1,3,2-Diazaphospha-[3]ferrocenophanes. Molecular Structures and Multinuclear Magnetic Resonance Studies

Bernd Wrackmeyer, Elena V. Klimkina, and Wolfgang Milius

Laboratorium für Anorganische Chemie, Universität Bayreuth, D-95440 Bayreuth, Germany

Reprint requests to Prof. Dr. B. Wrackmeyer. E-mail: b.wrack@uni-bayreuth.de

Z. Naturforsch. **2009**, *64b,* 1401 – 1412; received July 11, 2009

Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday

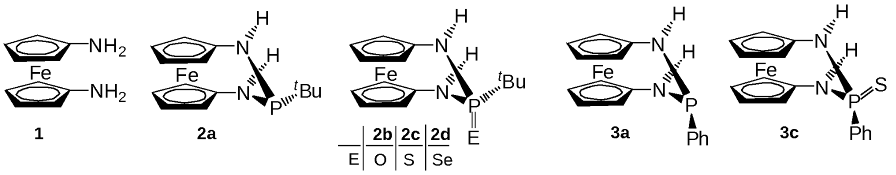
2-Phenoxy-1,3,2-diazaphospha-[3]ferrocenophane and related derivatives (oxide, sulfide, selenide) were prepared, characterized in solution by multinuclear magnetic resonance methods (1D and 2D ^{1}H, ^{13}C, ^{15}N and ^{31}P NMR) and in the solid state by X-ray structural analysis. The conformation of the 2-phenoxy derivative differs from that of the 2-*tert*-butyl compound. For further comparison, 2-R-2,3-dihydro-*1H*-1,3,2-diazaphospha-phenalene derivatives R = ^{t}Bu, PhO were prepared and studied by the same NMR techniques. The molecular structure of a selenide was determined, and together with the NMR evidence, it was concluded that the conformation of these heterocycles is independent of the respective substituent at the phosphorus atom.

Key words: Aminophosphanes, 1,1′-Diaminoferrocene, [3]Ferrocenophanes, NMR Spectroscopy, Crystal Structure

Introduction

The multifaceted chemistry of phosphorus-nitrogen compounds has attracted much attention for many years [1], and the coordination number of phosphorus may range from 1 to 6. In most cases, the chemistry is concerned with phosphorus in the formal oxidation state P(III) or P(V), and frequently it is fairly convenient to convert the P(III) into P(V) compounds if they are the final target. Otherwise it is also easy to start from a P(V) compound, if readily availabe, and form the respective P–N bond by appropriate reactions. Thus, aminophosphanes as P(III) compounds as well as the corresponding P(V) compounds are well studied in many respects, including their molecular structures [2] and numerous NMR properties [3]. Cyclic P-N compounds are of interest with respect to their conformation and molecular dynamics which are most efficiently studied by NMR spectroscopy, mostly by ^{1}H, ^{13}C and ^{31}P NMR [3 – 6]. In the case of cyclic aminophosphanes, only few examples with NH functions have been studied since their preparation is often accompanied by numerous side reactions. If the organic backbone of the diamine and (or) the third substituent at phosphorus are sufficiently bulky such side reactions may be less serious. However, experimental solid-state molecular structures are scarce [7, 8], and conclusive solution-state NMR data are either absent, incomplete or wrong [7, 9, 10], in particular with respect to the NH functions.

1,1′-Diaminoferrocene (**1**) [11, 12] (Scheme 1) is a potentially useful starting material to prepare novel cyclic diaminophosphanes, since the 1,1′-ferrocenediyl group is bulky and may provide a fairly rigid backbone in 1,3,2-diazaphospha-[3]ferrocenophanes. In a preliminary report [13], we have disclosed the synthesis and molecular structures of **2a** and **2d**, and it was pointed out that the 2-phenyl derivative **3a** may have a different structure as far as the mutual orientation of the P–C and the N–H bonds



Scheme 1. 1,1′-Diaminoferrocene [11, 12] and four 1,3,2-diazaphospha[3]ferrocenophanes reported in a preliminary study [13].

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Table 1. ^{13}C, ^{31}P, ^{77}Se and ^{1}H NMR data[a,b] of the 2-phenoxy-1,3,2-diazaphospha-[3]ferrocenophanes **4**.

Compound PR	**4a** P–OPh	**4c** P(S)OPh	**4d**[d,e] P(Se)OPh	**4a** P(O)OPh
δ^{31}P	132.1	73.9	71.3 [888.8]	19.9 (br)
δ^{13}C(PR)	119.3 (9.7) C_o	120.3 (6.5) C_o	120.3 (6.4) C_o	119.6 (6.0) C_o
	122.4 (< 0.5) C_p	124.9 (0.9) C_p	125.1 (< 0.5) C_p	124.5 (< 0.5) C_p
	129.7 (< 0.5) C_m	130.0 (< 0.5) C_m	130.1 (< 0.5) C_m	129.9 (< 0.5) C_m
	155.7 (9.0) C_i	151.8 (6.5) C_i	152.0 (6.2) C_i	151.2 (5.8) C_i
δ^{13}C(fc-C^1)	93.9 (8.1)	91.2 (10.6)	91.4 (12.9)	89.4 (5.3)
δ^{13}C(fc-C^2)	65.3 (< 0.5)[c]	70.3 (4.6)	70.3 (3.6)	69.9 (5.1)
δ^{13}C(fc-C^3)	65.5 (< 0.5)[c]	67.1 (0.7)	67.2 (br)	66.9
δ^{13}C(fc-C^4)	68.5 (< 0.5)[c]	69.1 (< 0.5)	69.3 (br)	68.4
δ^{13}C(fc-C^5)	69.6 (< 0.5)[c]	63.7 (< 0.5)	64.0 (br)	63.4
δ^{1}H(NH)	2.57 {+44.8}	3.46 {19.6} ([D$_8$]toluene)	4.23 {21.2}	4.27 {12.3}

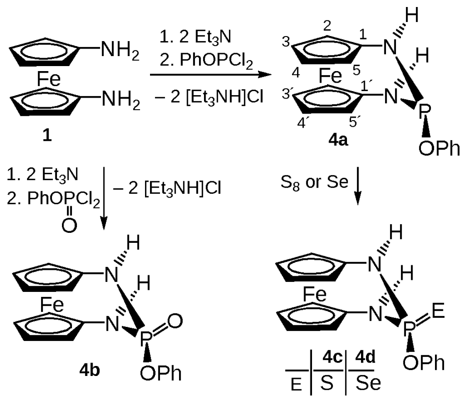
[a] The assignment of the NMR signals is based on ^{1}H-^{1}H NOESY [26], and 2D ^{1}H/^{13}C gHSQC [19] experiments; [b] measured in [D$_8$]toluene (**4a**), CD_2Cl_2 (**4c**, **4d**), $CDCl_3$ (**4b**); coupling constants $^nJ(^{31}P,^{13}C)$ (±0.5 Hz) are given in parentheses, $^2J(^{31}P,^1H)$ in braces, $^1J(^{77}Se,^{31}P)$ in brackets; [c] assignment might be reversed; [d] δ^{77}Se = −292.8 [888.8]; for comparison: δ^{77}Se (**2d**) = −186.4 [792.5] corrects a misprint in ref. [13]; [e] δ^{57}Fe = 1115.1 (ref. [25]).

are concerned. To the best of our knowledge, there are no fully characterized cyclic diaminophosphanes which differ in their principal conformation owing to effects exerted by substituents at the phosphorus atom. These properties might be of interest in further studies of such aminophosphanes as ligands in transition metal chemistry. The question of alternative structures raised previously [13] is addressed here in more detail, including the 2-phenoxy group, by using multinuclear 1D and 2D magnetic resonance techniques, and by taking advantage of the results of X-ray structural analysis for two further examples, in addition to those already reported [13] for **2a** and **2d**.

Results and Discussion

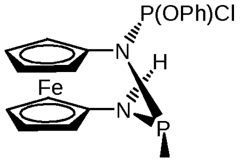
Synthesis

The synthesis of **4a**, **c**, **d** (Scheme 2) followed the conventional method reported for **2a**–**2d** [13], whereas **4b** was prepared by using the phenoxyphosphoryl dichloride by an analogous procedure as described for **4a**. These bulky aminophosphanes are of low reactivity, except for hydrolysis, since the reaction of neither **2a** (Et_2O, 4 d, r. t.) nor **4a** (toluene, 20 h at r. t., 1 h at 70 °C) with trimethylsilyl azide failed to afford the corresponding P(V) compounds. Compounds **4** were obtained in pure state as orange crystalline solids or, without further purification, as moisture-sensitive yellow-orange oils or yellow-greenish solids. Their solution-state structures follow from the consistent NMR data (Table 1 and Experimental Section), and the conformation has been confirmed by various more sophisticated NMR experiments (*vide infra*).



Scheme 2. Reactions of 1,1′-diaminoferrocene (**1**) with phenoxyphosphorus dichlorides towards 2-phenoxy-1,3,2-diazaphospha-[3]ferrocenophanes.

The crude product from the reaction to give **4a** contained in repeated experiments a small amount of about 2 % of a second defined compound, for which the structure of the diastereomers **5**/**5′** is proposed, as indicated by ^{31}P NMR spectra (see Experimental and Ref. [13] for the corresponding P-^{t}Bu compounds).



5,5′ (2 %)

Table 2. ^{13}C, ^{31}P, ^{77}Se and ^{1}H NMR data[a] of the 2-R-2,3-dihydro-1*H*-1,3,2-diazaphospha-phenalenes **6a**, **6d**, **7a** and **7d**.

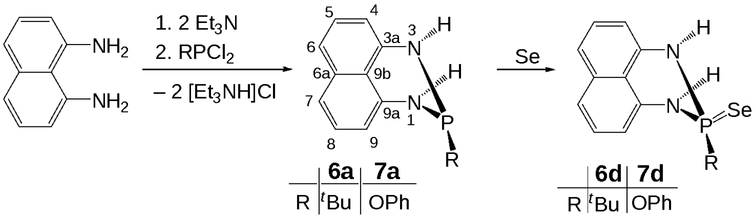
	δ^{13}C											
6 (R = ^{t}Bu)	C-3a,9a	C-4,9	C-5,8	C-6,7	C-6a	C-9b	CH$_3$		P–C		δ^{31}P	δ^{1}H(NH)
6a	138.6	108.4	126.2	117.9	134.9	115.6	24.2 (18.2)		38.2 (24.5)		71.3	5.06
P–^{t}Bu	(6.1)	(< 0.5)	(0.5)	(< 0.5)	(< 0.5)	(2.9)						{+38.0}
6d[b]	137.3	109.7	127.2	120.8	135.4	113.4	24.9 (2.4)		44.3 (71.3)		70.6	5.60
P(Se)^{t}Bu	(5.8)	(7.4)	(1.3)	(< 0.5)	(< 0.5)	(5.5)					(71.6) [815.3]	{12.6}
7 (R = OPh)	C-3a,9a	C-4,9	C-5,8	C-6,7	C-6a	C-9b	C$_i$	C$_o$	C$_m$	C$_p$		
7a	135.5	108.9	127.0	119.7	135.4	108.9	153.1	121.5	127.0	121.5	85.7	5.50
P–OPh	(5.3)	(1.3)	(1.1)	(< 0.5)	(< 0.5)	(1.3)	(3.2)	(6.8)	(1.1)	(6.8)		{+36.9}
7d[c]	135.6	110.4	127.1	121.6	135.4	115.1	150.3	122.2	129.4	125.5	42.7	6.27
P(Se)OPh	(7.1) ⟨1.6⟩	(8.7)	(1.1)	(< 0.5)	(0.8)	(7.6)	(9.2) ⟨1.6⟩	(4.2)	(2.1)	(2.4)	[928.5]	{14.3}

[a] Measured in CD$_2$Cl$_2$ (**6a**, **6d**), CDCl$_3$ (**7a**, **7d**); coupling constants $^{n}J(^{31}P,^{13}C)$ (±0.5 Hz) are given in parentheses, $^{3}J(^{77}Se,^{13}C)$ in ⟨⟩, $^{2}J(^{31}P,^{1}H)$ in braces; $^{1}J(^{77}Se,^{31}P)$ in brackets; [b] δ^{77}Se = −251.7 [814.2]; [c] δ^{77}Se = −268.7 [928.3].

Table 3. ^{15}N NMR data[a] of the 2-R-1,3,2-diazaphospha-[3]ferrocenophanes **2**–**4** and of the 2-R-2,3-dihydro-1*H*-1,3,2-diazaphospha-phenalenes **6a**, **6d**, **7a** and **7d**.

Compound	**4a**	**4c**	**4d**	**2a**	**2b**	**2c**	**2d**	**3a**	**6a**	**6d**	**7a**	**7d**
PR	P–OPh	P(S)OPh	P(Se)OPh	P–^{t}Bu	P(O)^{t}Bu	P(S)^{t}Bu	P(Se)^{t}Bu	P–Ph	P–^{t}Bu	P(Se)^{t}Bu	P–OPh	P(Se)OPh
δ^{15}N	−328.8	−324.3	−320.6	−341.8	−341.4	−335.9	−335.0	−344.7	−323.6	−310.0	−295.6	−290.6
$^{1}J(^{31}P,^{15}N)$, Hz	+72.2	6.8	3.5	+78.2	n. o.	27.0	29.7	+72.8	+52.8	10.9	+60.2	5.5
$^{1}J(^{15}N,^{1}H)$, Hz	−82.7	−86.1	−86.4	−71.1	–	–	−78.5	–	−86.7	−87.5	−86.9	−88.9

[a] Measured in [D$_8$]toluene (**4a**), CD$_2$Cl$_2$ (**4c**, **4d**, **6a**, **6d**, **2a**, **2c**, **3a**), CDCl$_3$ (**7a**, **7d**, **2d**), [D$_8$]DMSO (**2b**); n. o. = not observed.



Scheme 3. Synthesis of 2-substituted 2,3-dihydro-*1H*-1,3,2-diazaphospha-phenalene derivatives.

Two other cyclic diaminophosphanes **6a** and **7a** and their selenides **6d** and **7d** were prepared (Scheme 3) for comparison of NMR spectroscopic properties (Table 2), and in the case of the selenide **6d**, the molecular structure was determined by single crystal X-ray diffraction (*vide infra*). The molecular structure of 2-ethoxy-2,3-dihydro-*1H*-1,3,2-diazaphospha-phenalene **8a** has been reported [7a], the ethoxy group being in *anti* position (as the phenoxy group in **4**) relative to the N–H bonds. In contrast with the [3]ferrocenophanes **2a** and **4a**, which possess different ring conformations, the corresponding 1,3,2-diazaphospha-phenalene derivatives **6a** and **7a** [7a, 14] appear to have alike conformations, most likely the one which was determined in the solid state for the 2-ethoxy derivative **8a** [7a]. This assumption is further confirmed by the molecular structure of **6d**.

NMR studies and calculations

In addition to ^{1}H, ^{13}C and ^{31}P NMR data of the [3]ferrocenophanes **4** (Table 1) and comparable 1,3,2-diazaphospha-phenalene derivatives **6** and **7** (Table 2), the ^{15}N NMR parameters of **2**, **4**, **6** and **7** are of interest (Table 3). The major question regarding the solution-state structures of the 1,3,2-diazaphospha-[3]ferrocenophanes concerns the mutual orientation of the bond vectors of the P substituent and the N–H bonds. In the case of **2a**, ^{1}H-^{1}H NOE difference experiments indicated *syn* orientation (see Scheme 1), the same as determined by X-ray structural analysis [13]. Expectedly, this orientation did not change with oxidation, as shown by the molecular structure of **2d** [13]. Apparently, the magnitude of the coupling constants $|^{2}J(^{31}PN^{1}H)|$ serves as an unambiguous criterion to decide between the alternative solution-state structures of

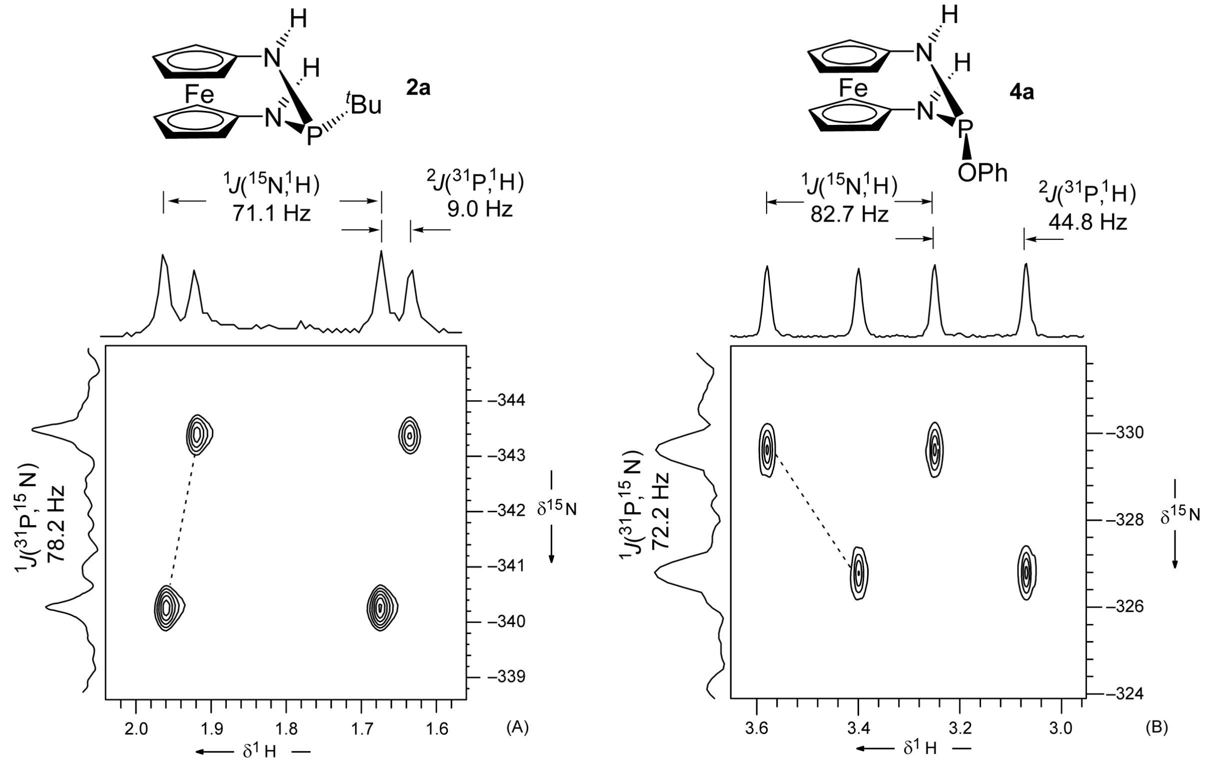


Fig. 1. Contour plot of the 25.4 MHz $^1H/^{15}N$ heteronuclear shift correlation (HMQC, refocused) for **2a** and **4a** (both in CD_2Cl_2 at 23 °C). Note the positive and negative tilt of the cross peaks for **2a** and **4a**, respectively (see text).

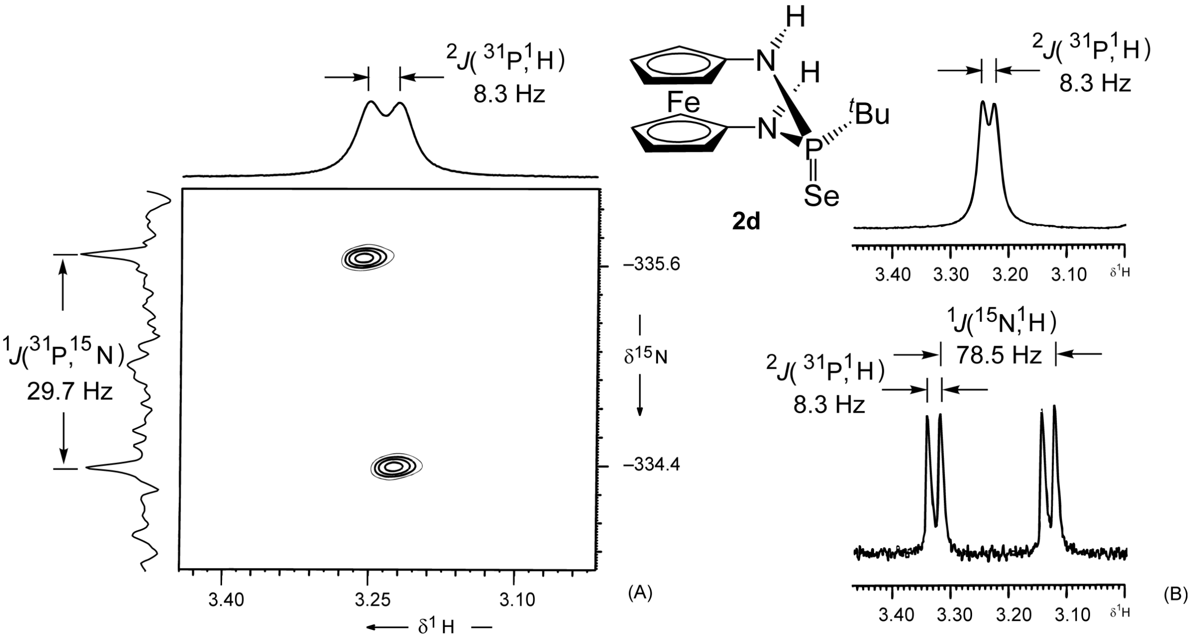


Fig. 2. (A) 40.5 MHz $^{15}N/^1H$ heteronuclear shift correlation (gHSQC [19] with ^{15}N decoupling in F_1) of **2d** ($CDCl_3$ at 23 °C). (B) The results of the corresponding 1D experiment with (upper trace) and without ^{15}N decoupling (lower trace).

the P(III) compounds **2a** and **4a**. This suggests that the conformation of **2a** is opposite from that of **4a**. It is known that in the case of comparable coupling constants $^2J(^{31}P,^{13}C)$ [15], magnitude and sign depend on the analogous geometrical factors. Therefore, 2D $^1H/^{15}N$ inverse correlation experiments were performed to compare the signs of the coupling constants $^1J(^{31}P,^{15}N)$ and $^2J(^{31}PN^1H)$ (Figs. 1 and 2).

For the correct interpretation of the results of such experiments, the negative sign of the gyromagnetic ratio $\gamma(^{15}N)$ must be considered, and it is more advisable to use the concept of reduced coupling constants $K(AB) = 4\pi^2 J(A,B)\ (\gamma_A \gamma_B\ h)^{-1}$. Thus, the positive tilt of the cross peaks [16] in the $^1H/^{15}N$ correlation for **2a** proves alike signs of $^1K(^{31}P,^{15}N)$ and $^2K(^{31}PN^1H)$, whereas the analogous experiment for **4a** reveals opposite signs, indicated by the negative tilt of the cross peaks. Since $^1K(^{31}P,^{15}N)$ in aminophosphanes is invariably negative [17, 18], it follows that $^2K(^{31}PN^1H)$ in **2a** is relatively small and negative, in contrast with large and positive $^2K(^{31}PN^1H)$ in **4a**. Since both gyromagnetic ratios $\gamma(^{31}P)$ and $\gamma(^1H)$ are > 0, the signs of ^2K and ^2J are the same.

In the cases of the P(V) compounds in the series **2** or **4**, the magnitude of the coupling constants $|^2J(^{31}PN^1H)|$ is less diagnostic, considering that they are small and may be of either sign, as is frequently observed for geminal coupling constants. Although the 2D $^{15}N/^1H$ correlation experiment for **2d** in Fig. 2 proves opposite signs of $^1K(^{31}P,^{15}N)$ and $^2K(^{31}PN^1H)$ (negative tilt of the cross peaks), this result is less straightforward to analyze in a general way, since the sign of $^1K(^{31}P,^{15}N)$ may be negative or positive in P(V)-N compounds [17, 18].

A sample of **2d** was selected to analyze the $^{31}P\{^1H\}$ NMR spectrum for satellites (Fig. 3) due to spin-spin coupling of ^{31}P with spin-1/2 nuclei other than ^1H. In the case of ^{77}Se, this is more of a routine nature, and many data $^1J(^{77}Se,^{31}P)$ are listed in the literature [20]. Of course, information on coupling constants $^nJ(^{31}P,^{13}C)$ are also readily obtained from $^{13}C\{^1H\}$ NMR spectra, although the measurements of these data from ^{31}P NMR spectra may be an alternative, in particular if isotope-induced chemical shifts [21] $^n\Delta^{12/13}C(^{31}P)$ are of interest. In the case of $^1J(^{31}P,^{15}N)$, the measurement of ^{15}N NMR spectra sometimes may be time consuming, whereas an excellent signal-to-noise ratio in ^{31}P NMR spectra is readily accomplished. Moreover, isotope-induced chemical shifts $^1\Delta^{14/15}N(^{31}P)$ cover a fairly large range [22, 23] and deserve more attention. In general, ^{31}P NMR signals of P-N compounds are more or less severely broadened owing to partially relaxed (unresolved) ^{31}P-^{14}N spin-spin coupling, and the broadening depends on the number of ^{14}N nuclei linked to ^{31}P, the magnitude of $^1J(^{31}P,^{14}N)$ and the quadrupole-induced nuclear spin relaxation times $[T^Q(^{14}N)]$. In order to reduce the relative intensity of the central ^{31}P NMR signal, it has been proposed to enhance the ^{31}P magnetization by polarization transfer and extend this pulse sequence by a Hahn echo with appropriate delays (HEED experiments) [22]). This is most effective if there is only one ^{14}N linked to the ^{31}P nucleus. However, it also can help to reduce the line width of the ^{31}P NMR signal of an ^{14}N-^{31}P-^{15}N isotopomer, and therefore allows to detect the ^{15}N satellites more readily, as shown in Fig. 3, where the ^{15}N satellites are somewhat less broad, and their height is similar even greater than for ^{13}C satellites, in spite of the three-times lower natural abundance of ^{15}N.

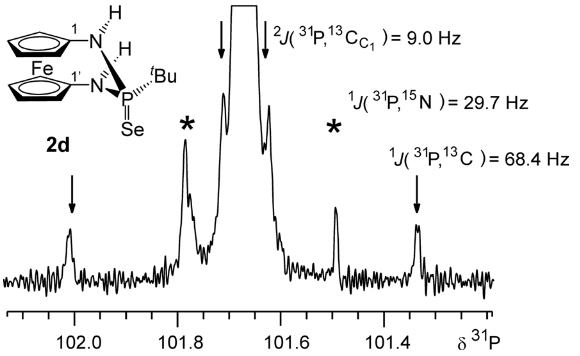


Fig. 3. 101.3 MHz $^{31}P\{^1H\}$ NMR spectra (refocused INEPT [27] with Hahn echo extension [22]) of **2d** ($CDCl_3$ at 23 °C; Hahn echo delay 0.05 s). The ^{13}C satellites for $^nJ(^{31}P,^{13}C)$ are marked by arrows. The ^{15}N satellites for $^1J(^{31}P,^{15}N)$ are marked by asterisks.

The proposed conformation of the 1,3,2-diazaphospha-phenalene derivatives **6** and **7** in solution follows from ^1H-^1H NOE difference experiments. A typical example is shown in Fig. 4 for **7d**. There is no NOE for the $^1H(OPh)$ NMR signals upon irradiation of the $^1H(NH)$ transitions and *vice versa*, whereas an NOE is observed for the $^1H^{ortho}(OPh)$ NMR signals (along with the expected strong NOE for the $^1H(NH)$ and of other ^1H(CH-phenalene) NMR signals) upon irradiation of the $^1H^{4,9}$ transitions.

The calculations [24] of both sign and magnitude of the coupling constants $^2J(^{31}PN^1H)$ for the optimized geometries of the model compounds **9M**(*syn*)

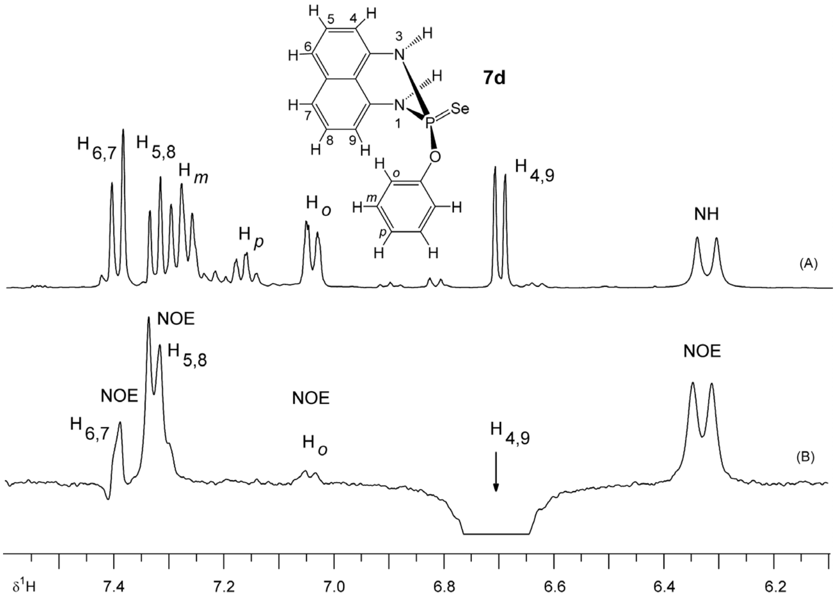


Fig. 4. 399.8 MHz ^{1}H-^{1}H NOE difference spectra (gradient enhanced [26]) of **7d** (in CD_2Cl_2 at 23 °C; relaxation delay 2.0 s; mixing time 0.9 s). (A) Normal ^{1}H NMR spectrum. (B) Irradiation of $^1H^{4,9}$; response: ^{1}H(NH), $^1H^{5,8}$, $^1H^{6,7}$, and $^1H^{ortho}$(OPh).

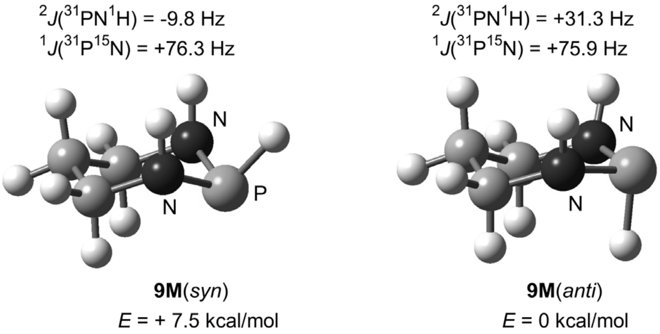


Fig. 5. Optimized geometries (B3LYP/6-311+G(d,p) [24]) of the 1,3,2-diazaphosphorinanes **9M**, together with calculated coupling constants $^2J(^{31}PN^1H)$ [24].

and **9M**(*anti*) is in complete agreement with the experimental findings (Fig. 5). It is of interest to note that the magnitude of $^1J(^{31}P,^{15}N)$, in contrast with $^2J(^{31}PN^1H)$, is hardly affected by the different conformations. This has been noted previously for some non-cyclic aminophosphanes [3b].

*Solid-state structural studies of the 2-phenoxy-1,3,2-diazaphospha-[3]ferrocenophanes **4a**, **4b** and 2-tert-butyl-2,3-dihydro-1H-1,3,2-diazaselenophosphoryl-phenalene **6d***

The molecular structures of **4a** and **4b** are shown in Fig. 6, and selected structural parameters are given in Table 4, together with data for **2a** for comparison. In the case of **4a**, intermolecular interactions are weak or negligible, whereas the molecules of **4b** are linked by N–H···O hydrogen bonds in slightly different zig-zag chains, of which one is picked out in part in Fig. 7. The structural data of **4a** and **2a** are well comparable except for the different conformation. The *anti* orientation of P–OPh and N–H bonds in **4a** enforces widening of the bond angles P–N–C(1,6) (127.0(3)°, 125.9(2)°), in contrast to the *syn* conformation of P–^{t}Bu and N–H bonds in **2a** (115.0(4)°, 113.4(4)°). Oxidation of phosphorus to give **4b** causes the usual changes in bond lengths and angles in the surroundings of the phosphorus atom.

The molecular structure of **6d** (Fig. 8; see Table 5 for structural parameters) shows that N–H bonds and the P-^{t}Bu group are in *anti*-position, which is most likely true also for the P(III) compound **6a**, in agreement with the findings for the N–H bonds and the P-OEt group in **8a** [7a]. It is therefore concluded that this particular conformation is usually observed irrespective of the substituent at the phosphorus atom. Thus,

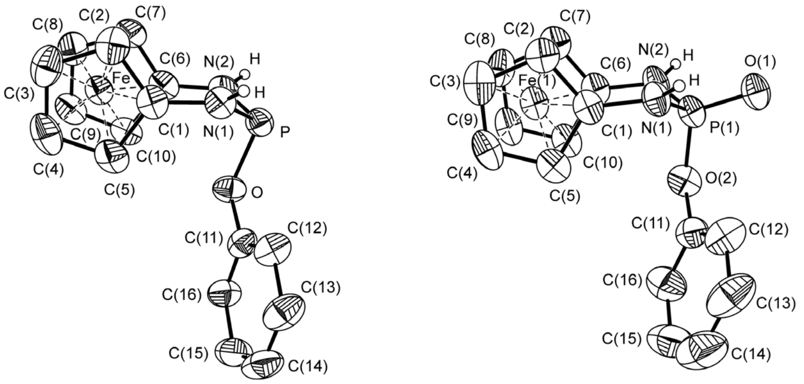


Fig. 6. Molecular structures of **4a** (left) and **4b** (right) in the solid state (ORTEP, 40 % probability ellipsoids; hydrogen atoms (except NH) omitted for clarity). For selected distances and angles see Table 5.

Table 4. Selected bond lengths (pm) and angles (deg)[a] of the 2-phenoxy-1,3,2-diazaphospha-[3]ferrocenophanes **4a**, **4b**, and of the 2-*tert*-butyl-1,3,2-diazaphospha-[3]ferrocenophane **2a**[b] for comparison.

	4a R = OPh	**4b**[c] R = OPh E = O		**2a** R = ^{t}Bu
P–N(1)	169.4(3)	162.5(3)	P–N(1)	172.1(5)
P–N(2)	170.0(3)	161.4(3)	P–N(2)	174.4(4)
P–O	166.1(3)	159.6(3)	P–C(11)	185.9(6)
C(1)–N(1)	141.3(5)	142.6(4)	C(1)–N(1)	142.7(7)
C(6)–N(2)	139.8(6)	143.4(4)	C(6)–N(2)	143.1(6)
P–O(1)		146.3(2)		
N(1)···N(2)	272.3	267.5	N(1)···N(2)	274.3
C(1)···C(6)	307.4	308.2	C(1)···C(6)	312.3
N(1)–P–N(2)	106.68(16)	111.40(16)	N(1)–P–N(2)	104.7(2)
N(1)–P–O	100.13(17)	107.30(15)	N(1)–P–C(11)	101.8(2)
N(2)–P–O	94.44(16)	100.68(15)	N(2)–P–C(11)	101.4(2)
N(1)–P–O(1)		111.95(15)		
N(2)–P–O(1)		112.19(16)		
P–N(1)–C(1)	127.0(3)	124.4(2)	P–N(1)–C(1)	115.0(4)
P–N(2)–C(6)	125.9(2)	124.2(2)	P–N(2)–C(6)	113.4(4)
P–O–C(11)	124.5(3)	127.5(3)		
O(1)–P–O(2)		112.73(15)		
C_5 / C_5 (α)	9.2	9.1	C_5 / C_5 (α)	8.9
C_5 / N(1) (β_1)	4.5	4.6	C_5 / N(1) (β_1)	5.5
C_5 / N(2) (β_2)	2.1 towards iron	4.8 towards iron	C_5 / N(2) (β_2)	1.8 towards iron
C_5-Fe-C_5 (γ)	172.4	173.7	C_5-Fe-C_5 (γ)	171.9
C_5 / C_5 (twist) (τ)	0.3	0.1	C_5 / C_5 (twist) (τ)	0

[a] The definition of the angles α, β, γ and τ is given in refs. [25, 28]; [b] ref. [13]; [c] one of two crystallographically independent molecules selected.

the 1,3,2-diazaphospha-[3]ferrocenophane is a special case, where a bulky substituent such as a ^{t}Bu group at the phosphorus atom prefers the steric repulsion by the N-H groups over that exerted by the C-H units of the ferrocenediyl group.

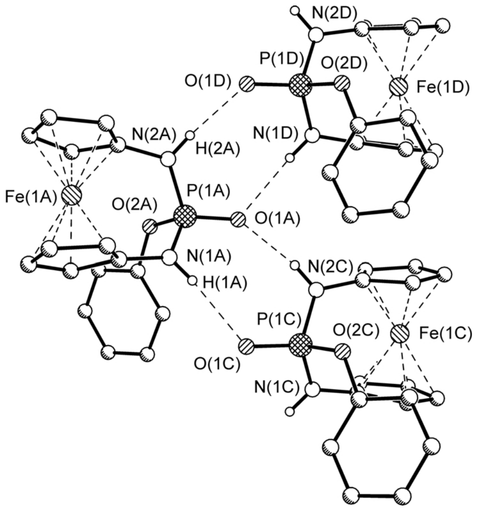


Fig. 7. View of the arrangement of molecules of **4b** in the crystal lattice (ball and stick model), showing close intermolecular contacts: N(1A)···O(1C) 302.9 pm, O(1C)···H(1A) 219.1 pm, N(1A)–H(1A)–O(1C) 164.5°; N(2A)···O(1D) 286.3 pm, O(1D)···H(2A) 205.7 pm, N(2A)–H(2A)–O(1D) 155.6°. The second independent arrangement of **4b** is similar, and in both cases, no hydrogen bonds are present between the zig-zag chains.

Conclusions

1,3,2-Diazaphospha-[3]ferrocenophanes are unique cyclic diaminophosphanes, since they exist in solution and in the solid state in different conformations, depending on the bulkiness of the substituent at the phosphorus atom, as shown by determination of the structure in solution by various 1D and 2D NMR spectroscopic techniques and in the solid state by X-ray structural analysis. These conformations remain unchanged after oxidation of the phosphorus atom.

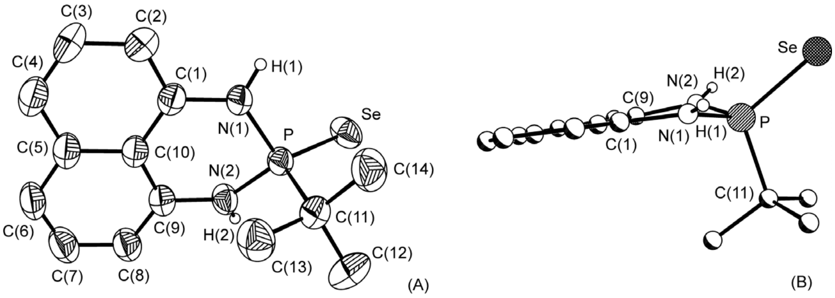


Fig. 8. Two views of the molecular structure of **6d** in the solid state (A: Ortep, 40 % probability ellipsoids; B: ball and stick model; hydrogen atoms (except NH) are omitted for clarity). See Table 5 for structural parameters.

Table 5. Selected bond lengths (pm) and angles (deg) of 2-*tert*-butyl-2,3-dihydro-1*H*-1,3-diaza-2-selenophosphoryl-phenalene **6d** and of 2-ethoxy-2,3-dihydro-*1H*-1,3,2-diazaphospha-phenalene **8a** (ref. [7a]) for comparison.

	6d R = ^{t}Bu		**8a** R = OEt
P–N(1)	165.8(4)	P–N(1)	170.1(4)
P–N(2)	165.7(4)	P–N(2)	167.4(5)
P–Se	210.78(13)		
C(1)–N(1)	140.9(5)	C(1)–N(1)	140.3(6)
C(9)–N(2)	141.3(6)	C(3)–N(2)	140.8(6)
P–C(11)	184.1(5)	P–O	162.3(3)
N(1)–P–N(2)	100.45(19)	N(1)–P–N(2)	95.1(2)
N(1)–P–C(11)	108.3(2)	N(1)–P–O	105.2(2)
N(2)–P–C(11)	108.7(2)	N(2)–P–O	105.9(2)
N(1)–P–Se	112.35(15)		
N(2)–P–Se	113.53(14)		
P–N(1)–C(1)	126.1(3)	P–N(1)–C(1)	126.9(3)
P–N(2)–C(9)	125.3(3)	P–N(2)–C(3)	128.5(4)
Se–P–C(11)	112.79(16)		

Experimental Section

General

All preparative work as well as handling of the samples was carried out observing precautions to exclude traces of air and moisture. Carefully dried solvents and oven-dried glassware were used throughout. The deuterated solvents CD_2Cl_2 and $CDCl_3$ were distilled over CaH_2 in an atmosphere of argon. All other solvents were distilled from Na metal in an atmosphere of argon. 1,1′-Diaminoferrocene (**1**) was prepared according to the published procedure [12]. Triethylamine was distilled from Na prior to use. Other starting materials were purchased from Aldrich (^{t}BuPCl$_2$) or Acros (PhOPCl$_2$, PhOP(O)Cl$_2$), and used without further purification. NMR measurements: Bruker ARX 250: ^{1}H, ^{13}C, ^{31}P, ^{77}Se, and ^{15}N NMR; Varian INOVA 400: ^{1}H, ^{13}C, ^{31}P NMR; Bruker DRX 500: ^{1}H, ^{13}C, ^{31}P NMR; chemical shifts are given with respect to SiMe$_4$ [δ^1H (CHCl$_3$/CDCl$_3$) = 7.24; (CDHCl$_2$) = 5.33; ((CDH$_2$)$_2$SO) = 2.50; δ^{13}C (CDCl$_3$) = 77.0; (CD$_2$Cl$_2$) = 53.8; ((CD$_3$)$_2$SO) = 39.4]; external aqueous H$_3$PO$_4$ (85 %) [δ^{31}P = 0 for $\Xi(^{31}$P) = 40.480747 MHz], external neat MeNO$_2$ [δ^{15}N = 0 for $\Xi(^{15}$N) = 10.136767 MHz]. The assignments of ^{1}H and ^{13}C NMR signals are based on ^{1}H-^{1}H NOE difference [26], and 2D ^{1}H/^{13}C gHSQC experiments [19]. For special purposes (see. Fig. 3), ^{31}P{^{1}H} NMR spectra were recorded using the refocused INEPT pulse sequence [27] extended by an appropriate Hahn echo delay [22, 23f]. IR spectra: Perkin Elmer Spectrum 2000 FTIR. EI-MS spectra: Finnigan MAT 8500 spectrometer (ionisation energy 70 eV) with direct inlet, the *m/z* data refer to the isotopes ^{1}H, ^{12}C, ^{14}N, ^{56}Fe, ^{16}O, ^{32}S and ^{80}Se. The melting points (uncorrected) were determined using a Büchi 510 melting point apparatus. All calculations were carried out using the Gaussian program package [24].

*2-Phenoxy-1,3,2-diazaphospha-[3]ferrocenophane (**4a**)*

A suspension of 1,1′-diaminoferrocene **1** (287 mg, 1.33 mmol) in Et$_2$O (25 mL) together with triethylamine (0.44 mL, 3.16 mmol) was prepared. The suspension was cooled to 0 °C, and PhOPCl$_2$ (259 mg, 1.33 mmol) dissolved in Et$_2$O (5 mL) was injected slowly through a syringe. The reaction mixture was stirred at 0 °C for 2 h; then it was allowed to reach ambient temperature and kept stirring for 20 h. Insoluble materials were filtered off, and volatile materials were removed from the filtrate *in vacuo*. The remaining yellow solid was dissolved in Et$_2$O (20 mL), and the solution was filtered. After removing of the solvent *in vacuo* the product **4a** (287 mg; 64 %) was left as a yellow-orange oily material (together with some **5**/**5′**, < 2 %). Orange single crystals of **4a** suitable for X-ray diffraction were grown from toluene solution after 2 weeks at −20 °C (m. p. 226 – 229 °C).

4a: ^{1}H NMR (250.1 MHz, [D$_8$]toluene, 23 °C): δ = 2.57 (br. d, 2H, NH, $^2J(^{31}$PN^{1}H) = 44.8 Hz), 3.63, 3.84, 3.95 and 3.97 (all m, 8H, H$^{2-5,2'-5'}$), 6.86 (m, 1H, Ph), 7.00 – 7.25 (m, 4H, Ph). – ^{1}H NMR (250.1 MHz, CD$_2$Cl$_2$, 23 °C): δ = 3.48 (br. d, 2H, NH, $^2J(^{31}$PN^{1}H) = 44.5 Hz), 3.99, 4.01 and 4.13 (all m, 2H, 4H, 2H, H$^{2-5,2'-5'}$), 7.10 (m, 1H, Ph), 7.20 – 7.45 (m, 4H, Ph).

5: ^{31}P NMR (101.3 MHz, CDCl$_3$, 23 °C): δ = 116.2 (d, 1P, $^2J(^{31}$P, ^{31}P) = 394.2 Hz), 135.2 (d, 1P, $^2J(^{31}$P, ^{31}P) = 394.2 Hz).

Table 6. Crystallographic data of the 2-phenoxy-1,3,2-diazaphospha-[3]ferrocenophanes **4a**, **4b** and of 2-*tert*-butyl-2,3-dihydro-*1H*-1,3-diaza-2-selenophosphoryl-phenalene **6d** [29].

	4a	**4b**	**6d**
Formula	$C_{16}H_{15}FeN_2OP$	$C_{16}H_{15}FeN_2O_2P$	$C_{14}H_{17}N_2PSe$
Crystal	orange prisms	yellow needles	light-yellow rhombs
Dimensions, mm^3	$0.22 \times 0.18 \times 0.08$	$0.25 \times 0.18 \times 0.08$	$0.26 \times 0.18 \times 0.15$
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1$	$P2_1/n$	$P\bar{1}$
Lattice parameters			
a, pm	606.91(12)	1805.5(4)	849.29(17)
b, pm	1257.7(3)	680.44(14)	918.20(18)
c, pm	944.13(19)	2558.0(5)	1079.2(2)
α, deg	90	90	65.68(3)
β, deg	99.34(3)	106.73(3)	71.60(3)
γ, deg	90	90	86.24(3)
Z	2	8	2
Absorption coefficient μ, mm^{-1}	1.2	1.1	2.7
T, K	293		
Diffractometer	Stoe IPDS I (MoK_α, λ = 71.073 pm), graphite monochromator		
Measuring range ϑ, deg	2.2 – 28.1	2.4 – 28.1	2.2 – 26.0
Reflections collected	6081	6918	5395
Independent reflections [$I \geq 2\sigma(I)$]	3043	6918	2633
Absorption correction	none[a]	none[a]	numerical
Max. / min. transmission	–	–	0.7672 / 0.5530
Refined parameters	190	397	163
$wR2/R1$ [$I \geq 2\sigma(I)$]	0.103 / 0.043	0.072 / 0.040	0.131 / 0.055
Absolute structure parameter	0.01(2)	–	–
Max./min. residual electron density, e pm$^{-3} \cdot 10^{-6}$	0.748 / −0.553	0.438 / −0.230	0.901 / −0.336

[a] Absorption corrections did not improve the structure refinement.

5′: ^{31}P NMR (101.3 MHz, $CDCl_3$, 23 °C): δ = 118.7 (d, 1P, $^2J(^{31}P, ^{31}P)$ = 345.9 Hz), 134.4 (d, 1P, $^2J(^{31}P, ^{31}P)$ = 345.9 Hz).

*2-Phenoxy-1,3,2-diaza-thiophosphoryl-[3]ferrocenophane (**4c**)*

A solution of **4a** (110 mg, 0.33 mmol) in CH_2Cl_2 (5 mL) was added at r. t. to an excess of dry and degassed elemental sulfur (35 mg). The solution was stirred for 1 d and then filtered to separate most of the unreacted sulfur. The solvent was removed *in vacuo*, the remaining yellow-green solid was dissolved in toluene (10 mL), and the solution was filtered. The solvent was removed *in vacuo* to give 98 mg (81 %) of **4c** as a yellow-green solid (m. p. 160 – 165 °C, decomp.). – ^{1}H NMR (250.1 MHz, [D$_8$]toluene, 23 °C): δ = 3.45 (br. d, 2H, NH, $^2J(^{31}PN^1H)$ = 19.2 Hz), 3.57, 3.73 and 3.80 (all m, 2H, 2H, 4H, $H^{2-5,2'-5'}$), 6.86 (m, 1H, Ph), 7.02 (m, 2H, Ph), 7.37 (m, 2H, Ph). – EI-MS (70 eV) for $C_{16}H_{15}N_2OPSFe$ (370.0): *m/z* (%) = 370 (100) [M]$^+$, 290 (5), 276 (50) [M–C_6H_5OH]$^+$, 197 (10), 134 (10).

*2-Phenoxy-1,3,2-diaza-selenophosphoryl-[3]ferrocenophane (**4d**)*

A solution of **4a** (90 mg, 0.27 mmol) in toluene (5 mL) was added at room temperature to an excess of dry and degassed elemental selenium (63 mg, 0.80 mmol). The solution was stirred for 1.5 d, filtered, and the solvent was removed *in vacuo* to give 82 mg (74 %) of **4d** as a yellow solid (m. p. 165 – 174 °C, decomp.). – ^{1}H NMR (250.1 MHz, CD_2Cl_2, 23 °C): δ = 3.96, 4.05, 4.13 and 4.23 (all m, 8H, $H^{2-5,2'-5'}$), 4.23 (br. d, 2H, NH, $^2J(^{31}PN^1H)$ = 21.2 Hz), 7.20 (m, 1H, Ph), 7.32 – 7.47 (m, 4H, Ph). – EI-MS (70 eV) for $C_{16}H_{15}N_2OPSeFe$ (417.94): *m/z* (%) = 418 (100) [M]$^+$, 324 (30) [M–C_6H_5OH]$^+$, 244 (50) [M–C_6H_5OH–Se]$^+$, 229 (14), 214 (12), 182 (10), 134 (18).

*2-Phenoxy-1,3,2-diaza-phosphoryl-[3]ferrocenophane (**4b**)*

A suspension of 1,1′-diaminoferrocene (**1**) (194 mg, 0.9 mmol) in Et_2O (25 mL) together with triethylamine (0.3 mL, 2.15 mmol) was cooled to −20 °C, and PhOP(O)Cl_2 (189 mg, 0.9 mmol) dissolved in Et_2O (3 mL) was injected slowly through a syringe. The reaction mixture was stirred at −20 °C for 2 h; then it was allowed to reach ambient temperature and kept stirring for 1.5 d. Insoluble materials were filtered off, and volatile materials were removed from the filtrate *in vacuo*. The remaining yellow solid was dissolved in Et_2O (20 mL) and toluene (10 mL), and the solution was filtered. After removing of the solvent *in vacuo* the product **4b** (115 mg; 36 %) was left as a yellow-green solid. Orange single crystals of **4b** suitable for X-ray diffraction were grown from CH_2Cl_2 after 1 week at −30 °C (m. p. 235 – 250 °C, decomp.). – ^{1}H NMR (250.1 MHz, $CDCl_3$, 23 °C): δ = 4.02, 4.08 and 4.20 (all m, 4H, 2H, 2H, $H^{2-5,2'-5'}$), 4.27 (br. d, 2H, NH, $^2J(^{31}PN^1H)$ = 12.3 Hz), 7.15 (m, 1H, Ph), 7.30–7.45 (m, 4H, Ph). – EI-MS (70 eV) for $C_{16}H_{15}N_2O_2PFe$ (354.02): *m/z* (%) = 354 (100) $[M]^+$, 274 (8), 260 (50) $[M–C_6H_5OH]^+$, 198 (15), 182 (12), 134 (15). IR ($CHCl_3$): ν = 3390 (N–H) cm^{-1}.

2-tert-Butyl-2,3-dihydro-1H-1,3,2-diazaphospha-phenalene (6a)

A solution of 1,8-diaminonaphtalene (224 mg, 1.42 mmol) in toluene (15 mL) together with triethylamine (0.45 mL, 3.2 mmol) was cooled to 0 °C, and $^tBuPCl_2$ (225 mg, 1.42 mmol) dissolved in hexane (3 mL) was injected slowly through a syringe. The reaction mixture was stirred at 0 °C for 2 h, allowed to reach ambient temperature and kept stirring for 20 h. Insoluble materials were filtered off, and volatile materials were removed from the filtrate *in vacuo*. The resulting mixture contained **6a** (*ca.* 70 %) and some starting material (1,8-diaminonaphtalene) as a crimson-colored material, a mixture of an oil with a solid. **7a** was obtained in the same way; the remaining rose-white-colored solid was dissolved in hexane/CH_2Cl_2 (3 : 1.2), filtered off, and the solid was dried *in vacuo* to give **7a** as a white solid.

6a: ^1H NMR (250.1 MHz, CD_2Cl_2, 23 °C): δ = 0.96 (d, 9 H, $3CH_3$, $^3J(^{31}P,^1H)$ = 13.6 Hz), 5.06 (br. d, 2H, NH, $^2J(^{31}PN^1H)$ = 38.0 Hz), 6.58 – 6.61 (m, 2H), 7.05 – 7.15 (m, 4H). – EI-MS (70 eV) for $C_{14}H_{17}N_2P$ (244.11): *m/z* (%) = 244 (5) $[M]^+$, 205 (13), 187 (100) $[M–(CH_3)_3C]^+$, 186 (48) $[M–(CH_3)_3CH]^+$.

7a: ^1H NMR (250.1 MHz, $CDCl_3$, 23 °C): δ = 5.50 (br. d, 2H, NH, $^2J(^{31}PN^1H)$ = 36.9 Hz), 6.48 – 6.52 (m, 2H), 6.90 – 6.98 (m, 2H), 7.0 – 7.1 (m, 1H), 7.15 – 7.3 (m, 6H). – EI-MS (70 eV) for $C_{16}H_{13}N_2OP$ (280.08): *m/z* (%) = 280 (23) $[M]^+$, 232 (7), 187 (100) $[M–C_6H_5O]^+$, 186 (92) $[M–C_6H_5OH]^+$, 140 (9).

The selenides **6d** and **7d** were prepared in the same way as **4d**, using toluene and ether, respectively, as the solvents.

Orange single crystals of **6d** suitable for X-ray diffraction were grown from $CDCl_3$, at −30 °C (m. p. 245 – 250 °C).

6d: ^1H NMR (250.1 MHz, CD_2Cl_2, 23 °C): δ = 1.19 (d, 9H, $3CH_3$, $^3J(^{31}P,^1H)$ = 19.7 Hz), 5.60 (br. d, 2H, NH, $^2J(^{31}PN^1H)$ = 12.6 Hz), 6.68 – 6.72 (dd, 2H, 6.4 Hz, 1.8 Hz), 7.05 – 7.13 (m, 4H). – EI-MS (70 eV) for $C_{14}H_{17}N_2PSe$ (324.03): *m/z* (%) = 324 (15) $[M]^+$, 267 (5) $[M–(CH_3)_3C]^+$, 187 (100) $[M–(CH_3)_3C–Se]^+$, 186 (37) $[M–(CH_3)_3CH–Se]^+$.

7d: (m. p. 170 – 173 °C, decom.): ^1H NMR (250.1 MHz, $CDCl_3$, 23 °C): δ = 6.27 (br. d, 2H, NH, $^2J(^{31}PN^1H)$ = 14.3 Hz), 6.65 – 6.68 (dd, 2H, 7.1 Hz, 1.2 Hz, $H^{4,9}$), 7.02 – 7.08 (m, 2H, H_o), 7.10 – 7.20 (m, 1H, H_p), 7.9 (m, 2H, H_m), 7.34 (m, 2H, $H^{5,8}$), 7.40 (dd, 2H, 8.3 Hz, 1.2 Hz, $H^{6,7}$). – ^1H NMR (399.8 MHz, CD_2Cl_2, 23 °C): δ = 6.32 (br. d, 2H, NH, $^2J(^{31}PN^1H)$ = 14.3 Hz), 6.70 (dd, 2H, 7.3 Hz, 0.8 Hz, $H^{4,9}$), 7.04 (dm, 2H, 8.4 Hz, H_o), 7.17 (m, 1H, H_p), 7.26 – 7.30 (m, 2H, H_m), 7.32 (m, 2H, $H^{5,8}$), 7.39 (dm, 2H, 8.1 Hz, $H^{6,7}$). – EI-MS (70 eV) for $C_{16}H_{13}N_2OPSe$ (359.99): *m/z* (%) = 360 (35) $[M]^+$, 267 (11) $[M–C_6H_5O]^+$, 203 (11), 187 (86) $[M–C_6H_5O–Se]^+$, 186 (100) $[M–C_6H_5OH–Se]^+$, 140 (9).

Acknowledgement

Support of this work by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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[29] CCDC 739348 (**4a** at 293 K), CCDC 739349 (**4b** at 293 K) and CCDC 739350 (**6d** at 293 K) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.