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Oxidation Reactions of 1,8-Bis(phosphino)naphthalenes: Syntheses and Molecular Structures of Bis(phosphine oxides) and of a Bis(phosphine sulfide)

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ABSTRACT: *A series of naphthalenediyl-1,8-bis(phosphine oxides) 1-RR′P(:O)($C_{10}H_6$)-8-P(:O)RR′ (R = R′ = Me (***2a***), Et (***2b***), iPr (***2c***), Cy (***2d***), Ph (***2f***) and R = tBu, R′ = Ph (***2e***) was prepared by oxidation of the corresponding bis(phosphines)* **1a–f** *with molecular oxygen or $H_2O_2 \cdot (H_2N)_2C(:O)$ and characterized by NMR and IR spectroscopy, mass spectrometry, and elemental analysis (***2a, 2b, 2d–f***). X-ray crystal structure analyses were performed for 1,8-bis(dimethylphosphinyl)naphthalene (***2a***), (RR,SS)-1,8-bis-(phenyl-tert-butylphosphinyl)naphthalene (***2e***) and 1,8-bis(diphenylphosphinyl)naphthalene (***2f***). Treatment of 1,8-bis(diphenylphosphino)naphthalene (dppn,* **1f***) with an excess of sulfur in hot toluene afforded the bis(phosphine sulfide) 1-Ph_2P(:S) ($C_{10}H_6$)-8-P(:S)Ph_2 (dppnS_2,* **3f***) the structure of which was elucidated by X-ray crystal structure analysis. The geometries of the compounds* **2a, 2e, 2f***, and* **3f** *revealed an increase of strain from the corresponding bis(phosphines). In each case, the proximity of the P(:X)R_2 groups (X = O, S) led to distortion, the main feature of which was the out-of-plane displacement of the P atoms.* © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:102–113, 2001

INTRODUCTION

Steric strain associated with 1,8-disubstituted naphthalenes (*peri*-substitution) has received much attention [1,2]. Relief of such strain may be accomplished by in- and out-of-plane deflection of the substituents and distortion or buckling of the aromatic framework. Moreover, the close proximity of NMR-active nuclei endows these compounds with unique NMR-spectroscopic properties [3].

Recently, we described the molecular structures of some 1,8-bis(dialkylphosphino)naphthalenes (**1a–d**), a 1,8-bis(alkylarylphosphino)naphthalene (**1e**) and a 1,8-bis[(dialkylamino)phosphino]naphthalene (**1g**) [4] (Scheme 1). These compounds can be regarded as phosphorus analogues of 1,8-bis(dimethylamino)naphthalene, known as *proton sponge* [5]. There is considerable interest in bis(phosphines) with a rigid C_3-backbone as bidentate ligands in transition metal–catalyzed reactions, because their pal-

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Dedicated to Professor Richard Neidlein on the occasion of his 70th birthday.

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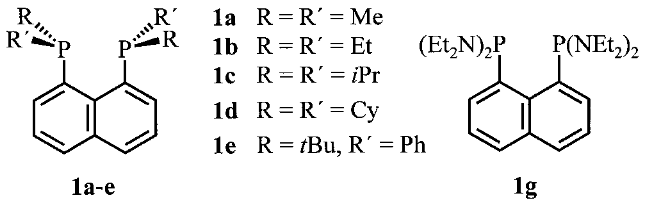
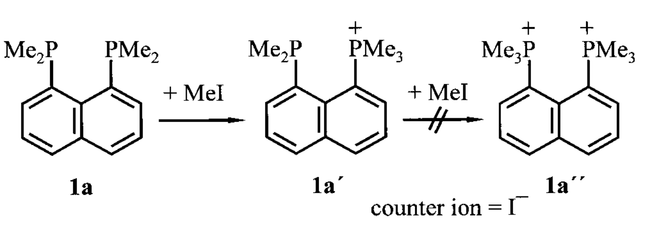
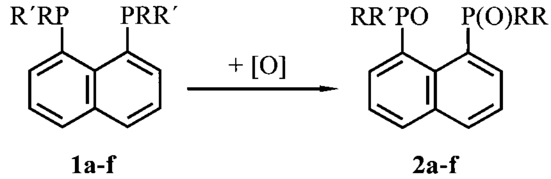


SCHEME 1 1,8-Bis(phosphino)naphthalenes.



SCHEME 2 Quaternization of 1,8-bis(dimethylphosphino)naphthalene **1a** [3a].



[O] = air (**2a-d, 2f**) or $H_2O_2 \cdot (H_2N)_2C(:O)$ (**2e**)

	a	b	c	d	e	f
R	Me	Et	*i*Pr	Cy	*t*Bu	Ph
R′	Me	Et	*i*Pr	Cy	Ph	Ph

SCHEME 3 Oxidation of **1a–f** with air or $H_2O_2 \cdot (H_2N)_2C(:O)$.

ladium(II) chelates turned out to be active catalysts for CO/ethylene copolymerization [6]. The ligand 1,8-bis(diphenylphosphino)naphthalene (dppn, **1f**), in particular, was reported to have high catalytic activity in the cyanation of vinylic halides and in the alkylation of heteroarenes [7].

Quaternization of the trivalent phosphorus atoms, for example, by oxidation, should drastically increase the steric strain in 1,8-bis(phosphino) naphthalenes. However, Schmidbaur and Costa [3a] found that two-fold quaternization of 1,8-bis-(dimethylphosphino)naphthalene (**1a**) by alkylation with methyl iodide failed because of the unfavorable steric and electronic situation in the expected dication **1a**″ (Scheme 2).

As part of our interest in 1,8-bis(phosphino)-naphthalene ligands, we have also studied their behavior toward oxygen, sulfur, selenium and tellurium. The resulting phosphine chalcogenides are useful model compounds for the resolution of racemic, pro-chiral phosphines, such as **1e**, with chirality at phosphorus [8], and may be used for the complexation of coinage metals [9] and in metal extraction [10].

RESULTS AND DISCUSSION

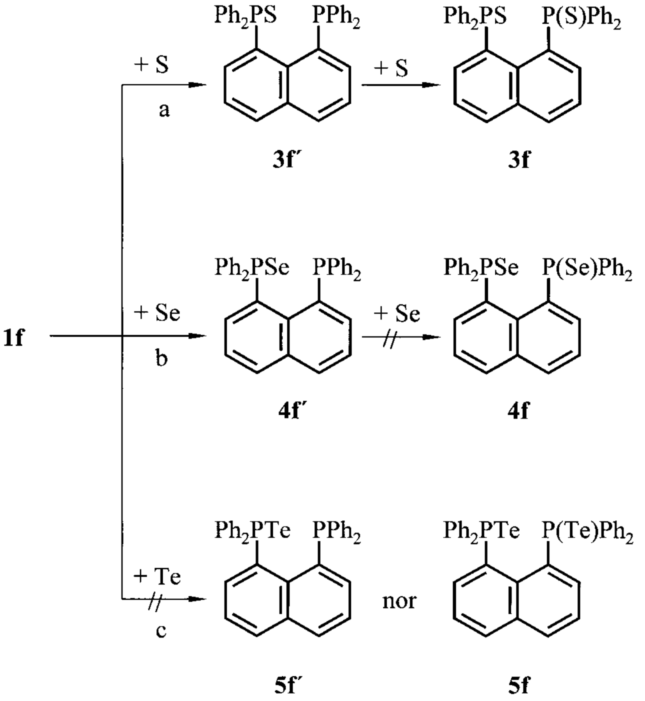
Oxidation Reactions of 1,8-Bis(phosphino)naphthalenes

In contrast to previous reports [3a,3c,7], in which 1,8-bis(dimethylphosphino)naphthalene (**1a**) and 1,8-bis(diphenylphosphino)naphthalene (**1f**) were described as air-stable solids, we found that, apart from the bulky 1,8-bis(phenyl-*tert*-butylphosphino)naphthalene (**1e**), 1,8-bis(diorganophosphino)naphthalenes **1a–d** and **1f** were air sensitive, even in the solid state. We ascribed this behavior to a mutual enhancement of basicity of the phosphino groups caused by their spatial proximity [4a].

The bis(phosphine oxides) **2a–d** and **2f** were thus prepared by exposing the corresponding bis(phosphines) **1a–d** and **1f** to air, while **2e** was obtained by oxidation of **1e** with $H_2O_2 \cdot (H_2N)_2C(:O)$ in dichloromethane (Scheme 3). The bis(phosphine oxides) **2a**, **2b**, **2d–f** are colorless solids, which are readily soluble in chlorinated solvents ($CHCl_3$, CH_2Cl_2) but poorly soluble in ethers (THF, Et_2O) and in alcohols (MeOH, EtOH).

Treatment of **1f** with two equivalents of sulfur in toluene at +80°C selectively afforded the bis(phosphine sulfide) **3f** (dppnS_2). The reaction proceeded via the phosphine sulfide **3f**′, which was completely transformed to **3f** in the presence of sulfur (Scheme 4a). Compound **3f** was isolated as a yellow, air-stable solid, which is soluble in all common nonpolar organic solvents.

The reaction of **1f** with two equivalents of grey selenium powder, carried out under standard conditions [11], did not afford the bis(phosphine selenide) **4f**. Instead, only the phosphine selenide **4f**′ (dppnSe) was obtained (Scheme 4b). Even after prolonged heating of **4f**′ with excess selenium in toluene, formation of **4f** could not be observed. Similarly, treatment of **1f** with elemental tellurium in boiling toluene afforded neither the bis(phosphine telluride) **5f** nor the phosphine telluride **5f**′ (Scheme 4c). We ascribe this behavior to the bulk of the seleno- and the tellurophosphinyl groups and to the inherent instability of the latter [12]. All isolated new compounds were characterized by a combination of ^{1}H, ^{13}C, and $^{31}P\{^{1}H\}$ (**2c**) NMR spectroscopy, IR spectroscopy, electron impact–mass spectrometry (EI-MS),



SCHEME 4 Reaction of **1f** with elemental sulfur, selenium, and tellurium.

and elemental analysis. X-ray crystal structure determinations were carried out for **2a**, *RR/SS*-**2e**, **2f**, and **3f**.

The phosphine chalcogenides **3f**′ and **4f**′ have potential significance as hemilabile, mixed-donor ligands in coordination chemistry. Compound **3f**′ could even play a role in homogeneous catalysis [13]. Their preparation and characterization together with their coordination chemistry is described in another article [14].

^{13}C NMR Spectra

The ^{13}C NMR data of compounds **2a, 2b, 2d–f**, and **3f** are summarized in Table 1. The atom numbering (C, H, P) is explained in Scheme 5. The assignment of the signals and the evaluation of the coupling constants are based on 2D experiments (HH, CH correlation spectroscopy [COSY], correlation spectroscopy in long-range coupling [COLOC] [2f], and CH H-detected heteronuclear multiple quantum, coherence via direct coupling [HMQC]/heteronuclear multiple bond connectivity by 2D multiple quantum NMR [HMBC] [2e,3f]) or on a comparison of the NMR data of **2a, 2b**, and **2d** with those of **2e**.

The quaternary carbon atoms C-4a, C-8a, and C-1,8 of the naphthalenediyl unit gave rise to characteristic signals. For C-4a and C-8a, which experience coupling to both phosphorus nuclei P-1 and P-2 because of their symmetrical orientation, triplets were observed at $\delta_C \approx 133$–136 (C-4a) and $\delta_C \approx 131$–134 (C-8a) with typical values of $^3J_{CP} \approx 8$–10 Hz and $^2J_{CP} \approx 4$–8 Hz. For C-1 and C-8 doublets of doublets with $^1J_{CP} \approx 95$–108 Hz and $^3J_{CP} \approx 2$–3 Hz due to coupling to P-1 and P-2 were observed between $\delta_C \approx 121$ and $\delta_C \approx 133$. In the ^{13}C NMR spectrum of **2d**, $^3J_{CP}$ was unresolved. Interestingly, a doublet of doublets with a small coupling of $^4J_{CP} = 1.3$ Hz was observed for C-2,7 in the spectrum of **2b**.

In the spectra of the parent phosphines **1a–f**, the carbon atoms C-α, C-β, and C-γ, as well as C-i in **1e** showed some interesting NMR-spectroscopic features. For C-α in **1a** and **1e**, C-β and C-β' in **1b–e**, C-γ and C-γ' in **1d**, and C-*i* in **1e**, virtual triplets were observed. This was interpreted as direct coupling through space that resulted from a considerable P-P interaction via the nonbonding electron pairs at P-1 and P-2 [3a,4a]. In the bis(phosphine oxides), no nonbonding electron pairs were available for through space interactions. Thus, for C-α in **2a, 2b**, and **2e**; C-β in **2b**; C-γ in **2d**; C-*i*, C-*o*, C-*m*, and C-*p* in **2f** and **3f**; only doublets were observed that resulted from direct coupling to the next phosphorus nucleus. Surprisingly, the ^{13}C NMR spectrum of **2e** showed a doublet of doublets for C-*i* with $^1J_{CP} \approx 52$ Hz and $^5J_{CP} \approx 3$ Hz.

As was expected, the δ(C-α) values of the substituents R and R′ at phosphorus increased in the order Me < Et < Cy < *t*Bu/Ph (**2a** < **2b** < **2d** < **2e**) (β-effect) whereas J(CP) values decreased in the order $^1J_{CP} > {}^3J_{CP} > {}^2J_{CP} > {}^4J_{CP}$.

At room temperature, the ^{13}C (and ^{1}H) NMR spectra of **2d** and **3f** displayed broad signals indicative of dynamic behavior. In the ^{1}H NMR spectrum of **3f**, the signal for *o*-H was broad and unresolved, and therefore C-*o* could not be observed in the CH HMQC and CH HMBC experiments. We suggest that in dppnS$_2$ (**3f**) rotation of the phenyl groups about the P-C(phenyl) bond is hindered compared to rotation of the phenyl groups in the less bulky dppnO$_2$ (**2f**).

^{1}H NMR Spectra

The ^{1}H NMR spectra of **2a** and **2b** showed the expected ABC signal pattern for the aromatic protons of the 1,8-naphthalenediyl units with typical *J*-values (without ^{31}P: [AA′BB′CC′] spin systems). Due to the presence of naphthalenediyl and phenyl groups, the aromatic region in the ^{1}H NMR spectra of **2e, 2f**, and **3f** was complex.

In the ^{1}H NMR spectra of the phosphines **1a–e** the aliphatic region was complicated by (a) coupling of protons with P-1 and P-2 (X and X′), and (b) dias-

TABLE 1 $^{31}P\{^1H\}$ and ^{13}C NMR[a] Data of 1,8-Naphthalenediyl-bis(phosphine oxides) **2a, 2b, 2d–f** and of the Bis(phosphine sulfide) **3f** [in $CDCl_3$, rel. H_3PO_4 (ext. = 0) and $CDCl_3$ (int. = 77.05): δ, J_{PC} in Hz and multiplicity in (O)]

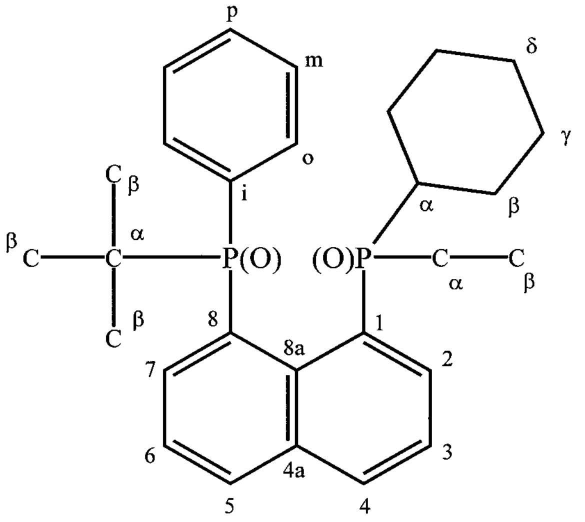
Compound (δ_P^b)	*C-1,8*	*C-2,7*	*C-3,6*	*C-4,5*	*C-4a*	*C-8a*	*C-i*	*C-o*	*C-m*	*C-p*	*C-α*	*C-β*
2a	132.70	131.72	124.54	131.96	134.06	131.18	—	—	—	—	21.17	—
	102.4, 2.5	12.8	15.8	2.9	8.8	5.3					73.8	
(39.9)	(dd)	(d)	(d)	(d)	(t)	(t)					(d)	
2b	131.18	131.80	124.41	131.60	133.80	133.18	—	—	—	—	25.00	6.10
	95.3, 2.3	12.0, 1.3	14.4	3.1, 1.3	8.3	4.2					70.3	5.5
(48.9)	(dd)	(dd)	(d)	(dd)	(t)	(t)					(d)	(d)
2d[d]	127.91	131.24	124.39	—	133.19	134.09	26.18	38.43	26.51	—	—	—
	101	—	13.2		8	4	31.1	br	12.8			
(46.3)	(d)	(br, m)	(d)		(t)	(t)	(d)	(m)	(d)			
2e	130.74	134.24	124.09	132.35	133.76	133.70	130.72	131.53	127.58	131.02	36.99	25.63
	98.2, 2.2	—	13.9	—	8.1	covered	51.9, 2.9	8.5	11.5	—	72.2	—
(38.6)	(dd)	(s)	(d)	(s)	(t)	(t)	(dd)	(d)	(d)	(s)	(d)	(s)
2f	129.96	137.63	123.99	132.78	134.30	134.44	137.85	131.41	137.72	130.42	—	—
	107.7, 2.4	12.2	14.9	2.9	9.0	6.0	106.8	9.4	12.2	2.4		
(31.5)	(dd)	(d)	(d)	(d)	(t)	(t)	(d)	(d)	(d)	(d)		
3f	121.40	142.21	126.11	138.36	135.60	133.00	126.70	131.80	129.67	134.12	—	—
	97.5, 3.2	13.6	15.2	—	9.7	7.5	112.5	10.8	13.3	2.9		
(46.2)	(vdd)	(d)	(d)	(s, br)	(t)	(t)	(d)	(d)	(d)	(d)		

[a] Recorded at 50.3 MHz; assignments are based on CH COSY, COLOC (**2f**) and HC HMBC, HC HMQC (**2e, 3f**) determinations at 100.61 MHz or on comparison (**2a, 2b, 2d**, with **2e**).

[b] *2c*: $\delta_P = 52.4$.

[c] ^{31}P NMR: $\delta_P = 48.9$ [m_c (≈ octet), $J_{PH} \approx 13$ Hz].

[d] C-*i*, -*o*, -*m*, -*p* denote C-α, -β, -γ, -δ, respectively.



SCHEME 5 The atom numbering (C, H, P) in 1,8-bis(phosphinyl)naphthalenes.

tereotopy of methylene and/or methyl protons in the case of **1b–e** [4a]. The spectra of the bis(phosphines) thus displayed signals corresponding to spin systems of the type $[A_6A'_6XX']$ (**1a**) [3a], $[A_6A'_6B_4B'_4XX']$ (**1b**), $[A_2A'_2B_4B'_4C_4C'_4D_2D'_2XX']$ (**1d**) and $[A_9A'_9XX']$ (**1e**) (diastereotopy of protons was not taken into account). Hence, for the methyl protons in **1a** and **1e**, virtual triplets were observed, whereas the methyl protons in **1b** gave a virtual quintet. In the ^{31}P-decoupled spectra, the virtual triplets were simplified to singlets and the virtual quintet was reduced to a virtual triplet. Similarly, in the bis(phosphine oxides), doublets (**2a, 2e**) and a doublet of triplets (**2b**) were observed for the methyl protons, formally corresponding to $[A_6X]$–(**2a**), $[A_9X]$–(**2e**) and $[A_6B_4X]$–(**2b**) spin systems. This again illustrates how the nuclear magnetic through space interaction in the bis(phosphines) was reduced by oxidation of the phosphorus atoms. Our results support the explanation of magnetic through space interactions in 1,8-bis(phosphino)naphthalenes by (1) a mutual overlap of the nonbonding electron pairs on phosphorus or (2) an H-contact with the electron pair on the neighboring P atom by rotation of the R_2P group about the P–C(naphthyl)-axis [3a].

The proton NMR spectrum of **2d** showed very complex, unresolved, broad multiplets between $\delta_H = 0.50$ and $\delta_H = 4.00$ and at $\delta_H = 7.65$. Apparently, a thorough ^1H and ^{13}C NMR spectroscopic investigation of **2d** is complicated by line-broadening caused by dynamic processes.

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

The $^{31}P\{^1H\}$ NMR spectra of the bis(phosphine oxides) **2a–f** (recorded in $CDCl_3$) showed sharp singlets. The δ_P values (Table 1) were in a range typical of phosphine oxides and sulfides [15] (cf. $Ph_3P(:O)$,

δ_P = 27.0 and Ph$_3$P(:S), δ_P = 42.6). The δ_P values of **2a–f** were shifted to high energy in the order [R,R′]: [Ph,Ph] (**2f**); [*t*Bu,Ph] (**2e**); [Me,Me] (**2a**); [Cy, Cy] (**2d**); [Et,Et] (**2b**); [*i*Pr, *i*Pr] (**2c**). For **2c** and particularly **2d**, the signals were considerably broader than those of the corresponding bis(phosphines), indicating hindered rotation about the P–C(naphthyl) bonds.

Mass Spectrometry and IR Spectroscopy

For further structural characterization, compounds **2a, 2b, 2d–f**, and **3f** were subjected to a EI mass spectrometric investigation (see Table 2). Molecular ions [M]$^+$ or [M-H]$^+$ were observed for all the products. Fragmentation occurred mainly by stepwise loss of the alkyl or aryl groups via P–C bond cleavage or elimination of the chalcogenide atoms. In the spectra of compounds **2a, 2b, 2e**, and **2f**, the ions that resulted from loss of one phosphinyl group formed the base peak (100% intensity), whereas in **2d** and **3f** the ions [M-R]$^+$ and [M-2X-2R]$^+$ were observed with 100% intensity.

In the IR spectra of the bis(phosphine oxides), **2a, 2b**, and **2d–f**, characteristic strong absorption bands were observed between 1170 cm^{-1} (**2e**) and 1195 cm^{-1} (**2f**). The bis(phosphine sulfide) **3f** showed typical absorptions at 663 (w) and 644 (m) cm^{-1} [15].

X-Ray Crystal Structure Determinations

The molecular structures of **2a**, (*S,S*)-**2e**, **2f**, and **3f** are shown in Figures 1–3.

Whereas (*S,S*)-**2e** and **3f** display crystallographic two-fold symmetry, the structures of **2a** and **2f** display only approximate noncrystallographic C$_2$-symmetry about the C9–C10 bond (Figure 3). Perhaps surprisingly, the compounds **2f** and **3f** are not isostructural. The P(:O)RR′ groups in **2a**, (*S,S*)-**2e**, and **2f** lie close to each other, with P···P distances between 337.9 and 347.9 pm (Table 3), still well within 380 pm, the double van der Waals radius of phosphorus [16], and O···O distances between 291.9 and 298.3 pm. In the bis(phosphine sulfide) **3f**, the P···P [374.6 pm] and the S···S [368.5 pm] distances are considerably larger than the P···P and the O···O distances in the bis(phosphine oxides) (see following section). As in the phosphines **1a**/**1a′** (**1a′** denotes a second independent molecule), **1e**, and **1f**, the close proximity of the two bulky *peri*-substituents leads to in-plane and out-of-plane displacement of the P atoms, the latter being the main feature of the structures studied in this article. We were particularly interested in the effects of quaternization of the bis(phosphines) by the addition of an oxygen or sulfur atom on the geometry of the bis(phosphine chalcogenides) compared to the bis(phosphines).

As in the bis(phosphines), the twisting of the molecules is evident in the torsion angles P1–

TABLE 2 Mass Spectrometric data of 1,8-phosphinyl-substituted naphthalenes **2a, 2b, 2d–f** (X = O) and the phosphine sulfide **3f** (X = S)

	2a	**2b**	**2d**	**2e**	**2f**	**3f**
Fragment	$R = R' = CH_3$	$R = R' = C_2H_5$	$R = R' = C_6H_{11}$	$R = C_4H_9, R' = C_6H_5$	$R = R' = C_6H_5$	$R = R' = C_6H_5$
[M]$^+$	{280}	{336}	{552}	488 (0.4)	528 (0.6)	560 (6)
[M-H]$^+$	279 (6)	335 (.24)	551 (0.50)	—	—	—
[M-X][a]		321[b] (.06)	—	472 (0.2)	—	528 (20)
[M-R][a]	265 (20)	307 (45)	**469 (100)**	431 (73)	451 (2.8)	483 (1)
[M-X-R]$^+$	249 (1)	—	—	415 (2)	435 (1.8)	451 (50)
[M-2R]$^+$	—	279[a] (2)	387[b] (11)	375[b] (20)	—	—
[M-X-2R]$^+$	—	—	—	—	—	375 (31)
[M-2X-R]$^+$	—	—	—	—	—	419[b] (33)
[M-2X-2R]$^+$	—	—	—	—	—	**343**[b] (**100**)
[M-P(:X)RR′]$^+$	**203**[c] (**100**)	**231 (100)**	339 (79)	**307 (100)**	**327 (100)**	—
[M-2R-R′]$^+$	235 (<1)	250[a] (4)	305[b] (25)	297 (44)	—	—
[M′-R]$^+$[d]	189[b] (4)	203[a] (2)	—	251[b] (46)	249 (24)	—
[M′-R-X]$^+$[d]	—	—	—	233 (30)	—	—
[M′-R-R′]$^+$[d]	173 (16)	173 (15)	—	173 (30)	—	—
[M′-R-R′-X]$^+$[d]	157 (3)	157 (11)	—	157 (12)	—	—
[M-2P(:X)R$_2$]$^+$	127 (3)	128[b] (4)	—	—	—	—

Note: { }, not observed; bold, base peak; intensity indicated by values in parentheses.

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

[b] + 1H.

[c] − 1H.

[d] [M′] = [M-P(:X)RR′].

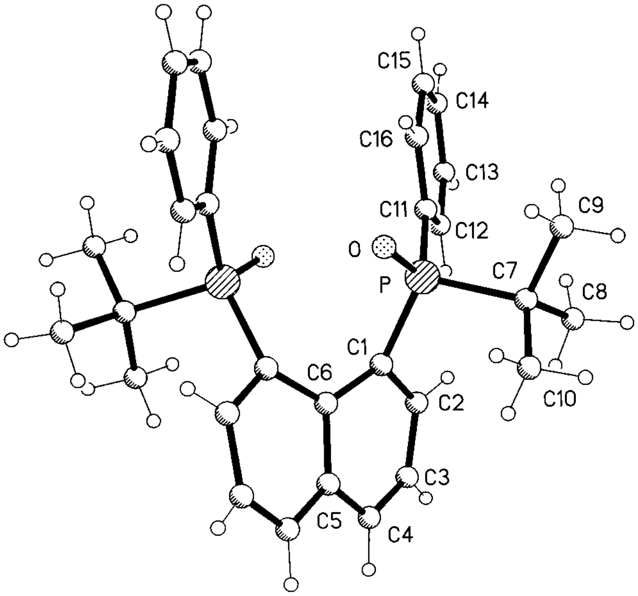


FIGURE 1 Molecular structure of **2e** in the crystal; (*S,S*)-enantiomer.

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 39.8 (1)° in the bis(diphenylphosphine oxide) **2f** to values as high as 63.8 (1)° in the bis(*tert*-butylphenylphosphine oxide) (*S,S*)-**2e**, the largest value that has been observed in 1,8-P,P-disubstituted naphthalenes to date. The out-of-plane distortion in the bis(dimethylphosphine oxide) **2a** is unexpectedly large, compared to the bis(diphenylphosphine oxide) **2f** (Table 3). It should be noted that the pseudo-torsion angle P1–C1 ··· C8–P2 in **2a** [48.45 (7)°] is even larger than the angle in the bulky bis(*tert*-butylphenylphosphine) **1e** [46.54 (7)°]. Again, there seems to be no simple correlation between out-of-plane distortion in the bis(phosphine oxides) and the steric bulk of the P(:O)RR′ groups. Apart from the out-of-plane distortion, in-plane distortion of the P(:X)RR′ groups, which is indicated by a widening of the bay angles P1–C1–C9, P2–C8–C9 and C1–C9–C8 is apparent in **2a, 2f**, and **3f** (Table 4). Widening of the bay angles was also observed in **1a**/**1a′** and **1f**. Again, there is no obvious trend relating in-plane distortion and steric bulk of the $P(:X)R_2$ groups. It should be noted that in **2e** the angles P1–C1–C9 and P2–C8–C9 are smaller than the ideal sp^2 angle of 120°. This observation was also made for the corresponding bis(phosphine) **1e**.

The displacement of the phosphinyl 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 8.6 pm in **2a** to 13.0 pm in **3f**. The *peri*-carbon atoms C1 and C8 and also C4 and C5 show a displacement 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 angle in naphthalene (119–121° [17]).

The conformations of the phosphinyl and the thiophosphinyl groups relative to the naphthalene plane (Figure 3) can be described by the orientation of the P = X bonds toward that plane. Torsion angles X–P1–C1–C2 and X–P2–C8–C7 of 180° indicate a bisecting conformation [4a] of the $P(:X)R_2$ groups relative to the C_{10}-plane, whereas angles of about 120° indicate an eclipsed conformation (Scheme 6 and Table 5). These angles range from − 149.7 (2)° at P1 in **2f** to − 168.00 (13)° in **2e**. In the case of **2e**, the conformation is approximately bisecting, in the other molecules the conformation lies between the ideal forms bisecting and eclipsed. In all four molecules, the chalcogenide atoms point to opposite faces of the naphthalene plane.

The CPC bond angles vary from 101.8(1)° (C17–P1–C11 in **2f**) to 105.84(8)° (C11–P–C7 in **2e**). P–C(sp^2) and P–C(sp^3) bond lengths are normal [18]; the longer P–C(*t*Bu) bond in **2e** [186.6(2) pm] lies in the usual range for P–C(*t*Bu) bonds found from a CCDC search [17] (11 hits, mean value: 185.5 pm, min.: 182.2 pm, max.: 187 pm).

In all four structures, nonclassical hydrogen bonds (C–H ··· X) were found (Table 6). In **2f**, there is a short [250 pm] and approximately linear [170.6°] hydrogen bond. In **3f**, because sulfur is a weaker acceptor, only a weak C–H ··· S contact [294.0 pm, 143.2°] was observed, which may be the reason for the nonisostructural crystallization.

In summary, the structures of the bis(phosphine chalcogenides) **2a, 2e, 2f**, and **3f** are more strongly distorted than those of the corresponding bis(phosphines) **1a**/**1a′**, **1e**, and **1f**. A comparison between the oxidized and the sulfurated compounds **2f** and **3f** shows a significantly bigger distortion in **3f**. As in the case of the bis(phosphines), there is no simple correlation between the type and extent of distortion and the steric bulk of the organic substituents on phosphorus in the bis(phosphine chalcogenides).

EXPERIMENTAL

General experimental methods were as described previously [4a]. The 1,8-bis(diorganophosphino)

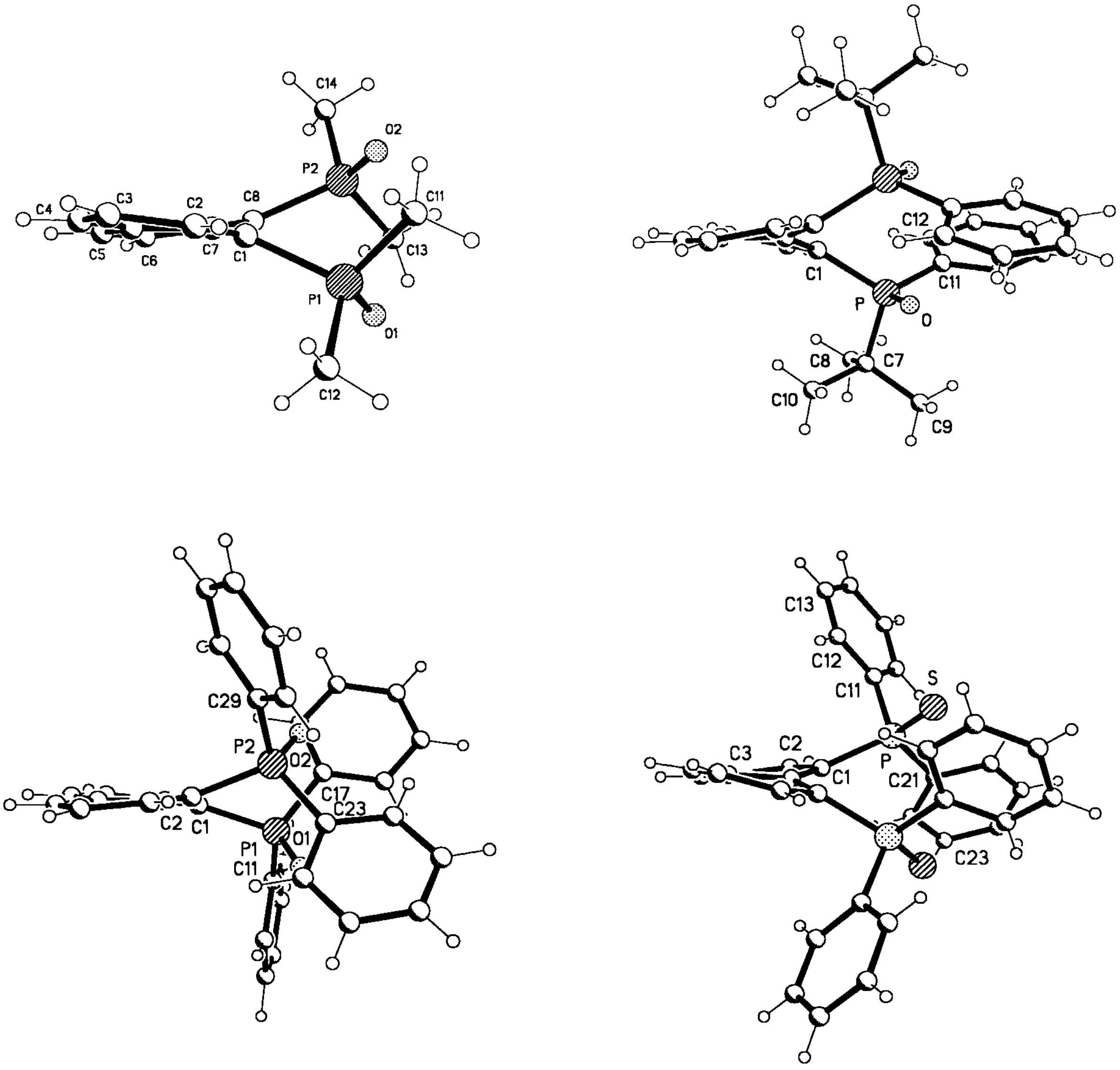


FIGURE 2 Molecular structures of **2a**, (*S,S*)-**2e**, **2f**, and **3f** viewed along the C2···C9···C7 axis to illustrate the amount of out-of-plane displacement of the P(:X)R_2 groups (X = O, S).

naphthalenes **1a–f** were prepared by literature methods [3a,4a,7]. $H_2O_2 \cdot (H_2N)_2C(:O)$ was obtained from Merck-Schuchhardt, Darmstadt, and elemental, grey selenium (99.5%) from Acros Chemicals, Gelnhausen, Germany. NMR: Bruker AC 200 (^{1}H: 200.1 MHz, ^{13}C: 50.3 MHz, ^{31}P: 81.0 MHz), Bruker AM 400 and DRX 400 (^{1}H: 400.13 MHz, ^{13}C: 100.61 MHz). $CDCl_3$ was used throughout as solvent. Reference substances were $SiMe_4$ (TMS) or $CHCl_3$ (int.) at δ_H = 7.25 for ^{1}H and δ_C = 77.05 for ^{13}C NMR spectra and 85% H_3PO_4 (ext.) at δ_P = 0 for ^{31}P NMR spectra. The atom numbering (C, H, P) is summarized in Scheme 5. Assignments were supported by CH correlation spectroscopy (COSY) and COLOC experiments (AM 400) (**2f, 3f**) or HC HMBC and HC HMQC experiments (DRX 400) (**2e**); m_c denotes a complex multiplet. Elemental analyses were carried out by Analytisches Laboratorium des Instituts für Anorganische und Analytische Chemie, Analytisches Laboratorium des Instituts für Pharmazeutische Chemie der Technischen Universität Braunschweig, and by Pracownia Mikroanalizy, Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, Łódź, Poland.

*Preparation of 1,8-Bis(diphenylphosphinyl) naphthalene (dppnO$_2$) (**2f**).*

Dppn **1f** (0.6 g, 1.21 mmol) was stored in air. After three weeks, the intensive yellow color had faded,

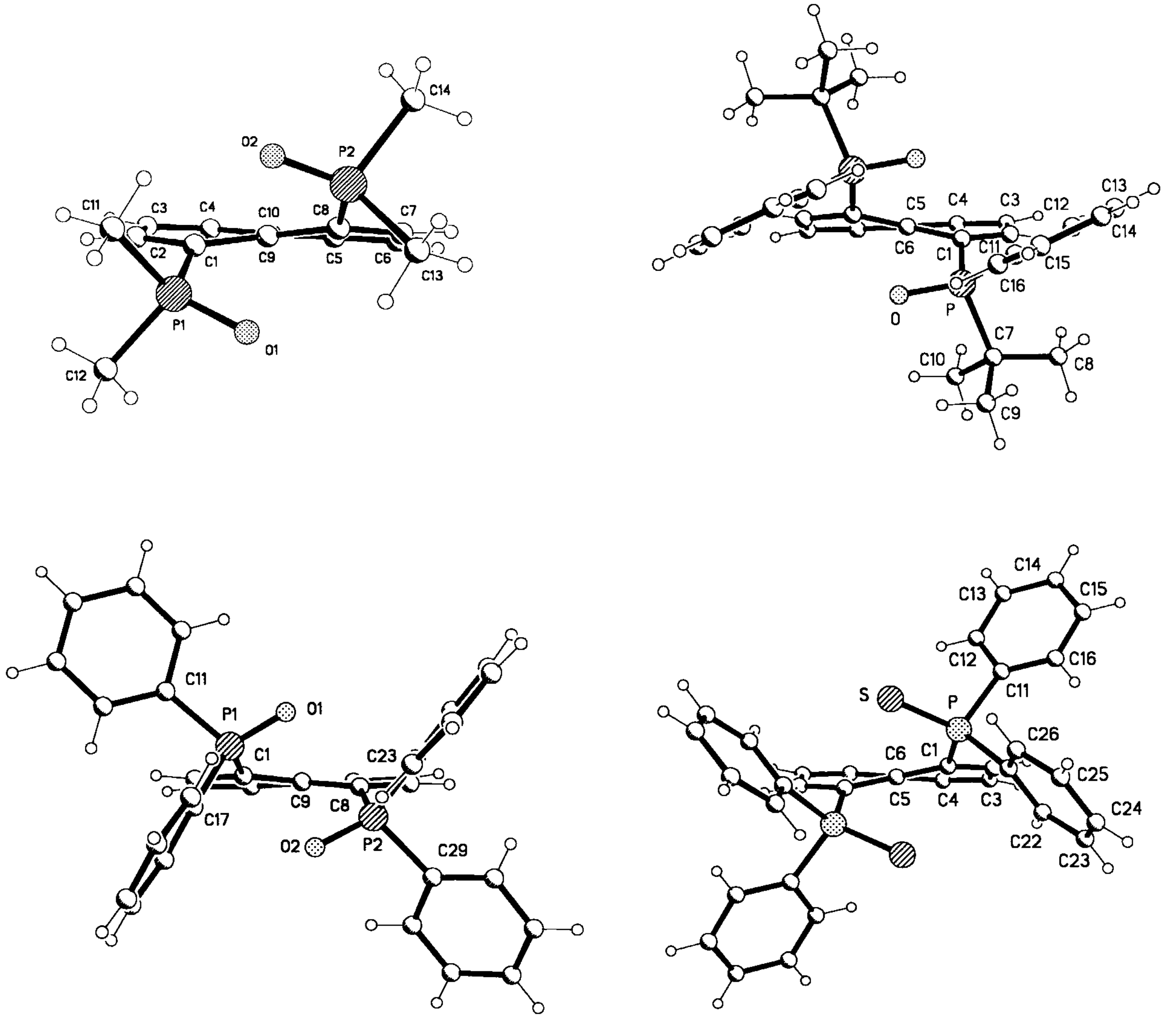


FIGURE 3 Molecular structures of **2a**, (*S,S*)-**2e**, **2f**, and **3f** viewed along the C9–C10 bond to illustrate the amount of out-of-plane displacement of the P(:X)R$_2$ groups (X = O, S), their conformation relative to the naphthalene ring, and the exact or approximate C$_2$ symmetry. Because of crystallographic symmetry, the bond is labeled as C5–C6 on the right-hand side of the figure.

and a colorless product was formed. After three months, oxidation was almost complete, as was observed from the ^{31}P{^{1}H} NMR spectrum. In order to take the oxidation to completion, the crude product was dissolved in 10 mL of dichloromethane. The solution was saturated with air and stirred at room temperature for 12 hours. After removal of the solvent in vacuo 0.611 g (1.16 mmol, 96%) of a colorless, crystalline solid were obtained (m.p. > 230°C, decomp.). Alternatively, **2f** can also be prepared by oxidation of **1f** with (1) $H_2O_2 \cdot (H_2N)_2C(:O)$ or (2) aqueous H_2O_2: (1) To a solution of 0.490 g (0.987 mmol) dppn in 15 mL of dichloromethane, 0.230 g (2.4 mmol, 2.5 eq) of $H_2O_2 \cdot (H_2N)_2C(:O)$ was added in small portions with stirring at room temperature. The mixture was stirred overnight. After removal of the urea adduct by filtration and following removal of the solvent, 0.507 g (0.96 mmol, 97%) of a colorless powder was obtained. (2) To a solution of 0.624 g (1.26 mmol) dppn in 20 mL of dichloromethane, 0.5 mL of aqueous H_2O_2 (35%) was added at room temperature. After stirring at room temperature overnight, drying with Na_2SO_4 (ca. 3 g), and removing the solvent, 0.648 g (1.23 mmol, 97%) of a colorless powder were obtained. Single crystals suitable for an X-ray structure analysis were obtained from a saturated solution of **2f** in dichloromethane/*n*-hexane by slow evaporation at room temperature. See Table 1 for ^{13}C and ^{31}P NMR data and Scheme 5 for the numbering of the H- and C-atoms. ^{1}H NMR (400

TABLE 3 Out-Of-Plane Distortion in Bis(phosphines) **1a**/**1a**′[a] [4b], **1e** [4a], and **1f** [3c], in Their Oxides **2a, 2e**, and **2f**, and in dppnS_2 (**3f**), 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 Carbon Atoms

	Torsion Angles			*Out-Of-Plane Disp.*		*Mean Devn.*	*Nonbonded Distances*	
Compound	*P1–C1···C8–P2*	*P1–C1–C9–C8*	*P2–C8–C9–C1*	*P1*	*P2*	*C1 to C10*	*P1···P2*	*X1···X2*[b]
1a[a]	30.7 (2)	18.0 (4)	18.0 (4)	+37.8 (5)	−37.8 (5)	1.0	307.0 (1)	—
1a′	20.0 (2)	11.9 (2)	11.9 (2)	+29.7 (6)	−29.7 (6)	<0.1	303.6 (1)	—
1e	46.5 (1)	26.7 (2)	26.5 (2)	+88.9 (2)	−91.2 (2)	9.6	305.6 (1)	—
1f[c]	17.7	13.4 (7)	7.7 (7)	+34	−50	6.6	305.2	—
2a	−48.5 (1)	−29.4 (4)	−28.1 (4)	94.1 (3)	−93.9 (3)	10.2	343.2 (1)	293.0 (3)
2e	63.8 (1)	36.5 (1)	−36.5 (1)[d]	−121.1 (1)	121.1 (1)[d]	14.6	347.9 (1)	298.3 (2)
2f	39.8 (1)	22.2 (4)	25.5 (4)	70.3 (3)	−81.5 (3)	7.8	337.9 (1)	291.9 (3)
3f	−53.4 (1)	−32.4 (1)	32.4 (1)[d]	107.8 (1)	−107.8 (1)[d]	14.9	374.6 (1)	368.5 (6)

Note: Angles in degrees; distances in pm.

[a] The structure of 1,8-bis(dimethylphosphino)naphthalene consists of two independent molecules denoted as **1a** and **1a**′.

[b] **2a, 2e, 2f**: X = O; **3f**: X = S.

[c] Values taken from Ref. [3c] or calculated from deposited data; standard deviations were not available for some values.

[d] By symmetry.

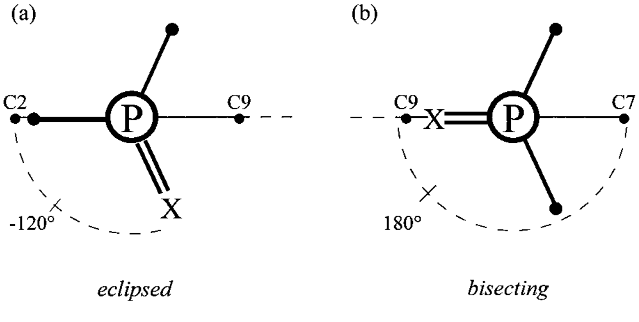
TABLE 4 In-Plane Distortions in Bis(phosphines) **1a**/**1a**′[a] [4b], **1e** [4a], and **1f** [3c], in Their Oxides **2a, 2e**, and **2f**, and in dppnS_2 (**3f**) as Indicated by the Bay Angles P1–C1–C9, P2–C8–C9, and C1–C9–C8 (in °)

Compound	*P1–C1–C9*	*P2–C8–C9*	*C1–C9–C8*
1a	121.6 (4)[b]	121.6 (4)[c]	125.5 (6)
1a′	123.1 (9)[b]	123.1 (9)[c]	125.5 (6)
1e	118.1 (1)	118.4 (1)	123.5 (1)
1f	124.5 (3)	123.0 (4)	125.3
2a	123.0 (2)	121.9 (2)	126.3 (3)
2e	117.8 (1)[b]	117.8 (1)[c]	126.0 (2)
2f	123.2 (2)	124.1 (2)	127.3 (3)
3f	125.1 (1)[b]	125.1 (1)[c]	128.1 (1)

[a] **1a** and **1a**′ denote two independent molecules.

[b] Labelled as P1–C1–C6 in Figures 1–3 because of crystallographic symmetry.

[c] By symmetry.



SCHEME 6 Idealized *eclipsed* (a) and *bisecting* (b) conformations of 1,8-bis(phosphinyl)naphthalenes. Numerical values are pseudo torsion angles (see text).

TABLE 5 Conformations of the P(:X)R_2 Groups, Relative to the C_{10}-Plane, Described by the Orientation of the P=X Bonds (°)

Compound *Torsion Angle*	**2a**	**2e**	**2f**	**3f**
X–P1–C1–C2	157.5 (2)	−168.00 (13)	−149.7 (2)	158.42 (7)
X–P2–C8–C7	162.5 (2)	−168.00 (13)[a]	−153.8 (2)	158.42 (7)[a]

[a] By symmetry.

MHz): $\delta = 7.30$–7.44 [m_c, 14H, H-*o* or H-*m*, H-*p*, and H-3], 7.48 [m_c, 8H, H-*o* or H-*m*], 7.71 [m_c ($\approx$ ddd), $^3J(H_2H_3) = 7.2$ Hz, $^4J(H_2H_4) = 1.0$ Hz, 2H, H-2], 7.90 [$m_c \approx$ dd, $^3J(H_3H_4) \approx 8.1$ Hz, $^4J(H_2H_4) \approx 1.3$ Hz, 2H, H-4]; IR (KBr): $\tilde{\nu}(\mathrm{cm}^{-1}) = 3052$ (w), 1556 (w), 1482 (w), 1435 (m), 1322 (w), 1217 (w, sh), 1195 (vs, $\nu_{P=O}$), 1158 (w), 1112 (m), 1101 (m), 891 (m), 822 (w), 772 (m), 748 (m), 713 (s), 692 (s), 566 (s), 520 (s), 434 (m); EI-MS: see Table 2; Anal. found: C, 77.03%; H, 5.17%; P, 11.64%. Calcd for $C_{34}H_{26}O_2P_2$ (528.53): C, 77.27%; H, 4.96%; P, 11.72%. The preparation of compounds **2a, 2b, 2d**, and **2e** was conducted analogously to the preparation of **2f** [method (1)]:

1,8-Bis(dimethylphosphinyl)naphthalene (**2a**)

Starting from 2.17 g (8.74 mmol) of 1,8-bis(dimethylphosphino)naphthalene (**1a**), CH_2Cl_2 (10 mL) and 1.80 g (19 mmol, 2.2 eq) of $H_2O_2 \cdot (H_2N)_2C(:O)$, 2.11 g (7.53 mmol, 86%) of a colorless solid (m.p. > 200°C, decomp.) were obtained by recrystallization from CH_2Cl_2/Et_2O. Crystals suit-

TABLE 6 Non-Classical Hydrogen Bonds for **2a, 2e, 2f** and **3f** [pm] and [°]

Compound	*D–H···A*	*d(D–H)*	*d(H···A)*	*d(D···A)*	*<(DHA)*	*Sym. Transformations for Equiv. Atoms*
2a	C11-H11B···O1#1	98	239	335.4 (4)	168.5	#1 0.5 − x, − 0.5 + y,.z #2 − x, 0.5 + y,.0.5 − z
	C6-H6···O2#2	95	251	331.2 (4)	142.7	
2e	C3-H3···O#1	95	260	351.0 (2)	159.9	#1 x, − y,.0.5 + z #2 x, 1 − y,.0.5 + z
	C14-H14···O#2	95	252	343.5 (2)	161.1	
2f	C27-H27···O1#1	95	250	344.1 (4)	170.6	#1 − x, y,.0.5 − z
3f	C13-H13···S#1	95	294	374.2 (1)	143.2	#1 2.5 − x, 0.5 − y,.1 − z

able for X-ray diffraction were obtained from $CDCl_3$ by slow evaporation of the solvent. See Table 1 for ^{13}C and ^{31}P NMR data and Scheme 5 for the numbering of the H- and C-atoms. ^1H NMR (200 MHz): $\delta = 1.78$ [d, $^2J(PH) = 12.8$ Hz, 12H, α-H, $P(:O)C\underline{H}_3$], 7.42 [m_c ($\approx$ ddd), $^3J(H_2H_3) \approx 7.6$ Hz, $^4J(H_2H_4) \approx 2.0$ Hz, 2 H, 2-H], 7.61 [m_c ($\approx$ ddd), $^3J(H_3H_4) \approx 7.9$ Hz, $^3J(H_2H_3) \approx 7.0$, $^4J(PH) \approx 1.1$ Hz, 2 H, 3-H], 7.81 [m_c ($\approx$ dq), $^3J(H_3H_4) \approx 8.0$ Hz, $^4J(H_2H_4) \approx 1.6$ Hz, 2 H, 4-H]; IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3053 (w), 3023 (m), 2972 (m), 2912 (m), 1487 (m), 1293 (s), 1189 (s, $\nu_{P=O}$), 1166 (s), 1060 (w), 1005 (w), 946 (s), 859 (m), 831 (s), 727 (m), 463 (w), 406 (m), 360 (m), 309 (m); EI-MS: see Table 2; Anal. found: C, 59.25%; H, 6.57%. Calcd. for $C_{14}H_{18}O_2P_2$ (280.24): C, 60.00%; H, 6.47%.

*1,8-Bis(diethylphosphinyl)naphthalene (**2b**)*

From 302 mg (0.99 mmol) of 1,8-bis(diethylphosphino)naphthalene (**1b**), CH_2Cl_2 (5 mL), and 200 mg (2.13 mmol, 2.15 eq) $H_2O_2 \cdot (H_2N)_2C(:O)$, 246 mg (0.73 mmol, 74%) of a colorless solid (m.p. 164°C) were obtained by recrystallization from CH_2Cl_2/Et_2O. See Table 1 for ^{13}C and ^{31}P NMR data and Scheme 5 for the numbering of the H- and C-atoms. ^1H NMR (200 MHz): $\delta = 0.89$ [m_c ($\approx$dt), $J(PH) = 16.3$ Hz, $J(HH) = 7.6$ Hz, 12 H, $CH_2C\underline{H}_3$, β-H (AA′-part)], 2.15 [m_c, 8 H, $C\underline{H}_2CH_3$, α-H (BB′-part)], 7.41 [m_c ($\approx$ ddd), $^3J(H_2H_3) \approx 7.5$ Hz, $^4J(H_2H_4) \approx 2.3$ Hz, 2 H, 2-H], 7.55 [m_c ($\approx$ ddd), $^3J(H_3H_4) \approx 7.7$ Hz, $^3J(H_2H_3) \approx 7.0$, 2 H, 3-H], 7.80 [m_c ($\approx$ dq), $^3J(H_3H_4) \approx 7.9$ Hz, $^4J(H_2H_4) \approx 1.5$ Hz, 2 H, 4-H]; ^{31}P NMR ($CDCl_3$): $\delta = 48.9$ [m_c ($\approx$voctet), $J \approx 14$ Hz]; IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3052 (w), 2966 (vs), 2933 (s), 2912 (m), 2878 (s), 1938 (m), 1456 (m), 1322 (w), 1179 (s, $\nu_{P=O}$), 1034 (m), 891 (m), 829 (m); EI-MS: see Table 2; Anal. found: C, 63.79%; H, 7.75%. Calcd. for $C_{18}H_{26}O_2P_2$ (336.35): C, 64.28%; H, 7.79%.

*1,8-Bis(dicyclohexylphosphinyl)naphthalene (**2d**)*

From 260 mg (0.5 mmol) 1,8-bis(dicyclohexylphosphino)naphthalene (**1d**), CH_2Cl_2 (5 mL) and 110 mg (1.2 mmol, 2.3 eq) $H_2O_2 \cdot (H_2N)_2C(:O)$, 227 mg (0.41 mmol, 82%) of a colorless solid (m.p. 153 °C) were obtained by recrystallization from CH_2Cl_2/Et_2O. See Table 1 for ^{13}C and ^{31}P NMR data and Scheme 5 for the numbering of the H- and C-atoms. ^1H NMR (400.1 MHz): $\delta = 0.10$–4.00 [m_c, 44 H, cyclohexyl-$C\underline{H}$ and -$C\underline{H}_2$], 7.43 [m_c ($\approx$ t), $^3J(HH) \approx 6.5$ Hz, 2H, 3-H], 7.66 [m_c, br, 2H, 2-H], 7.80 [m_c ($\approx$ d), $^3J(HH) \approx 7.7$ Hz, 2 H, 4-H]; IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3048 (w), 2930 (vs), 2850 (vs), 1448 (m), 1277 (w), 1215 (w), 1181 (m, $\nu_{P=O}$), 1106 (w), 885 (w), 772 (w), 564 (w); EI-MS: see Table 2; Anal. found: C, 73.33%; H, 9.24%. Calcd for $C_{34}H_{50}O_2P_2$ (552.72): C, 73.88%; H, 9.12%.

*rac-1,8-Bis(phenyl-tert-butylphosphinyl)naphthalene (**2e**)*

From 0.158 g (0.35 mmol) *rac*-1,8-bis(phenyl-*tert*-butylphosphino)naphthalene (**1e**), CH_2Cl_2 (5 mL), and 0.98 g (1 mmol, 1.4 eq) $H_2O_2 \cdot (H_2N)_2C(:O)$, 0.140 g (0.28 mmol, 80%) of a colorless solid (m.p. 325–330°C, decomp.) were obtained by recrystallization from CH_2Cl_2/Et_2O. See Table 1 for ^{13}C and ^{31}P NMR data and Scheme 5 for the numbering of the H- and C-atoms. ^1H NMR (200 MHz): $\delta = 0.57$ [d, $J(PH) = 13.6$ Hz, 18 H, $C(C\underline{H}_3)_3$, β-H], 7.50–7.60 [m_c, 8 H, arom. H], 7.93 [m_c ($\approx$ dd), $^3J(H_3H_4) = 8.3$ Hz, $^3J(H_2H_3) = 7.1$ Hz, 2 H, 3-H], 8.06–8.17 [m_c, 6 H, arom. H]; IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3085 (w), 3055 (m), 2981 (s), 2947 (s), 2900 (m), 2865 (m), 1472 (m), 1442 (m), 1360 (w), 1170 (s, $\nu_{P=O}$), 1106 (m), 1009 (w), 878 (w), 750 (m), 691 (m), 611 (m), 566 (m), 537 (m), 513 (m), 397 (w); EI-MS: see Table 2; Anal. found: C, 71.85%; H, 7.41%; P, 11.67%. Calcd for $C_{30}H_{34}O_2P_2$ (488.55): C, 73.76%; H, 7.01%; P, 12.68%.

*Formation of 1,8-Bis(diisopropylphosphinyl)naphthalene (**2c**).*

A small portion of $H_2O_2 \cdot (H_2N)_2C(:O)$ was added to an NMR sample of 1,8-bis(diisopropylphosphino) naphthalene (**1c**) dissolved in $CDCl_3$. The resulting mixture was investigated by $^{31}P\{^1H\}$ NMR spectroscopy. $^{31}P\{^1H\}$ NMR: $\delta = 52.4$.

*Preparation of 1,8-Bis(diphenylthiophosphinyl)naphthalene (**3f**)*

Dppn **1f** (1.24 g, 2.5 mmol) and 0.2 g (6.2 mmol, 2.5 eq) of elemental sulfur were slurried in 20 mL of toluene and heated under reflux for 17 hours. The reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. In the first step, the phosphine sulfide **3f′** was formed, which reacted to the bis(phosphine sulfide) **3f** upon heating in the presence of sulfur (Scheme 4a). After removal of the solvent by rotary evaporation, a yellow solid was obtained, which was taken up in dry methanol. The crude product was purified by recrystallization from a 1:1 mixture of CH_2Cl_2 and *n*-hexane. Yield: 0.66 g (1.18 mmol, 47%) of a colorless solid (m.p. 237–239°C). See Table 1 for ^{13}C and ^{31}P NMR data and Scheme 5 for the numbering of the H- and C-atoms. ^1H NMR (400 MHz): $\delta = 7.10$–7.25 [m_c, 12 H, H-*m*, H-*p*], 7.30 [m_c ($\approx$ dt), $^3J(H_2H_3) \approx 6.9$ Hz, $^3J(H_3H_4) \approx 8.3$ Hz, 2 H, H-3], 7.40 [m_c, 8 H, H-*o*], 7.76 [m_c ($\approx$ ddd), $^3J(H_2H_3) = 7.1$ Hz, $^4J(H_2H_4)$ not resolved, 2 H, H-2], 7.85 [m_c ($\approx$ dq), $^3J(H_3H_4) \approx 8.0$ Hz, $^4J(H_2H_4) \approx 1.0$ Hz, 2 H, H-4]; IR (KBr): $\tilde{\nu}$ (cm^{-1}): 3046 (w), 1479 (w), 1437 (s), 1304 (w), 1096 (m), 879 (w), 817 (w), 766 (m), 742 (m), 721 (s), 700 (m), 663 (w), 644 (m), 616 (w), 538 (w), 521 (w), 498 (s), 454 (w), 423 (m); EI-MS: see Table 2; Anal. found: C, 73.00%; H, 4.51%; P, 10.94%; S, 11.53%. Calcd for $C_{34}H_{26}P_2S_2$ (560.66): C, 72.84%; H, 4.67%; P, 11.05%; S 11.44%.

Reaction of Dppn with Elemental Selenium

Dppn **1f** (0.80 g, 1.60 mmol), grey selenium (0.30 g, 3.80 mmol), and a catalytic amount of $AlCl_3$ were slurried in 20 mL of toluene and heated under reflux for 23 hours. The reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. In the first step, the phosphine selenide **4f′** was formed, which did not react to the bis(phosphine selenide) **4f** upon heating in the presence of an excess of selenium (Scheme 4b). A catalytic amount of AIBN was added, and the mixture was refluxed for 7 hours. No further reactions were observed.

Reaction of Dppn with Elemental Tellurium

A suspension of 0.15 g (0.30 mmol) dppn (**1f**), 0.038 g (0.30 mmol) elemental tellurium, and a catalytic

TABLE 7 Crystallographic Data for **2a, 2e, 2f**, and **3f**

Compound	**2a**	**2e**	**2f**	**3f**
Formula	$C_{14}H_{18}O_2P_2$	$C_{30}H_{34}O_2P_2$	$C_{34}H_{26}O_2P_2$	$C_{34}H_{26}P_2S_2$
M_r	280.22	488.51	528.49	560.61
Crystal habit	colourless prism	colourless, irregular	colourless tablet	colourless prism
Crystal size (mm)	0.75 × 0.50 × 0.30	0.65 × 0.65 × 0.50	0.70 × 0.60 × 0.30	0.44 × 0.22 × 0.15
Temperature (°C)	−100	−100	−130	−130
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	Pbca	C2/c	C2/c	C2/c
Cell constants				
a (pm)	1655.94(14)	1846.0(2)	3459.0(8)	1162.32(12)
b (pm)	1011.15(10)	1159.54(12)	870.2(2)	1522.62(16)
c (pm)	1683.7(2)	1229.36(12)	1921.9(4)	1573.67(16)
β (°)	90	98.954(8)	112.38(2)	93.63(3)
U (nm^3)	2.8192(5)	2.5994(5)	5.349(2)	2.7794(5)
Z	8	4	8	4
D_x ($Mg\ m^{-3}$)	1.320	1.248	1.312	1.340
μ (mm^{-1})	0.300	0.193	0.193	0.330
F(000)	1184	1040	2208	1168
$2\theta_{max}$ (°)	24.99	25.00	25.04	30.55
No. of reflections:				
Measured	2586	4568	8709	11797
Independent	2462	2286	4729	4264
R_{int}	0.019	0.0296	0.0417	0.0495
$wR(F^2$, all refl.)	0.1241	0.0877	0.1281	0.0879
$R(F, >4\sigma(F))$	0.0473	0.0342	0.0523	0.0321
No. of parameters	167	158	343	173
S	1.035	0.989	1.044	1.047
Max. Δ/σ	<0.001	<0.001	<0.001	<0.001
Max. $\Delta\rho$ ($e\ nm^{-3}$)	379	340	476	439

amount of pyridine in 20 mL of toluene was heated at reflux for 25 hours. The reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy.

Crystal Structure Analyses

Crystal data are summarized in Table 7.

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 **2a** and **2e**, Stoe STADI-4 for **2f**, both with LT-2 low temperature attachment, and Bruker SMART 1000 CCD with LT-3 low temperature attachment for **3f**). The orientation matrix for **2a** and **2e** was refined from setting angles of 70 (60) reflections in the 2θ range 5–25°. The cell constants for **2f** were refined from $\pm\omega$ angles of 52 reflections in the 2θ range 20–23° and for **3f** from 5973 reflections in the 2θ range 2–60° (monochromated Mo$K\alpha$ radiation).

Structure Solution and Refinement. The structures were solved by direct methods and refined anisotropically on F^2 (program system: SHELXL-93 for **2a**, **2e**, and **2f** and SHELXL-97 for **3f**, G. M. Sheldrick, University of Göttingen). H atoms were included using a riding model or rigid methyl groups. Weighting schemes of the form $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$, with $P = (F_o^2 + 2F_c^2)/3$ were employed. Full details of the structure determinations have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Rd., GB Cambridge CB2 1EZ, under the numbers 148131 (**2a**), 148132 (**2e**), 148133 (**2f**), and 148134 (**3f**). Copies may be obtained free of charge on application to the Director (Telefax: Int +12 23 33 60 33; e-mail: deposit@ccdc.cam.ac.uk).

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