and the bis(diphenylphosphine) **2f** are dominated by other than steric effects. In **2d,** the presence of γ-carbons results in a shift to low energy (γ-effect), which outweighs the shift to high energy caused by the β-carbons (β-effect, cf. *i*Pr substituents in **2c**). Although the phenyl substituents in **2f** are less bulky than the cyclohexyl substituents in **2d,** which resemble isopropyl groups sterically, the δ_P-value of the phenyl phosphine is shifted to higher energy. Such a low-field shift of aryl compared to alkyl phosphines is typical, *tert*-butyl phosphines being the only exception [17].

Mass Spectrometry

For further structural characterization, compounds, **2b–2f** were subjected to a mass spectrometric investigation (see Table 2). Because of the low stability of $[M]^+$ under EI conditions, which is typical of alkyl-substituted bisphosphines with a polymethylene backbone [19], parent ions appeared with low intensity only (**2d** and **2f**) or were not observed at all. The molecular ion cluster, resulting from the loss of the first substituent R, always formed the base peak in the spectrum. Further fragmentation occurred mainly by stepwise loss of alkyl or aryl groups via P–C bond cleavage or by elimination of an alkene (RH). Hence, $[M\text{-}nR]^+$ and $[M\text{-}(R\text{-}H)]^+$ ions, generated by hydrogen migration to phosphorus and elimination of an olefin RH, were observed. The presence of $[C_3H_7]^+$ [m/z = 43 (5%)] in the mass spectrum of **2c** confirms this interpretation.

X-ray Crystal Structure Determinations

The molecular structures of **2c, 2d,** and (*S,S*)-**2e** are shown in Figures 3, 4, and 5. Whereas 1,8-bis(dimethylphosphino)naphthalene **2a** [21] displayed crystallographic twofold symmetry, the ditertiary 1,8-bis(phosphino)naphthalenes described here have no crystallographic symmetry. However, the structures display approximate noncrystallographic C_2-symmetry about the C9–C10 bond (Figure 5). For compound **2c,** the asymmetric unit consists of two independent molecules (**2c** and **2c′**) that are not significantly different from each other ; a least-squares fit of the naphthalene carbon atoms gave a mean deviation of 1.5 pm. Therefore, only one of the molecules **2c** is discussed in detail in the text.

In **2a** and **2c–2f,** the PR_2 groups lie close to each other, with P ⋯ P distances between 293.5(1) (**2d**) and 307.0(1) pm (**2a**) (Table 3), well within the double van der Waals radius of about 380 pm [20]. The close proximity of the two bulky PR_2 groups leads to *in-plane* and *out-of-plane* displacement of the P atoms, the latter being the main feature of the structures of 1,8-bis(phosphino)naphthalenes. Similar distortions have been observed in 1,8-bis(dimethylphosphino)naphthalene, which crystallizes with two independent molecules **2a** and **2a′** [21], and 1,8-bis(diphenylphosphino)naphthalene **2f** [4c]. We were particularly interested in the effect of PR_2 groups with bulky organic substituents R on the geometry of the molecules. Here, the new structures are discussed in comparison with those published previously.

The twisting of the molecules is evident in the torsion angles P1–C1 ⋯ C8–P2, P1-C1-C9-C8 and P2-C8-C9-C1, as well as in the displacement of the phosphorus atoms to opposite faces of the best naphthalene plane (Table 3); the pseudo-torsion angles P1–C1 ⋯ C8–P2, for example, range from a low value of 5.12(7)° in the bis(dicyclohexylphosphine) **2d** to values as high as 46.55(7)° in the bis(*tert*-butylphenylphosphine) **2e.** Compared to **2c, 2d,** and **2f,** the out-of-plane distortion in the bis(dimethylphosphines) **2a** and **2a′** is unexpectedly large, and it is unexpectedly small in the bulky bis(dicyclohexylphosphine) **2d,** compared to the bis(diphenylphosphine) **2f** or even the bis(di-isopro-

TABLE 2 Mass spectrometric data of 1,8-bis(diorganophosphino)naphthalenes **2b–2f** [{} not observed; bold: base peak; () intensity].

Fragment	**2b** $R = R' = C_2H_5$	**2c** $R = R' = C_3H_7$	**2d** $R = R' = C_6H_{11}$	**2e** $R = C_4H_9$, $R' = C_6H_5$	**2f** $R = C_6H_5$
$[M]^+$	{304}	{360}	520 (0.22)	{456}	496 (5)
$[M-H]^+$	—	—	519 (0.50)	455 (1)	—
$[M-R]^+$	**275 (100)**	**317 (100)**	**437 (100)**	**399 (100)**	**419 (100)**
$[M-2R]^+$	246 (22)	274 (22)	355 (6)[b]	343[a] (66)	342 (8)
$[M-PR_2]^+$	—	—	—	—	311 (14)
$[M-2R-R']^+$	218[a] (22)	232[a] (12)	272 (9)	265 (40)	265 (18)
$[M-4R]^+$	189[a] (22)	189[a] (46)	190 (14)	—	—
$[M-R'-PRR']^+$	—	—	—	233[b] (22)	233 (28)
$[M-2R-PR_2]^+$	—	157 (2)	160 (2)	157 (2)	—
$[M-2PR_2]^+$	—	127 (10)	128 (2)	126 (2)	—

[a]Presumably H-transfer (+ 1H) and alkene elimination.
[b]1H.

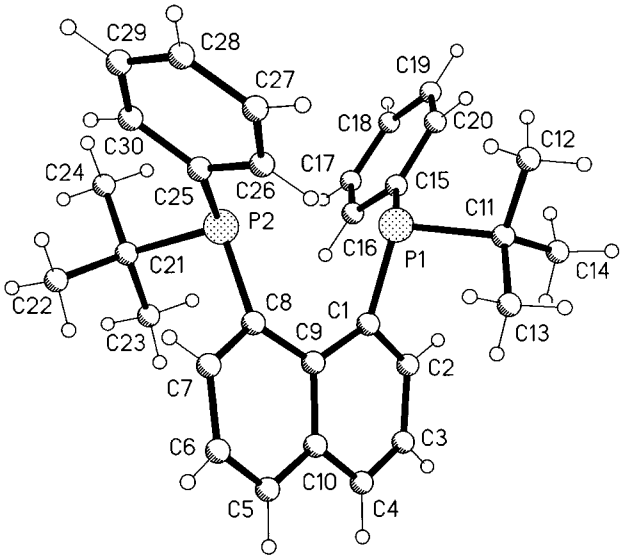


FIGURE 3 Molecular structure of **2e** in the crystal; (*S,S*)-enantiomer.

pylphosphine) **2c.** Apparently, out-of-plane distortion in 1,8-bis(phosphino)naphthalenes does not increase simply with the steric bulk of the PR_2 groups. Apart from the out-of-plane distortion, in-plane distortion of the PR_2 groups, which is indicated by a widening of the bay angles P1-C1-C9, P2-C8-C9, and C1-C9-C8 (Table 4), is apparent in **2c** and **2d** but, surprisingly, not in **2e** (Table 4). Widening of the bay angles was also observed in **2a**/**2a′** and **2f.** Again, there is no obvious trend relating in-plane distortion and steric bulk of the PR_2 groups. It should be noted that in **2e** the angles P1-C1-C9 and P2-C8-C9 are even smaller than the ideal sp^2 angle of 120°.

The displacement of the phosphino substituents is also associated with the distortion of the usually planar and rigid C_{10} unit by bond angle deformation and a twist into a nonplanar conformation. Mean deviations from the best plane (C1 to C10) range from <0.1 pm in **2a′** to 9.6 pm in **2e.** The *peri*-carbon atoms C1 and C8 as well as C4 and C5 show displacements from the best plane such that each C_6 ring is distorted to a flattened half boat. Bond angle deformation is indicated by a widening of the C1-C9-C8 angle (see Table 4), which deviates significantly from the standard C-C-C bond angles in naphthalene (119–121° [3b]).

As expected, in **2e** (*rac*), the bulky *t*Bu groups point to opposite faces of the naphthalene plane. The conformations of the phosphino groups relative to the naphthalene plane (Figure 6) can be described by the orientation of the nonbonding electron pairs at phosphorus toward that plane. The lone pair orientation is given by the pseudo-torsion angles *X*-P1-C1-C2 and *X*-P2-C8-C7, where *X* is the center of gravity of the atoms directly bonded to phosphorus, and P-*X* thus represents the opposite direction from the lone pair (Table 5). Small pseudo-torsion angles *X*-P1-C1-C2 and *X*-P2-C8-C7, ideally 0°, indicate a bisecting conformation of the PR_2 groups relative to the C_{10} plane, whereas angles of about 60° indicate an eclipsed conformation (Figure 5, Table 5). These angles range from −1.8° at P1 in **2e** to 37.0° at P2 in **2d.** The nonbonding electron pairs at P1 and P2 in **2c** and **2d** point to opposite faces of the naphthalene plane and are *gauche* with respect to that plane. In **2e,** they point in antiparallel directions and are almost eclipsed with respect to the naphthalene plane (Figure 5). Hence, the 1,8-bis(phosphino)naphthalenes described here adopt conformations between bisecting (**2e**) and eclipsed (**2d**), and the substituents at phosphorus point to opposite sides of the C_{10} plane.

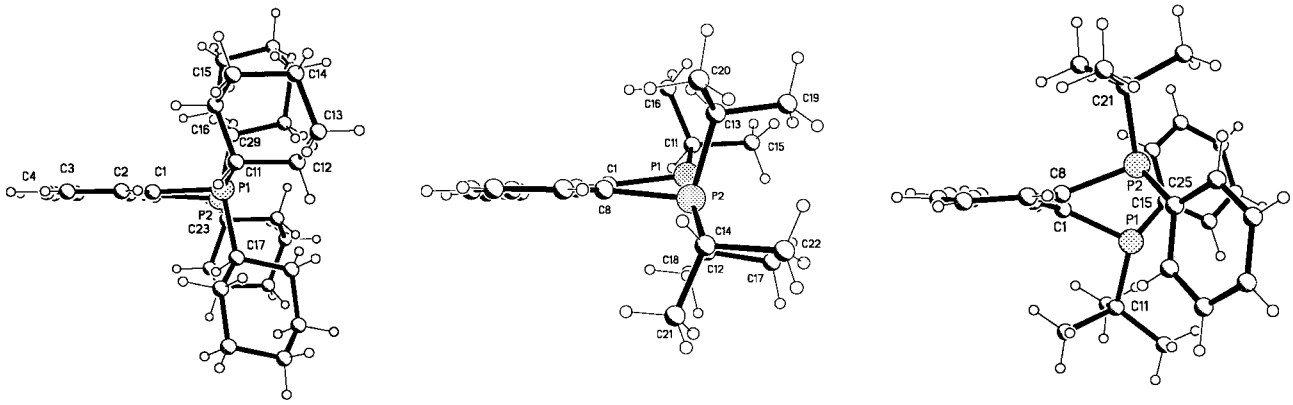


FIGURE 4 Molecular structures of **2d, 2c,** and **2e** viewed along the C2···C9···C7 axis to illustrate the extent of out-of-plane displacement of the PR_2 groups and the (eclipsed) conformation of the isopropyl and cyclohexyl groups in **2c** and **2d.**

The phosphorus atoms in **2c–2e** display the expected pyramidal coordination. Their displacement from the plane of their α substituents ranges from 77.4 pm (P2 in **2e**) to 81.6 pm (P1 in **2c**). The CPC bond angles vary from 98.22(7)° (C8-P2-C29 in **2d**) to as wide as 108.62(7)° (C25-P2-C21 in **2e**). P–C(sp^2) and P–C(sp^3) bond lengths are normal [22]; the long P–C(*t*Bu) bonds in **2e** [191.1(2) and 189.4(2) pm] are the only exception.

In summary, the PR_2 groups in **2c** and **2d** are mainly distorted in-plane but out-of-plane in **2e.** The known compounds **2a**/**2a′** and **2f** are distorted in- as well as out-of-plane. However, there is no simple correlation between the type and extent of distortion and the steric bulk of the PR_2 groups. Surprisingly, the bulky bis(dicyclohexylphosphine) **2d** displays only small distortions.

CONCLUSION

We have shown that the synthesis of 1,8-bis(phosphino)naphthalenes is not restricted to compounds with small organic substituents on phosphorus but can be extended to derivatives with substituents that are bulkier than the phenyl group. Reactivity and coordination properties of the new bisphosphines are currently under investigation. Of particular interest is the racemic bisphosphine **2e** whose enantiomers are potential ligands for transition-metal–catalyzed asymmetric reactions.

EXPERIMENTAL

All operations were carried out in standard Schlenk-type glassware under an atmosphere of dry nitrogen and, if necessary, with exclusion of moisture. Solvents were dried, purified, and stored according to common procedures [23]. Chloroform and ethanol, used for recrystallization, were degassed in vacuo and saturated with dry nitrogen. *n*-Butyllithium in *n*-hexane (1.6 M, 15%) was obtained from Chemetall GmbH. 1-Bromonaphthalene and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) were distilled prior to use (TMEDA from lithium aluminium hydride). The halophosphines RR′PX (X = Br, R = R′ = Et [24a]; X = Cl, R = R′ = Me [24b], *i*Pr [24c], Cy [24c] and R = *t*Bu, R′ = Ph [24d]) were prepared as described in the literature. Ph_2PCl (95%) was obtained commercially and used without further purification. Melting points were determined on a Büchi 530 melting point apparatus using sealed 0.1 mm capillary tubes and are uncorrected. NMR: Bruker AC 200 (^{1}H: 200.1 MHz, ^{13}C: 50.3 MHz, ^{31}P: 81.0 MHz) and Bruker AM 400 (^{1}H: 400.13 MHz, ^{13}C: 100.61 MHz). $CDCl_3$ was used as a solvent, unless stated otherwise. Reference substances were $SiMe_4$ (TMS) or, indirectly, $CHCl_3$ (int.) at δ = 7.25 for ^{1}H and δ = 77.05 for ^{13}C NMR spectra, and 85% H_3PO_4 (ext.) at δ = 0 for ^{31}P NMR spectra; high-field shifts are given negative signs, and low-field shifts, positive signs; m_c denotes a complex multiplet. Atom numbering (C, H, P) is summarized in Figure 1. Assignments were supported by CH-COSY and COLOC experiments (AM 400). MS: Finnigan MAT 8430; EI at 70 eV. Elemental analyses were carried out by Analytisches Laboratorium des Instituts für Anorganische und Analytische Chemie der Technischen Universität, Braunschweig. In vacuo (i.v.) refers to a pressure of 0.05 Torr at 25°C. The experimental details of the crystal structure determinations are summarized in Table 6. Yields have not been optimized.

General Procedure for the Preparation of Ditertiary 1,8-Bis(phosphino)naphthalenes **2a–2f.**

To a suspension of 1,8-dilithionaphthalene in *n*-hexane, prepared from 1-bromonaphthalene (mmol see

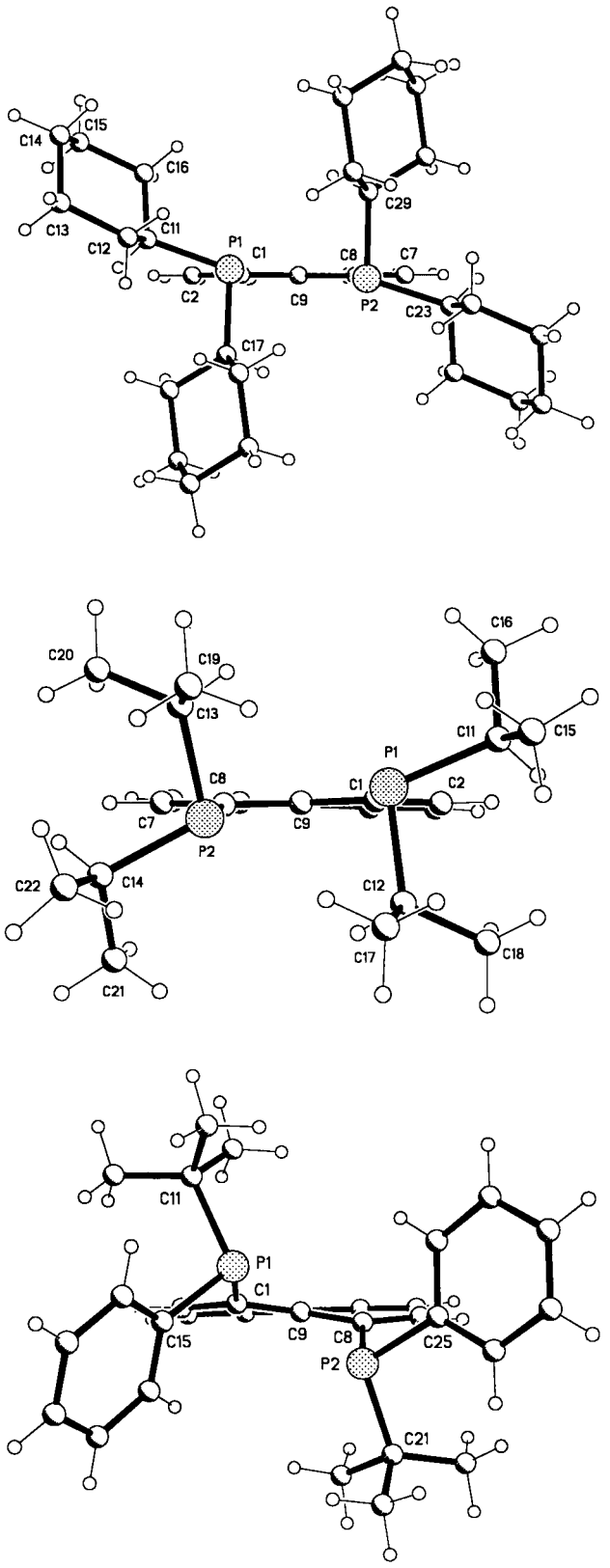


FIGURE 5 Molecular structures of **2d, 2c,** and **2e** viewed along the C9–C10 bond to illustrate the extent of out-of-plane displacement of the PR_2 groups, their conformation, relative to the naphthalene ring, and the approximate noncrystallographic C_2 symmetry.

below) by twofold lithiation with *n*-BuLi and TMEDA [7,9], dry THF (ca. 1 mL/mmol) was added between −10 and 0°C, and the resulting dark green mixture was cooled to −80°C with stirring. A solution of 2.5 equivalents of chlorophosphine (bromophosphine for **2b**) in THF (ca. 0.2 mL/mmol phosphine) was added dropwise over 30 minutes, while keeping the temperature between −50 and −70°C (slightly exothermic). After the addition, the resulting mixture was allowed to warm to room temperature with stirring. Stirring was continued overnight (12 h) (**2c:** 3 d) at room temperature, and the reaction mixture was subsequently hydrolyzed with deionized, carefully deoxygenated water (ca. 1.5–2 mL/mmol 1-bromonaphthalene). The organic layer was taken up with dichloromethane (to effect phase inversion) and was separated from the aqueous layer, which was exhaustively extracted with dichloromethane. After drying over $MgSO_4$ and removal of the solvents i.v., viscous, dark-red residues (**2b:** sticky, yellow solid) were obtained, which were recrystallized from THF (**2a**), ethanol (**2b**), dichloromethane/ethanol (**2c–2e,** ca. 1:1), or chloroform/ethanol (**2f**) to give yellow, crystalline (**2a, 2c, 2d**) or powdery (**2b, 2e, 2f**), air-sensitive (**2a–2d, 2f**) or air-stable (**2e**) solids.

1,8-Bis(dimethylphosphino)naphthalene (**2a**). Starting from 4.14 g (0.020 mol) of 1-bromonaphthalene, THF (20 mL) and 4.83 g (0.05 mol) of chlorodimethylphosphine in THF (5 mL), 2.70 g (0.011 mol, 54%) of a yellow solid were obtained by recrystallization from THF. ^{1}H and ^{31}P NMR data were in accordance with those published previously [4a]. For ^{13}C and ^{31}P NMR data, see Table 1, and see Figure 1 for the numbering of the H and C atoms. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.49 [m_c (≈t), 12H, J(PH) ≈ 3 Hz, PC$\underline{H}_3$, α-H], 7.50 [m_c (≈dd), $^3J(H_3H_4)$ ≈ 8.05 Hz, $^3J(H_2H_3)$ ≈ 7.10 Hz, 2H, 3-H], 7.79–7.89 [m, 4H, 2-H and 4-H]; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.49 [m_c (≈t), 12H, J(PH) ≈ 3 Hz, PC$\underline{H}_3$, α-H], 7.49 [m_c (≈t), ^3J(HH) ≈ 7.6 Hz, 2H, 3-H], 7.81 [m_c (≈d), $^3J(H_3H_4)$ ≈ 7.9 Hz, 2H, 4-H], 7.85 [m_c (≈"), $^3J(H_3H_4)$ ≈ 7.1 Hz, $^4J(H_2H_4)$ ≈ 1.8 Hz, 2H, 2-H]; EI–MS: see Table 2; anal. found: C, 67.15%; H, 7.46%. Calcd for $C_{14}H_{18}P_2$ (248.3): C, 67.74%; H, 7.31%.

1,8-Bis(diethylphosphino)naphthalene (**2b**). From 2.07 g (0.010 mol) of 1-bromonaphthalene, THF (10 mL) and 4.30 g (0.025 mol) of bromodiethylphosphine in THF (5 mL), 0.684 g (2.25 mmol, 23%) of a yellow solid (mp 36°C) were obtained by recrystallization from ethanol at −60°C. For ^{13}C and ^{31}P NMR data, see Table 1, and see Figure 1 for the numbering of the H and C atoms. ^{1}H NMR ($CDCl_3$,

TABLE 3 *Out-of-plane* distortion in 1,8-bis(diorganophosphino)naphthalenes **2a** and **2c–2f**, as indicated by the torsion angles P1–C1···C8–P2, P1-C1-C9-C8, P2-C8-C9-C1, and the out-of-plane displacement of P1 and P2 from the least-squares plane of the naphthalene carbons (angles in °, distances in pm).

	Torsion Angles			*Out-of-Plane Disp.*		*Mean Deviation*	*Distance*
Compound	*P1–C1···C8–P2*	*P1-C1-C9-C8*	*P2-C8-C9-C1*	*P1*	*P2*	*C1 to C10*	*P1···P2*
2a	30.7 (2)	18.0 (4)	18.0 (4)	+37.8 (5)	−37.8 (5)	1.0	307.0 (1)
2a′	20.0 (2)	11.88 (15)	11.88 (15)	+ 29.7 (6)	−29.7 (6)	<0.1	303.6 (1)
2c	12.49 (11)	6.4 (3)	8.3 (3)	−22.4 (3)	+30.2 (2)	3.4	294.4 (1)
2c′	13.71 (11)	5.4 (3)	10.8 (3)	+21.2 (2)	−35.2 (2)	3.8	292.7 (1)
2d	5.12 (7)	2.9 (2)	3.1 (2)	−11.3 (2)	+9.9 (2)	1.3	293.5 (1)
2e	46.54 (7)	26.7 (2)	26.5 (2)	+88.9 (2)	−91.2 (2)	9.6	305.6 (1)
2f[a]	17.7	13.4 (7)	7.7 (7)	+34	−50	6.6	305.2

[a]Values taken from Ref. [4c] or calculated from deposited data; standard deviations were not available for some values.

TABLE 4 In-plane distortion in 1,8-bis(diorganophosphino)naphthalenes **2a** and **2c–2f**, as indicated by the bay angles P1-C1-C9, P2-C8-C9, and C1-C9-C8 (in °).

Compound	*P1-C1-C9*	*P2-C8-C9*	*C1-C9-C8*
2a	121.6 (4)[a]	121.6 (4)	125.5 (6)
2a′	123.1 (9)[a]	123.1 (9)	125.5 (6)
2c	122.5 (2)	121.9 (2)	125.8 (2)
2c′	122.1 (2)	122.4 (2)	125.3 (2)
2d	122.23 (11)	122.46 (11)	125.90 (19)
2e	118.09 (11)	118.37 (11)	123.48 (13)
2f	124.5 (3)	123.0 (4)	125.3

[a]Labeled in Ref. [21] as P1-C1-C6.

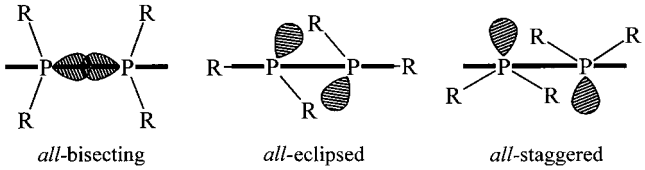


FIGURE 6 Idealized conformations of 1,8-bis(phosphino)naphthalenes.

TABLE 5 Conformations of the PR_2 groups, relative to the C_{10}-plane, described by the orientation of the nonbonding electron pairs at phosphorus. *X* is the center of gravity of the atoms directly bonded to phosphorus (see text).

Compound *Torsion Angle*	**2a**	**2a′**	**2c**	**2c′**	**2d**	**2e**	**2f**
X-P1-C1-C2	14.8	24.3	−32.5	30.9	36.4	−1.8	64.5
X-P2-C8-C7			−29.2	30.4	37.0	−7.4	23.6

200 MHz): δ = 0.92 [m_c (≈quint), J ≈ 7.6 Hz, 12H, $CH_2C\underline{H}_3$, β-H (AA′-part)], 1.81 [m_c (≈quintd), J ≈ 7 Hz, 8H, $C\underline{H}_2CH_3$, α-H (BB′-part)], 7.34 [m_c (≈t), J(HH) ≈ 7.2 Hz, 2H, 3-H], 7.66 [m_c (≈t), J(HH) ≈ 8 Hz, 4H, 2-H and 4-H]; $^1H\{^{31}P\}$ NMR ($CDCl_3$, 200 MHz): δ = 0.92 [t, J = 7.6 Hz, 12H, $CH_2C\underline{H}_3$, β-H (AA′-part)], 1.81 [m_c (≈quintd), J ≈ 7.6 Hz, 8H, $C\underline{H}_2CH_3$, α-H (BB′-part)], 7.34 [m_c (≈dd), J(HH) ≈ 7.2 Hz, 2H, 3-H], 7.65 [m_c ≈ t, J(HH) ≈ 8 Hz, 4H, H-2 and H-4]; ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.92 [m_c (≈quint), J ≈ 7.6 Hz, 12H, $CH_2C\underline{H}_3$, β-H (AA′-part)], 1.75 [m, 4H, $C\underline{H}_2CH_3$, α-H (BB′-part)], 1.87 [m, 4H, $C\underline{H}_2CH_3$, α'-H (BB′-part)], 7.34 [m_c (≈t), ^3J(HH) ≈ 7.6 Hz, 2H, 3-H], 7.63 [m_c (≈dd), $^3J(H_2H_3)$ ≈ 7.0 Hz, $^4J(H_2H_4)$ ≈ 1.5 Hz, 2H, 2-H], 7.68 [d, $^3J(H_3H_4)$ = 8.0 Hz, 2H, 4-H]; EI–MS: see Table 2; $C_{18}H_{26}P_2$ (304.35).

*1,8-Bis(diisopropylphosphino)naphthalene (***2c***).* Starting from 1.04 g (5 mmol) of 1-bromonaphthalene and 1.90 g (12.5 mmol) of chlorodiisopropylphosphine in THF (3 mL), 0.522 g (1.45 mmol, 29%) of yellow needles (mp 82°C) were obtained by crystallization from dichloromethane/ethanol at −20°C. For ^{13}C and ^{31}P NMR data, see Table 1, and see Figure 1 for the numbering of the H and C atoms. ^1H NMR ($CDCl_3$, 200 MHz): δ = 0.96 [dd, $^3J(H_\alpha H_\beta)$ = 7.1 Hz, $^3J(H_\beta P)$ = 13.2 Hz, 12H, $CH(C\underline{H}_3)_2$, β-H or β'-H], 1.28 [dd, $^3J(H_\alpha H_\beta)$ = 6.9 Hz, $^3J(H_\beta P)$ = 12.6 Hz, 12H, $CH(C\underline{H}_3)_2$, β'-H or β-H], 2.27 [m_c (≈ sept), $^3J(H_\alpha H_\beta)$ ≈ 7.0 Hz, 4H, $C\underline{H}(CH_3)_2$, α-H)], 7.37–7.54 [m, 2H, naphthalenediyl, 3-H], 7.70–7.78 [m, 4H, naphthalenediyl, 2-H and 4-H]; EI–MS: see Table 2 anal. found: C, 72.70%; H, 9.15%. Calcd for $C_{22}H_{34}P_2$ (360.4): C, 73.31%; H, 9.51%.

*1,8-Bis(dicyclohexylphosphino)naphthalene (***2d***).* From 1.04 g (5 mmol) of 1-bromonaphthalene, THF (10 mL), and 2.90 g (12.5 mmol) of chlorodicycloh-

TABLE 6 Crystallographic Data for **2c–2e**

Compound	***2c***	***2d***	***2e***
Formula	$C_{22}H_{34}P_2$	$C_{34}H_{50}P_2$	$C_{30}H_{34}P_2$
M_r	360.43	520.68	456.51
Crystal habit	colorless prism	colorless tablet	colorless prism
Crystal size (mm)	0.55 × 0.45 × 0.40	0.85 × 0.40 × 0.15	0.90 × 0.50 × 0.35
Temperature (°C)	−130	−100	−100
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$
Cell constants			
a (pm)	735.8(2)	1055.17(6)	1239.91(12)
b (pm)	3069.1(6)	1128.11(6)	1270.44(12)
c (pm)	1934.5(4)	1381.26(7)	1656.5(2)
α (°)	90	69.992(4)	90
β (°)	99.11(3)	82.329(4)	99.955(8)
γ (°)	90	73.862(4)	90
U (nm³)	4.313(2)	1.48272(14)	2.5701(4)
Z	8	2	4
D_x (Mg m^{-3})	1.110	1.116	1.180
μ (mm^{-1})	0.203	0.168	0.185
F (000)	1568	568	976
$2\theta_{max}$ (°)	50	50	50
No. of reflns.:			
Measured	8229	8355	6525
Independent	7603	5139	4508
R_{int}	0.030	0.017	0.015
$wR(F^2$, all refl.)	0.124	0.083	0.085
$R[F > 4\sigma(F)]$	0.046	0.032	0.032
No. of parameters	449	325	295
S	1.06	1.04	1.06
Max. Δ/σ	<0.001	<0.001	<0.001
Max. $\Delta\rho$ (e nm^{-3})	411	289	267

exylphosphine in THF (5 mL), 1.05 g (2 mmol, 41%) of an orange-yellow solid (mp 148°C) were obtained by crystallization from dichloromethane/ethanol at −20°C. For ^{13}C and ^{31}P NMR data, see Table 1, and see Figure 1 for the numbering of the H and C atoms. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.00–2.30 [m_c, 44H, cyclohexyl-C<u>H</u> and -C<u>H</u>$_2$], 7.40 [m_c (≈dd), J(HH) ≈ 7.5 Hz, 2H, 3-H], 7.73 [m_c (≈t), J(HH) ≈ 7.6/8.3 (ca. 8) Hz, 4H, 2-H and 4-H]; ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ = 1.11–2.06 [4m_c, 44H, cyclohexyl-C<u>H</u> and -C<u>H</u>$_2$], 7.40 [m_c (≈t), ^3J(HH) ≈ 7.55 Hz, 2H, 3-H], 7.71 [m_c (≈dd), ^3J(HH) ≈ 7.07 Hz, ^4J(HH) ≈ 1.09 Hz, 4H, 2-H], 7.75 [m_c (≈d), ^3J(HH) ≈ 7.94 Hz, 4H, 4-H]; EI–MS: see Table 2; anal. found: C, 77.18%; H, 9.85%. Calcd for $C_{34}H_{50}P_2$ (520.72): C, 78.43%; H, 9.68%.

*rac-1,8-Di(tert-butylphenylphosphino)naphthalene (***2e***).* From 2.07 g (0.010 mol) of 1-bromonaphthalene, THF (10 mL), and 5.02 g (0.025 mol) of (±)-chloro-*tert*-butylphenylphosphine in THF (5 mL), 1.90 g (4.17 mmol, 42%) of a yellow, powdery solid (mp 124°C) were obtained by crystallization from dichloromethane/ethanol at −20°C. The *meso*-compound could not be isolated from the mother liquor. For ^{13}C and ^{31}P NMR data, see Table 1, and see Figure 1 for the numbering of the H and C atoms. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 0.76 [m_c (≈t), J ≈ 6.4 Hz, 18H, C(C<u>H</u>$_3$)$_3$, β-H], 7.27–7.49 [m, 8H, arom. H], 7.73–7.96 [m, 8H, arom. H]; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.76 [m_c (≈t), J ≈ 6.4 Hz, 18H, C(C<u>H</u>$_3$)$_3$, β-H], 7.27 [m_c (≈t), $^3J(H_3H_4)$ ≈ 7.3 Hz, 2H, p-H], 7.33 [m_c (≈t), ^3J(HH) ≈ 7.3 Hz, 4H, m-H], 7.44 [m_c (≈t), ^3J(HH) ≈ 7.6 Hz, 2H, 3-H], 7.77 [m_c (≈dm), ^3J(HH) ≈ 7 Hz, 4H, o-H], 7.82 [m_c (≈d), ^3J(HH) ≈ 7.93 Hz, 2H, 4-H], 7.94 [m_c (≈dd), $^3J(H_2H_3)$ ≈ 7.06 Hz, $^4J(H_2H_4)$ ≈ 1.05 Hz, 2H, 2-H]; EI–MS: see Table 2; anal. found: C, 78.80%; H, 7.62%. Calcd for $C_{30}H_{34}P_2$ (456.55): C, 78.93%; H, 7.51%.

*1,8-Bis(diphenylphosphino)naphthalene (***2f***).* Prepared from 8.28 g (0.04 mol) of 1-bromonaphthalene and 22.06 g (0.10 mol) of chlorodiphenylphosphine, as described previously [7], and purified by recrystallization from chloroform/ethanol at 60°C. Yield: 10.42 g (0.021 mol, 53%) of a pale-yellow solid (mp 205°C).

^{1}H, ^{13}C, and ^{31}P NMR data were in accordance

with those published [7]. For a different assignment of some signals in the ^{13}C NMR spectrum see Table 1. In order to comply with the CH and COLOC spectrum, o-H and m-H have to be interchanged in Ref.[7].

Crystal Structure Analyses

Data Collection and Reduction. Crystals were mounted on glass fibers in inert oil and transferred to the cold gas stream of the diffractometer (Siemens P4 for **2d** and **2e,** Stoe STADI-4 for **2c,** both with LT-2 low-temperature attachment). The orientation matrix for **2d** and **2e** was refined from setting angles of 63 (42) reflections in the 2θ range 5–25°. The cell constants for **2c** were refined from $\pm\omega$ angles of 58 reflections in the 2θ range 20–23° (monochromated MoK_α radiation).

Structure Solution and Refinement. The structures were solved by direct methods and refined anisotropically on $\underline{F}^2$ (program system: SHELXL-93, G. M. Sheldrick, University of Göttingen). H atoms were included using a riding model or rigid methyl groups. Weighting schemes were of the form $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$, with $P = (F_o^2 + 2F_c^2)/3$. Full details of the structure determinations have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, from where this material may be obtained on quoting the full literature citation and the reference numbers CSD 406913 (**2c**), 406914 (**2d**), and 406915 (**2e**).

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