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The structures and electronic properties
of bulky electron-withdrawing phosphines

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Abstract

The crystal structures of the *N*-carbazolyl phosphines $\text{PPh}(\text{NC}_{12}\text{H}_8)_2$ and $\text{P}(\text{NC}_{12}\text{H}_8)_3$ have been determined. In the latter, large deviations from planarity are observed for one of the nitrogen atoms, which facilitate strong intermolecular $\text{C}\cdots\text{H}\cdots\pi$ and $\pi\cdots\pi$ interactions in the supramolecular structure. The compounds $\text{PPh}_{3-n}(\text{NC}_{12}\text{H}_8)_n$ ($n = 1-3$) react with selenium to give the phosphine selenides $\text{SePPh}_{3-n}(\text{NC}_{12}\text{H}_8)_n$. From the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, the $^1J_{\text{PSe}}$ coupling constants for these compounds are inversely related to the σ -basicity of the phosphines, which decreases with the increasing number of *N*-carbazolyl groups. The crystal structure of $0.65 \text{SeP}(\text{NC}_{12}\text{H}_8)_3 \cdot 0.35 \text{P}(\text{NC}_{12}\text{H}_8)_3$ contrasts with that for $\text{P}(\text{NC}_{12}\text{H}_8)_3$ as all of the nitrogen atoms are planar and $\pi\cdots\pi$ interactions are absent. The electronic differences between phenyl and *N*-pyrrolyl phosphines are borne out by the reaction of the diphosphine $\text{Ph}_2\text{PCH}_2\text{P}(\text{NC}_4\text{H}_4)_2$ with sulphur, which gives exclusively $\text{Ph}_2\text{P}(\text{S})\text{CH}_2\text{P}(\text{NC}_4\text{H}_4)_2$. **To cite this article:** A.D. Burrows *et al.*, *C. R. Chimie* 9 (2006).

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Résumé

Les structures cristallines des *N*-carbazolyl-phosphines $\text{PPh}(\text{NC}_{12}\text{H}_8)_2$ et $\text{P}(\text{NC}_{12}\text{H}_8)_3$ ont été déterminées. Dans la dernière, on observe une forte non-planarité pour l'un des atomes d'azote, qui facilite des interactions $\text{C}\cdots\text{H}\cdots\pi$ et $\pi\cdots\pi$ dans la structure supramoléculaire. Les composés $\text{PPh}_{3-n}(\text{NC}_{12}\text{H}_8)_n$ ($n = 1-3$) réagissent avec le sélénium pour donner des séléniures de phosphines $\text{SePPh}_{3-n}(\text{NC}_{12}\text{H}_8)_n$. Les constantes de couplage $^1J_{\text{PSe}}$ tirées des spectres RMN $^{31}\text{P}\{^1\text{H}\}$ sont inversement reliées à la basicité σ des phosphines, qui diminue avec l'augmentation du nombre de groupes *N*-carbazolyles. Dans la structure cristalline de $0,65 \text{SeP}(\text{NC}_{12}\text{H}_8)_3 \cdot 0,35 \text{P}(\text{NC}_{12}\text{H}_8)_3$, tous les atomes d'azote ont un environnement plan et les interactions $\pi\cdots\pi$ sont absentes, au contraire de la situation qui prévaut dans celle de $\text{P}(\text{NC}_{12}\text{H}_8)_3$. Les différences électroniques entre les phényl- et les *N*-pyrrolylphosphines sont confirmées par la réaction de la diphosphine $\text{Ph}_2\text{PCH}_2\text{P}(\text{NC}_4\text{H}_4)_2$ avec le soufre, qui conduit exclusivement à la formation de $\text{Ph}_2\text{P}(\text{S})\text{CH}_2\text{P}(\text{NC}_4\text{H}_4)_2$. **Pour citer cet article :** A.D. Burrows *et al.*, *C. R. Chimie* 9 (2006)

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1. Introduction

Tertiary phosphine ligands are ubiquitous in the realms of coordination chemistry and organometallic chemistry [1]. This is largely due to the wide range of steric and electronic properties that are accessible through variation of the substituents. The range of tertiary phosphines that are available provides a degree of control over the properties of transition metal complexes, and facilitating the ability to tune the activity and selectivity of a catalyst. A recent protocol for developing stereoelectronic maps for phosphorus ligands concluded that bulky electron-poor phosphines were largely unknown, so would be useful targets [2]. Such ligands have the potential to stabilise coordinatively unsaturated metals in low oxidation states [3].

We recently reported the synthesis of a range of *N*-carbazolyl phosphines $\text{PPh}_{3-n}(\text{NC}_{12}\text{H}_8)_n$ ($n = 1$, **1**; $n = 2$, **2**; $n = 3$, **3**) and their coordination chemistry with rhodium(I), palladium(II) and palladium(0) [4]. Some of these phosphines have also been reported by Jackstell et al. [5], who used them as ligands in Rh-catalysed hydroformylation reactions. The carbonyl stretching frequencies in the IR spectra of the $[\text{Rh}(\text{acac})(\text{CO})\{\text{PPh}_{3-n}(\text{NC}_{12}\text{H}_8)_n\}]$ complexes suggested that the *N*-carbazolyl phosphines have similar electronic properties to their *N*-pyrrolyl phosphine analogues $\text{PPh}_{3-n}(\text{NC}_4\text{H}_4)_n$ [6], though the presence of the *N*-carbazolyl groups ensures the ligands are much larger.

In this paper we report the crystal structures of **2** and **3**. The $^1J_{\text{PSe}}$ coupling constants in the phosphine

selenides provide a means of assessing phosphine electronic properties, so the synthesis and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the selenide derivatives $\text{SePPh}_{3-n}(\text{NC}_{12}\text{H}_8)_n$ ($n = 1$, **4**; $n = 2$, **5**; $n = 3$, **6**) are also detailed, along with the crystallographic characterisation of the co-crystal $0.65 \text{SeP}(\text{NC}_{12}\text{H}_8)_3 \cdot 0.35 \text{P}(\text{NC}_{12}\text{H}_8)_3$ **7**. Finally, we describe the reaction of the unsymmetrical diphosphine $\text{Ph}_2\text{PCH}_2\text{P}(\text{NC}_4\text{H}_4)_2$ with sulphur to form $\text{Ph}_2\text{P}(\text{S})\text{CH}_2\text{P}(\text{NC}_4\text{H}_4)_2$ **8**.

2. Crystal structures of **2**·MeC(O)Me and **3**

Slow evaporation of an acetone solution of $\text{PPh}(\text{NC}_{12}\text{H}_8)_2$, **2**, gave crystals suitable for X-ray crystallography. Analysis revealed the compound to be the acetone solvate **2**·MeC(O)Me, the structure of which is shown in Fig. 1. Selected bond distances and angles are presented in Table 1. The phosphine adopts a propeller-like conformation [7] in the solid state and the nitrogen atoms are both planar, with the respective sums of the angles around the nitrogen atoms ($\Sigma\angle\text{N}$) having values of 358° and 359° . The P–N bonds in **2** are longer than those in $\text{P}(\text{NC}_4\text{H}_4)_3$ [1.677(8)–1.710(8) Å] [8], which is likely to be a consequence of the increased steric requirements of the *N*-carbazolyl groups. Analysis of the supramolecular structure reveals the presence of C–H... π interactions between the carbazolyl and phenyl rings on neighbouring molecules.

Crystals of $\text{P}(\text{NC}_{12}\text{H}_8)_3$, **3**, suitable for crystallographic analysis were obtained by the slow diffusion

Table 1
Selected bond lengths (Å) and angles (°) for **2**·MeC(O)Me and **3**

	2		3
P(1)–N(1)	1.7216(14)	P(1)–N(1)	1.7476(16)
P(1)–N(2)	1.7320(15)	P(1)–N(2)	1.7159(16)
P(1)–C(25)	1.8153(18)	P(1)–N(3)	1.7159(16)
C(1)–N(1)–C(12)	106.67(13)	C(1)–N(1)–P(1)	116.67(12)
C(1)–N(1)–P(1)	133.38(12)	C(1)–N(1)–C(12)	105.44(14)
C(12)–N(1)–P(1)	119.29(12)	C(12)–N(1)–P(1)	118.26(12)
C(24)–N(2)–C(13)	107.13(14)	C(13)–N(2)–P(1)	115.53(12)
C(24)–N(2)–P(1)	134.43(12)	C(24)–N(2)–C(13)	105.94(15)
C(13)–N(2)–P(1)	116.33(12)	C(24)–N(2)–P(1)	135.08(13)
N(1)–P(1)–N(2)	102.89(7)	C(25)–N(3)–P(1)	132.87(13)
N(1)–P(1)–C(25)	103.33(8)	C(25)–N(3)–C(36)	106.62(15)
N(2)–P(1)–C(25)	103.90(8)	C(36)–N(3)–P(1)	118.11(13)
		N(2)–P(1)–N(3)	104.89(8)
		N(2)–P(1)–N(1)	100.94(8)
		N(3)–P(1)–N(1)	101.07(8)

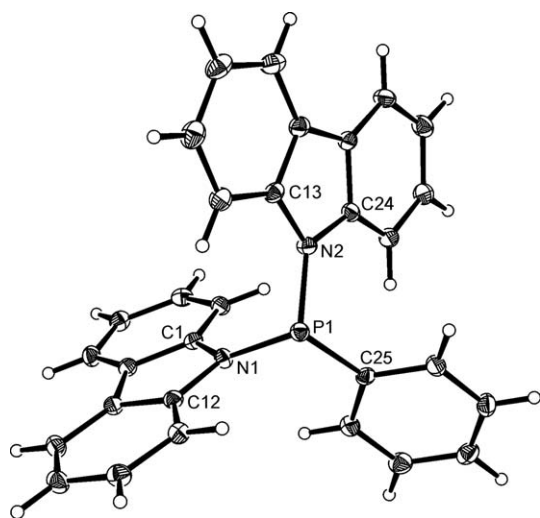


Fig. 1. The molecular structure of $\text{PPh}(\text{NC}_{12}\text{H}_8)_2 \cdot \text{MeC}(\text{O})\text{Me}$, $2 \cdot \text{MeC}(\text{O})\text{Me}$, with the acetone molecule omitted for clarity. Thermal ellipsoids are shown at the 30% probability limit.

of hexane into a dichloromethane solution. The structure of **3** is shown in Fig. 2 and selected bond angles and distances are given in Table 1. In contrast with the structure of $\text{P}(\text{anthracenyl})_3$ [9], **3** deviates from a propeller-like arrangement due to unequal rotations of the carbazoyl rings about the P–N bonds. The plane of the carbazoyl ring containing N(1) is almost perpendicular to the planes of the carbazoyl rings containing N(2) and N(3).

The most striking feature in the structure of **3** is the deviation in N(1) from the planarity expected for an sp^2 -hybridised nitrogen atom. The sum of the angles

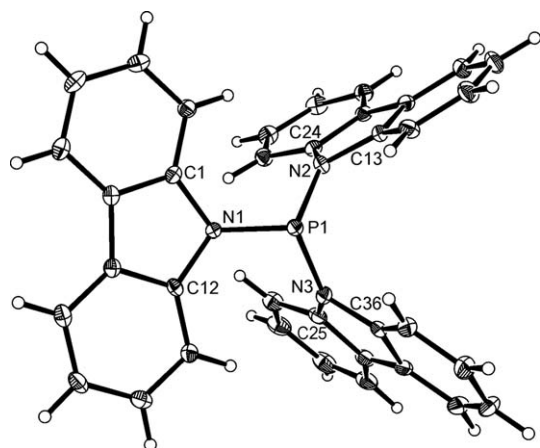


Fig. 2. The molecular structure of $\text{P}(\text{NC}_{12}\text{H}_8)_3$, **3**. Thermal ellipsoids are shown at the 30% probability limit.

($\Sigma\angle\text{N}$) around N(1) is only 340° , whereas for N(2) and N(3) the sums are 357° and 358° , respectively. N(1) is oriented such that its lone pair is *anti* to that of the phosphorus atom. These structural features are in contrast to those observed for tri(*N*-pyrrolyl)phosphine, $\text{P}(\text{NC}_4\text{H}_4)_3$, and tri(*N*-indolyl)phosphine, $\text{P}(\text{NC}_8\text{H}_6)_3$, both of which only contain nitrogen atoms that are virtually planar. The presence of a pyramidal nitrogen in **3** is reminiscent of the structures of many tris(dialkylamino)phosphines and their metal complexes [6,10]. For example, in the structure of $\text{P}(\text{NMe}_2)_3$ the phosphorus atom is bonded to two nearly planar nitrogen atoms ($\Sigma\angle\text{N}$ 353 – 359°) and one pyramidal nitrogen atom ($\Sigma\angle\text{N}$ 337 and 339° in the two independent molecules) [11]. In $\text{P}(\text{NMe}_2)_3$, the P–N bond involving the pyramidal nitrogen is longer (0.03–0.05 Å) than those to the planar nitrogen atoms. A similar increase in the P–N bond distance is observed for **3**, with P(1)–N(1) [1.7476(16) Å] approximately 0.03 Å longer than the two other P–N bonds, and also longer than the P–N distances in $\text{P}(\text{NC}_4\text{H}_4)_3$ [1.677(8)–1.710(8) Å] [8] and $\text{P}(\text{NC}_8\text{H}_6)_3$ [1.698–1.728 Å] [12].

The supramolecular structure of **3** reveals the presence of both C–H $\cdots\pi$ and $\pi\cdots\pi$ interactions. These interactions are shown in Fig. 3 which contains views approximately parallel and orthogonal to the plane of the carbazoyl ring containing N(1). Hydrogen–aromatic ring distances lie in the range 2.64–2.76 Å, whereas the closest distance between parallel carbazoyl rings is 3.54 Å. The pyramidal distortions in **3** facilitate these intermolecular interactions by placing the *N*-carbazoyl groups in the appropriate positions.

3. Phosphine selenides

In order to further investigate the electronic properties of **1–3**, the seleno derivatives $\text{SePPh}_{3-n}(\text{NC}_{12}\text{H}_8)_n$ ($n = 1$, **4**; $n = 2$, **5**; $n = 3$, **6**) were prepared by reaction of the phosphines with an excess of selenium powder in toluene. The conditions required for the reaction to reach completion become increasingly severe with more *N*-carbazoyl substituents, hence $\text{PPh}_2(\text{NC}_{12}\text{H}_8)$ reacts at room temperature while $\text{P}(\text{NC}_{12}\text{H}_8)_3$ requires 48 h at reflux. This trend is consistent with the increase in the electron-withdrawing nature of $\text{PPh}_{3-n}(\text{NC}_{12}\text{H}_8)_n$ with increasing n , and the accompanying decrease in the availability of the phosphorus lone pair. Compounds **4–6** were isolated in good yield as crystalline solids.

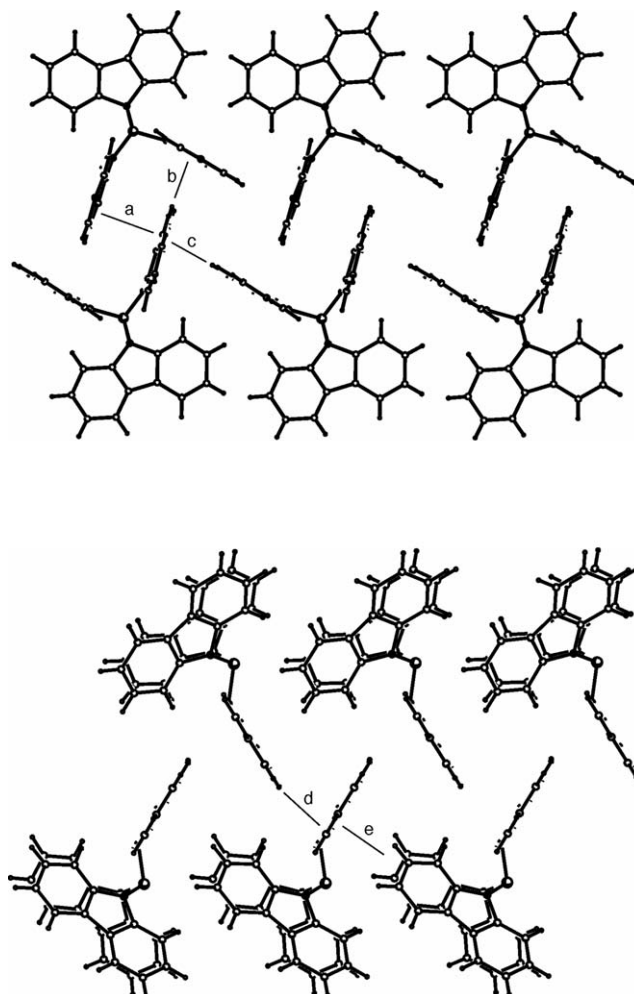


Fig. 3. Intermolecular $\pi\cdots\pi$ (a) and C–H $\cdots\pi$ (b–e) interactions within the crystal structure of **3**. Shortest distance from C or H to mean carbazoyl plane (a) 3.48, (b) 2.67, (c) 2.64, (d) 2.76, (e) 2.65 Å.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of compounds **4–6** consist of singlets with ^{77}Se satellites, and the spectral data are presented in Table 2 along with that for related compounds. There is a well established correlation between $^1J_{\text{PSe}}$ and the electronic properties of the parent phosphorus ligands, which takes the form of an inverse relationship with the σ -basicity [13–15]. Thus, as expected, the values of the $^1J_{\text{PSe}}$ coupling constant decrease in the order $6 > 5 > 4$ which is consistent with the anticipated decrease in σ -basicity of **1–3** as the number of carbazoyl substituents at the phosphorus atom increases. Further comparison shows that **6** and $\text{SeP}(\text{N-indolyl-3-CH}_3)_3$ have similar $^1J_{\text{PSe}}$ values, which are appreciably smaller than that for $\text{SeP}(\text{NC}_4\text{H}_4)_3$, suggesting that **3** is a better σ -donor than $\text{P}(\text{NC}_4\text{H}_4)_3$. This

contrasts with the $^{31}\text{P}\{^1\text{H}\}$ NMR and IR data observed for the compounds $[\text{Rh}(\text{acac})(\text{CO})(\text{L})]$ [$\text{L} = \mathbf{3}$, $\text{P}(\text{NC}_4\text{H}_4)_3$], indicating that **3** and $\text{P}(\text{NC}_4\text{H}_4)_3$ have similar electronic properties, though differences in the π -acceptor character may counterbalance those in the σ -basicity.

For the phosphines **1–3**, the trend in chemical shift is straightforward, and an increase in chemical shift accompanies the increase in the number of electron-withdrawing *N*-carbazoyl substituents. Thus, δ_{P} is 32.7, 52.9 and 77.6 for **1–3**, respectively. This can be rationalised on electronic grounds as simply being a consequence of increased deshielding of the phosphorus atom with the increasing number of *N*-carbazoyl groups, although steric effects leading to an increase the energy

Table 2
NMR parameters for selected phosphine selenide compounds

	δ_P	$^1J_{PSe}/\text{Hz}$	$\Delta\delta_P^a$	References
SePMe ₃	8.0	684	+70.0	[22,23]
SePMe ₂ Ph	15.1	710	+61.1	[22,23]
SePMePh ₂	22.3	725	+50.3	[22,23]
SePPh ₃	34.1	736	+41.5	[22,23]
SeP(NMe ₂) ₃	81.2	805	-40.3	[22,23]
SePPh ₂ (NC ₁₂ H ₈) 4	54.4	811	+21.7	this work
SePPh(NC ₁₂ H ₈) ₂ 5	50.3	873	-2.6	this work
SeP(NC ₁₂ H ₈) ₃ 6	30.1	942	-47.5	this work
SeP(<i>N</i> -indolyl-3-CH ₃) ₃	28.2	943	-36.6	[14]
SeP(OMe) ₃	77.5	963	-62.5	[22,23]
SeP(NC ₄ H ₄) ₃	43.0	970	-36.6	[6,14]
SeP(OPh) ₃	58.6	1027	-67.8	[23,24]
SeP{(NC ₄ H ₃) ₃ CH}	28.3	1032	-8.4	[13]

^a $\Delta\delta_P = \delta_P(\text{SePR}_3) - \delta_P(\text{PR}_3)$.

of the excited state, and hence the paramagnetic contribution, may also be a factor. However, the trend for the phosphine selenides is opposite: as shown in Table 2, the chemical shift *decreases* with the increasing number of *N*-carbazolyl substituents. For phosphine selenides such as SePMe₃ and SePPh₃, the difference in chemical shift between the selenide and the free phosphine ($\Delta\delta_P$) is large and positive, whereas for **6**, $\Delta\delta_P$ is large and negative. Similar observations have been made for the selenides of other electron-withdrawing phosphines such as P(NC₄H₄)₃ and P(*N*-indolyl-3-CH₃)₃ [13,14], and since P(NC₄H₄)₃ is similar in size to PPh₃ [6,16], the origin must be electronic rather than steric. A possible explanation for this lies in the relative importance of the R₃P=Se and R₃P⁺-Se⁻ resonance forms, since a decrease in the importance of the ionic resonance form for **6** would lead to reduced deshielding of the phosphorus nucleus, hence the observed upfield shift. However, the paramagnetic contribution may also be important as the R₃P=Se resonance form would better stabilise the ground state than the R₃P⁺-Se⁻ form.

4. Crystal structure of 0.65 SeP(NC₁₂H₈)₃·0.35 P(NC₁₂H₈)₃ **7**

Co-crystals of the phosphine selenide SeP(NC₁₂H₈)₃ and the phosphine P(NC₁₂H₈)₃ were grown from slow diffusion of hexane into a dichloromethane solution containing both **3** and **6**. On the basis of the X-ray structural analysis, the crystalline product was formulated

as 0.65 SeP(NC₁₂H₈)₃·0.35 P(NC₁₂H₈)₃, **7**, with the two compounds disordered. The phosphine selenide component of **7** is shown in Fig. 4 and selected bond distances and angles are given in Table 3. In contrast to **3**, the molecule adopts a propeller-like conformation with no strong pyramidal distortions at any of the nitrogen atoms; $\Sigma\angle N$ is in the range 354–360°. This contrasts with the structures of SeP(NC₄H₈)₃ and SeP(NMe₂)₃,

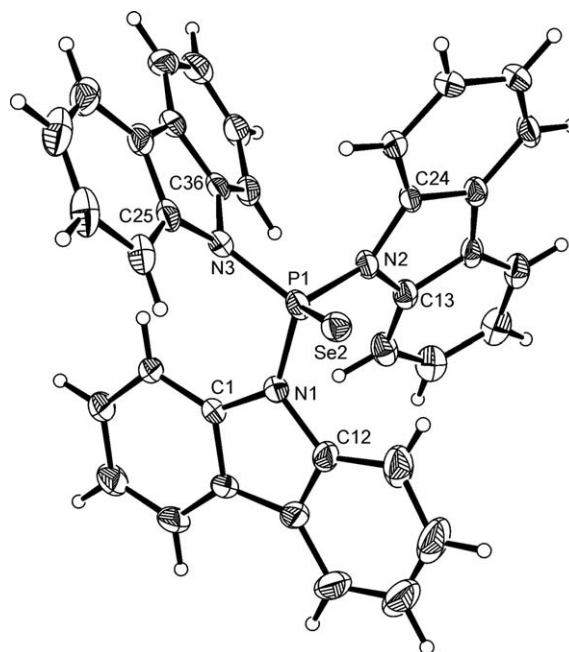


Fig. 4. Molecular structure of 0.65 SeP(NC₁₂H₈)₃·0.35 P(NC₁₂H₈)₃, **7**, with only the phosphine selenide component shown for clarity. Thermal ellipsoids are shown at the 30% probability limit.

Table 3
Selected bond lengths (Å) and angles (°) for **7**

P(1)–N(1)	1.683(3)
P(1)–N(2)	1.705(3)
P(1)–N(3)	1.701(3)
P(1)–Se(2)	2.0369(10)
C(1)–N(1)–C(12)	106.7(3)
C(1)–N(1)–P(1)	132.8(2)
C(12)–N(1)–P(1)	120.5(2)
C(24)–N(2)–C(13)	107.4(2)
C(24)–N(2)–P(1)	118.9(2)
C(13)–N(2)–P(1)	131.4(2)
C(36)–N(3)–C(25)	106.1(3)
C(36)–N(3)–P(1)	125.7(2)
C(25)–N(3)–P(1)	121.8(2)
N(1)–P(1)–N(3)	106.47(13)
N(1)–P(1)–N(2)	103.92(14)
N(3)–P(1)–N(2)	101.57(13)
N(1)–P(1)–Se(2)	110.48(10)
N(3)–P(1)–Se(2)	119.10(10)
N(2)–P(1)–Se(2)	113.89(10)

both of which contain one nitrogen atom with a strong pyramidal distortion ($\Sigma\angle N$ 342–344°), in a similar way to the free phosphines and their metal complexes. The absence of any pyramidal distortion in **7** is consistent with its observation in **3** being a consequence of the intermolecular interactions, rather than being intrinsic to the compound. In line with this argument, there are no $\pi\cdots\pi$ interactions present in the supramolecular structure of **7**. Instead, the extended structure is dominated by C–H $\cdots\pi$ interactions, as shown in Fig. 5.

The P–Se bond length in **6** of 2.0369(10) Å is one of the shortest observed between these atoms. A search of the Cambridge Structural Database [17] revealed the presence of 146 compounds containing P–Se bonds in which the selenium is not bonded to another atom, corresponding to 217 independent P–Se bond lengths. Of these, the average P–Se bond length is 2.100 Å. There is a correlation between the electronic nature of the substituents and the P–Se distance, with electron donating groups leading to larger bond lengths than electron-withdrawing groups. As with the chemical shift data, this can be understood on the basis of the two resonance forms $R_3P=Se$ and $R_3P^+-Se^-$. The ionic resonance form is stabilised by electron donating substituents, but is less important with electron-withdrawing groups such as *N*-carbazolyl. The short P–Se bond observed in **7** is therefore a consequence of the greater contribution of the $R_3P=Se$ resonance form.

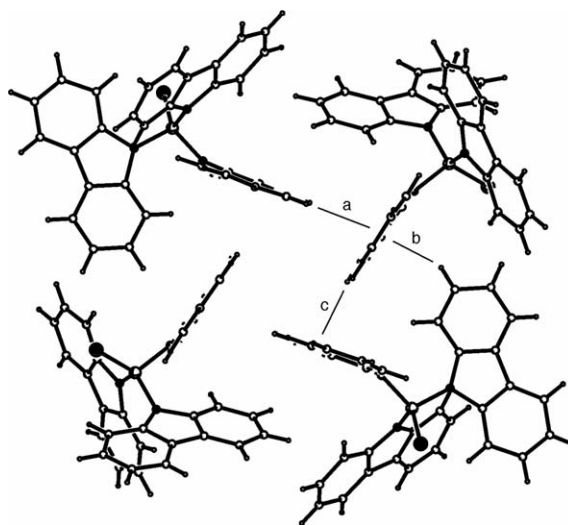


Fig. 5. Intermolecular C–H $\cdots\pi$ interactions within the crystal structure of **7**. Shortest distance from H to mean carbazolyli plane (a) 2.88, (b) 2.58, (c) 2.71 Å.

5. Reaction of $Ph_2PCH_2P(NC_4H_4)_2$ with sulphur

The diphosphine $Ph_2PCH_2P(NC_4H_4)_2$ contains two electronically different phosphino groups, with the di(*N*-pyrrolyl)phosphino group more electron-withdrawing than the diphenylphosphino group. Studies with late transition metals have shown that the reactivity of these groups differs, and the di(*N*-pyrrolyl)phosphino group is more readily displaced from a metal centre than the diphenylphosphino group [18]. In order to determine whether the electronic difference influences oxidation of the phosphorus atoms, the reaction between $Ph_2PCH_2P(NC_4H_4)_2$ and sulphur was investigated. The compounds were stirred together in dichloromethane for 4 h, and following removal of excess sulphur, the compound $Ph_2P(S)CH_2P(NC_4H_4)_2$ **8** was isolated by recrystallisation from dichloromethane–hexane.

The $^{31}P\{^1H\}$ NMR spectrum of **8** consists of doublets at δ 56.9 and δ 35.6, with a mutual coupling constant of 85 Hz. These resonances can be assigned on the basis of chemical shift and peak width to the phosphorus(III) and phosphorus(V) centres, respectively. The broader resonance at δ 56.9 is relatively close to that for the di(*N*-pyrrolyl)phosphino group in $Ph_2PCH_2P(NC_4H_4)_2$ (δ 66.1) [18], and the large peak width is a consequence of the quadrupolar nitrogen nucleus [6]. The doublet at δ 35.6 has shifted by $\Delta\delta$ +60.1 from that of the diphenylphosphino group in

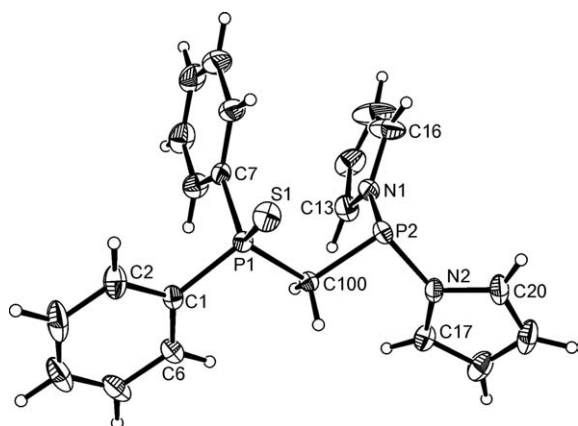


Fig. 6. Molecular structure of $\text{Ph}_2\text{P}(\text{S})\text{CH}_2\text{P}(\text{NC}_4\text{H}_4)_3$ **8**. Only one of the two independent molecules in the asymmetric unit is shown. Thermal ellipsoids are shown at the 30% probability limit.

$\text{Ph}_2\text{PCH}_2\text{P}(\text{NC}_4\text{H}_4)_2$, consistent with oxidation of this phosphorus atom.

Crystals of **8** suitable for X-ray analysis were obtained by the slow diffusion of hexane into a dichloromethane solution. The asymmetric unit contains two independent molecules, though there are only minor differences between them. The structure of **8** is shown in Fig. 6, and selected bond lengths and angles are given in Table 4. The structure concurs with the NMR data in that only the diphenylphosphino group has been oxidised. Both *N*-pyrrolyl groups contain planar nitrogen atoms, with the sums of the angles around both N(1) and N(2) being 360° . Intramolecular $\pi\cdots\pi$ interactions

are present between one of the pyrrolyl and one of the phenyl rings. Further intermolecular interactions between the two phosphino groups give rise to fourfold embraces in the supramolecular structure [19].

6. Conclusion

Analysis of the NMR spectra of the phosphine selenides **4–6** has revealed correlations of both the $^1J_{\text{PSe}}$ coupling constants and the δ_{P} chemical shifts with the electronic character of the parent phosphine. The pyramidal distortion observed around one of the nitrogen atoms in the crystal structure of **3** is not observed in the phosphine selenide **6**. This suggests that, in contrast to tris(dialkylamino)phosphines, it is not intrinsic to the phosphine, but rather a consequence of the intermolecular interactions. The reaction of $\text{Ph}_2\text{PCH}_2\text{P}(\text{NC}_4\text{H}_4)_2$ with sulphur to form **8** confirms that the diphenylphosphino group is easier to oxidise than the di(*N*-pyrrolyl)phosphino group.

7. Experimental

7.1. General experimental

Reactions were routinely carried out using Schlenk-line techniques under pure dry dinitrogen or argon, using dry dioxgen-free solvents unless noted otherwise. Microanalyses (C, H and N) were carried out by

Table 4
Selected bond lengths (Å) and angles ($^\circ$) for **8**

S(1)–P(1)	1.9528(6)	S(2)–P(3)	1.9523(6)
P(2)–N(1)	1.7126(18)	P(4)–N(3)	1.7173(18)
P(2)–N(2)	1.7287(17)	P(4)–N(4)	1.7312(17)
C(16)–N(1)–C(13)	106.9(2)	C(36)–N(3)–C(33)	107.06(18)
C(16)–N(1)–P(2)	121.64(18)	C(36)–N(3)–P(4)	130.86(14)
C(13)–N(1)–P(2)	131.08(15)	C(33)–N(3)–P(4)	122.67(16)
C(17)–N(2)–C(20)	107.60(18)	C(37)–N(4)–C(40)	107.42(18)
C(17)–N(2)–P(2)	132.12(14)	C(37)–N(4)–P(4)	131.83(13)
C(20)–N(2)–P(2)	120.19(16)	C(40)–N(4)–P(4)	120.74(16)
C(7)–P(1)–C(1)	105.30(8)	C(21)–P(3)–C(27)	104.92(8)
C(7)–P(1)–C(100)	105.72(8)	C(21)–P(3)–C(200)	106.54(8)
C(1)–P(1)–C(100)	106.65(8)	C(27)–P(3)–C(200)	107.22(9)
C(7)–P(1)–S(1)	114.15(7)	C(21)–P(3)–S(2)	112.08(6)
C(1)–P(1)–S(1)	111.91(6)	C(27)–P(3)–S(2)	113.35(7)
C(100)–P(1)–S(1)	112.51(6)	C(200)–P(3)–S(2)	112.21(6)
N(1)–P(2)–N(2)	102.00(8)	N(3)–P(4)–N(4)	101.93(8)
N(1)–P(2)–C(100)	101.14(8)	N(3)–P(4)–C(200)	100.55(8)
N(2)–P(2)–C(100)	98.48(7)	N(4)–P(4)–C(200)	98.42(7)

Mr. Alan Carver (University of Bath Microanalytical Service). NMR spectra were recorded on JEOL EX-270, Varian Mercury 400 and Bruker Avance 300 spectrometers referenced to TMS or 85% H_3PO_4 . Compounds **1–3** [4] and $\text{Ph}_2\text{PCH}_2\text{P}(\text{NC}_4\text{H}_4)_2$ [18] were prepared as previously reported.

7.2. Synthesis of $\text{SePPh}_2(\text{NC}_{12}\text{H}_8)$ **4**

A mixture of **1** (0.146 g, 0.41 mmol) and selenium powder (0.120 g, 1.50 mmol) in toluene was stirred overnight. The solution was filtered and the solvent eliminated under reduced pressure. The resulting white powder was recrystallised from dichloromethane–hexane. Yield: 0.144 g (81%). Calc. for $\text{C}_{24}\text{H}_{18}\text{NPSe}$: C, 67.0; H, 4.22; N, 3.25. Found: C, 67.3; H, 4.27; N, 3.30%. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CDCl_3): δ 54.4 (s, $^1J_{\text{Pse}}$ 811 Hz). ^1H NMR (300.2 MHz, CDCl_3): δ 8.07–8.00 (m, 6H, H_o , $\text{H}_{4,5}$), 7.64–7.59 (m, 2H, H_p), 7.55–7.49 (m, 4H, H_m), 7.26–7.22 (m, 2H, $\text{H}_{3,6}$), 7.11–7.05 (m, 2H, $\text{H}_{2,7}$), 6.68 (d, 2H, $^3J_{\text{HH}}$ 9 Hz, $\text{H}_{1,8}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl_3): δ 141.1 (d, $^2J_{\text{CP}}$ 4 Hz, $\text{C}_{10,13}$), 132.7 (d, $^2J_{\text{CP}}$ 12 Hz, C_o), 132.5 (d, $^2J_{\text{CP}}$ 3 Hz, C_i), 130.1 (s, C_p), 128.8 (d, $^3J_{\text{CP}}$ 14 Hz, C_m), 126.8 (d, $^3J_{\text{CP}}$ 5 Hz, $\text{C}_{11,12}$), 125.6 (s, $\text{C}_{2,7}$), 121.7 (s, $\text{C}_{3,6}$), 119.7 (s, $\text{C}_{4,5}$), 115.2 (d, $^3J_{\text{CP}}$ 3 Hz, $\text{C}_{1,8}$).

7.3. Synthesis of $\text{SePPh}(\text{NC}_{12}\text{H}_8)_2$ **5**

As for **4** using **2** (0.92 g, 0.21 mmol) and selenium powder (0.049 g, 0.63 mmol) in toluene heated at reflux for 24 h. Yield: 0.102 g (93%). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CDCl_3): δ 50.3 (s, $^1J_{\text{Pse}}$ 873 Hz). ^1H NMR (300.2 MHz, CDCl_3): δ 8.18–8.10 (m, 2H, H_o), 8.03 (bd, 4H, J 9.0 Hz, $\text{H}_{4,5}$), 7.75–7.69 (m, 1H, H_p), 7.59–7.52 (m, 2H, H_m), 7.29–7.16 (m, 8H, $\text{H}_{3,6}$, $\text{H}_{2,7}$), 7.11–6.99 (m, 4H, $\text{H}_{1,8}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl_3): δ 140.9 (d, $^2J_{\text{CP}}$ 6 Hz, $\text{C}_{10,13}$), 134.2 (d, $^2J_{\text{CP}}$ 12 Hz, C_o), 131.8 (d, $^2J_{\text{CP}}$ 4 Hz, C_i), 130.1 (s, C_p), 129.2 (d, $^3J_{\text{CP}}$ 14 Hz, C_m), 127.1 (d, $^3J_{\text{CP}}$ 6 Hz, $\text{C}_{11,12}$), 122.8 (s, $\text{C}_{2,7}$), 120.0 (s, $\text{C}_{4,5}$), 115.7 (s, $\text{C}_{1,8}$).

7.4. Synthesis of $\text{SeP}(\text{NC}_{12}\text{H}_8)_3$ **6**

As for **4** using **3** (0.125 g, 0.24 mmol) and selenium powder (0.880 g, 1.1 mmol) in toluene heated at reflux for 48 h. Yield: 0.110 g (75%). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CDCl_3): δ 30.1 (s, $^1J_{\text{Pse}}$ 942 Hz). ^1H NMR

(300.2 MHz, CDCl_3): δ 8.09–8.04 (m, 6H, $\text{H}_{4,5}$), 7.31–6.91 (m, 18H, $\text{H}_{1,8}$, $\text{H}_{2,7}$, $\text{H}_{3,6}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl_3): δ 138.2 (d, J 5 Hz), 125.3 (d, J 7 Hz), 119.8 (s), 118.2 (s), 117.8 (s), 114.3 (s).

7.5. Synthesis of $\text{Ph}_2\text{P}(\text{S})\text{CH}_2\text{P}(\text{NC}_4\text{H}_4)_2$ **8**

Sulphur (0.089 g, 2.8 mmol) was added to a dichloromethane solution of $\text{Ph}_2\text{PCH}_2\text{P}(\text{NC}_4\text{H}_4)_2$ (0.089 g, 0.25 mmol), and the mixture was stirred for 4 h. The solution was filtered to remove excess sulphur, and the volume of solvent halved under reduced pressure. On standing at -20 °C, yellow crystals of sulphur were obtained. These were separated by filtration, and the filtrate was recrystallised from dichloromethane–hexane to give a colourless powder, which was dried under reduced pressure. Yield 0.080 g (82%). Calc. for $\text{C}_{21}\text{H}_{20}\text{N}_2\text{P}_2\text{S}\cdot\text{CH}_2\text{Cl}_2$: C, 55.1; H, 4.63; N, 5.84. Found: C, 55.1; H, 4.54; N, 6.00%. $^{31}\text{P}\{^1\text{H}\}$ NMR (161.8 MHz, CDCl_3): δ 56.9 (d, $^2J_{\text{PP}}$ 85 Hz, P^{III}), 35.6 (d, $^2J_{\text{PP}}$ 85 Hz, P^{V}). ^1H NMR (399.8 MHz, CDCl_3): δ 7.74–7.68 (m, 4H, H_m), 7.47–7.36 (m, 6H, H_o , H_p), 6.87 (ps. quin, 4H, H_α), 6.17 (ps. t, 4H, H_β), 3.66 (dd, 2H, $^2J_{\text{HP}}$ 13.2, 1.2 Hz, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl_3): δ 131.7 (s), 131.5 (s), 130.7 (d, J 10 Hz), 128.5 (d, J 12 Hz), 123.4 (d, J 17 Hz, C_α), 112.3 (d, J 3 Hz, C_β), 37.4 (dd, $^1J_{\text{CP}}$ 50, 26 Hz, CH_2).

7.6. Crystallography

Single crystals of compounds **2**· $\text{CH}_3\text{C}(\text{O})\text{CH}_3$, **3**, **7** and **8** were analysed using a Nonius Kappa CCD diffractometer and molybdenum radiation throughout. Details of the data collections, solutions and refinements are given in Table 5. The structures were solved using SHELXS-97 [20] and refined using SHELXL-97 [21]. Absorption corrections (semi-empirical from equivalent reflections) were applied to data for **3**, **7** and **8**. [max./min. transmission factors 1.06 and 0.92, 0.88 and 0.81, and 0.90 and 0.83, respectively].

Compound **7** is an average of 65% $\text{SeP}(\text{NC}_{12}\text{H}_8)_3$ and 35% $\text{P}(\text{NC}_{12}\text{H}_8)_3$. Compound **8** crystallises with two independent molecules in the asymmetric unit.

The supplementary material has been sent to the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (CCDC 271732–271735) and can be obtained by contacting the CCDC.

Table 5
Crystallographic information for compounds 2-MeC(O)Me, 3, 7 and 8

Compound	2-MeC(O)Me	3	7	8
Formula	C ₃₃ H ₂₇ N ₂ OP	C ₃₆ H ₂₄ N ₃ P	C ₃₆ H ₂₄ N ₃ PSe _{0.65}	C ₂₁ H ₂₀ N ₂ P ₂ S
<i>M</i>	498.54	529.55	580.88	394.39
<i>T</i> /K	150(2)	170(2)	150(2)	150(2)
λ /Å	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	8.7170(1)	9.8160(2)	16.5450(3)	13.0640(1)
<i>b</i> /Å	15.2970(3)	7.8210(1)	9.3500(2)	14.2480(2)
<i>c</i> /Å	10.4140(2)	33.8940(6)	18.2990(4)	22.5130(3)
β /°	114.318(1)	93.507(1)	102.669(1)	104.201(1)
<i>U</i> /Å ³	1265.43(4)	2597.20(8)	2761.86(10)	4062.42(8)
<i>Z</i>	2	4	4	8
ρ_{calc} /g cm ⁻³	1.308	1.354	1.397	1.290
μ /mm ⁻¹	0.139	0.138	0.988	0.324
Crystal size/mm	0.20 × 0.20 × 0.20	0.50 × 0.40 × 0.20	0.40 × 0.10 × 0.10	0.60 × 0.50 × 0.40
Reflections collected	24,788	37,362	42,557	48,958
Independent reflections	5626	5923	4855	9168
	[<i>R</i> (int) = 0.0575]	[<i>R</i> (int) = 0.0954]	[<i>R</i> (int) = 0.0575]	[<i>R</i> (int) = 0.0457]
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)]	0.0372, 0.0810	0.0483, 0.1013	0.0476, 0.1044	0.0479, 0.1335
<i>R</i> indices (all data)	0.0509, 0.0864	0.1027, 0.1194	0.0635, 0.1093	0.0591, 0.1448
Flack parameter	−0.10(7)			

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