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Aminodiphenylphosphanes: Isotope-Induced Chemical Shifts $^1\Delta^{14/15}N(^{31}P)$, Coupling Constants $^1J(^{31}P,^{15}N)$, and Chemical Shifts $\delta^{15}N$ and $\delta^{31}P$

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ABSTRACT: *A series of aminodiphenylphosphanes* **1** *[Ph_2P-N(H)tBu (**a**), -NEt_2 (**b**), -$NiPr_2$ (**c**)],* **2** *[Ph_2P-NHPh (**a**), -NH-2-pyridine (**b**), -NH-3-pyridine (**c**), -NH-4-pyridine (**d**), NH-pyrimidine (**e**), NH-2,6-Me_2-C_6H_3 (**f**), NH-3-Me-2-pyridine (**g**)],* **3** *[Ph_2P-N(Me)Ph (**a**), -NPh_2 (**b**)], and N-pyrrolyldiphenylphosphane* **4** *(Ph_2P-NC_4H_4) was prepared and studied by NMR (^1H, ^{13}C, ^{31}P, ^{15}N NMR) spectroscopy. The isotope-induced chemical shifts $^1\Delta^{14/15}N(^{31}P)$ were determined at natural abundance of ^{15}N by using HEED INEPT experiments. A dependence of $^1\Delta^{14/15}N(^{31}P)$ on the substituents at nitrogen was found (alkyl < H < aryl; increasingly negative values). The magnitude and sign of the coupling constants $^1J(^{31}P,^{15}N)$ (positive sign) are dominated by the presence of the lone pair of electrons at the phosphorus atom. The X-ray structural analysis of* **2b** *is reported, showing the presence of dimers owing to intermolecular hydrogen bridges in the solid state.* © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:542–550, 2001

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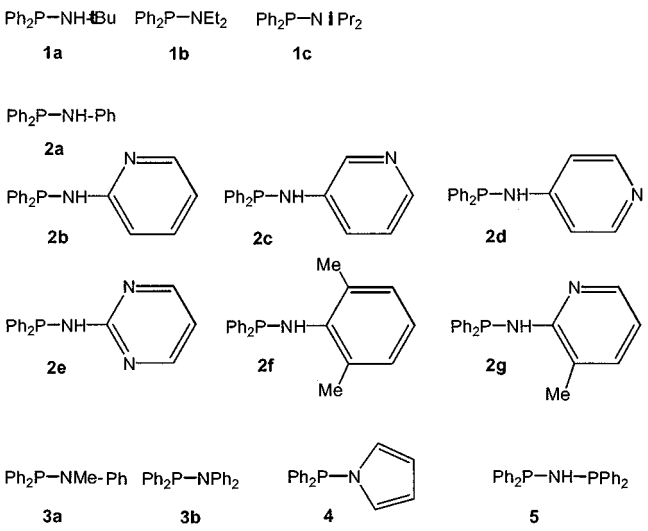
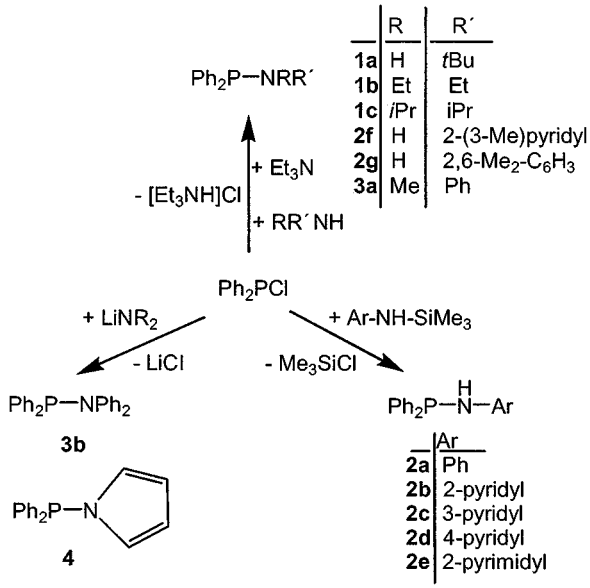
INTRODUCTION

Aminophosphanes have been in the center of various NMR studies, and there is a wealth of ^1H, ^{13}C, and ^{31}P NMR data available [1–4]. More recently, many of these studies were complemented by ^{15}N NMR measurements in order to provide $\delta^{15}N$ and $^1J(^{31}P,^{15}N)$ data [4,5]. ^{15}N chemical shifts are useful for assessing the nature of the PN bond, and they respond to the substituents at the nitrogen atoms. In the case of numerous representative aminophosphanes, the positive sign of the $^1J(^{31}P,^{15}N)$ values [the reduced coupling constants $^1K(^{31}P,^{15}N)$ are negative owing to $\gamma(^{15}N) < 0$] having been firmly established [6,7]. In contrast, a further NMR parameter, the isotope-induced chemical shift $^1\Delta^{14/15}N(^{31}P)$ has received



SCHEME 1 Numbering of aminodiphenylphosphanes studied.



SCHEME 2

only limited attention, although it can be determined now for many examples at natural abundance of ^{15}N (0.37%) using so-called HEED (Hahn-echo extended) polarization transfer experiments [8,9]. By using this technique, the set of data $^{1}\Delta^{14/15}N(^{31}P)$ is already steadily increasing and shows a considerable range, depending on the formal oxidation state of phosphorus, its coordination number, and on the substituents at the phosphorus and nitrogen atoms. In spite of the fact that many aminodiphenylphosphanes are known or can be readily prepared, only a single derivative, $(Ph_2P)_2NH$ **5** [10], has been studied so far with respect to $^{1}\Delta^{14/15}N(^{31}P)$. Therefore, we have prepared a series of these compounds with alkyl, hydrogen, or aryl groups linked to nitrogen (**1–4** in Scheme 1). In all cases it proved possible to determine the $^{1}\Delta^{14/15}N(^{31}P)$ data without ^{15}N labeling. The pyridine derivatives were of interest because of their potential use in coordination chemistry [11], and these derivatives were also useful to investigate a particular effect of the heteroaromatic system in comparison to a phenyl group. Compound **2b** was isolated in crystalline state, and an X-ray structural analysis [11] was carried out.

RESULTS AND DISCUSSION

Synthesis of the Aminodiphenylphosphanes

There are three methods (Scheme 2) that all work well to prepare aminodiphenylphosphanes of the type **1, 2**, and **3a**. *N,N*-diphenylaminodiphenylphosphane **3b** and the *N*-pyrrolyl derivative **4** are best obtained from the reaction of Ph_2PCl with the respective N-lithio derivatives. All phosphanes are colorless solids or oils, sensitive to moisture and well soluble in most hydrocarbons.

Molecular Structure of 2-Pyridylaminodiphenylphosphane **2b**

The crystal structure of **2e** has been reported [12], and recently, parallel to our work, the structure of **2b** was also published [11]. However, details of the structures were not discussed at all (**2e**) or very briefly summarized (**2b**). The crystal data, reported for **2b**, crystallized from $CDCl_3$ [11], differ from our data (single crystals of **2b** were obtained from benzene solution) as far as the cell dimensions, the space group, and the angle β are concerned. Otherwise, the results are very similar. The molecular structure of **2b** [13] is shown in Figure 2, which reveals that dimeric units are present in the lattice due to intermolecular hydrogen bridging. The main structural features of **2b** and **2e** are similar. The surroundings of the phosphorus atoms in **2b** are pyramidal, as expected; however, the bond angles are rather large (all >102°). The angle C(2)N(7)P(8) = 129.6(11)° at the amino nitrogen atom is wide, as a result of bonding to two fairly bulky groups and one hydrogen atom. The small angle (3.7°) between the planes N(1)C(2)C(3) and C(2)N(7)P(8) is at least in part enforced by the intermolecular hydrogen bridging in the solid state. However, even in the absence of these hydrogen bridges (e.g., in solution), one expects a fairly small dihedral angle in order to allow for efficient (pp)π interactions between the amino

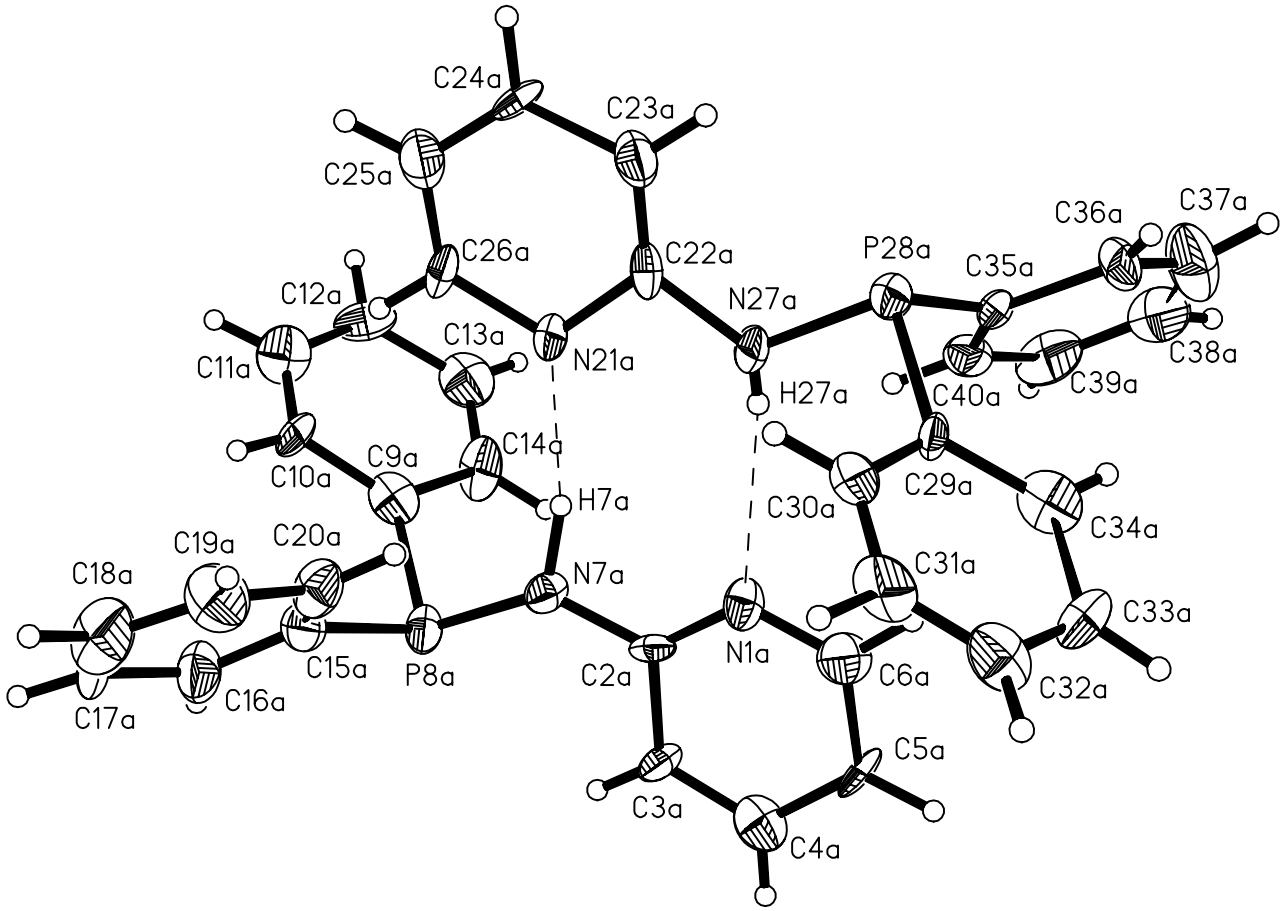


FIGURE 1 In the lattice, dimeric units of **2b** are formed, due to head-to-tail (P)N–H–N(py) intermolecular hydrogen bridging as indicated. Molecular structure of 2-pyridylaminodiphenylphosphane **2b**. Selected bond lengths (pm) and angles (°): P(8)N(7) 167.2(12), P(8)C(9) 184(2), P(8)C(15) 185(2), C(2)N(7) 135(2), N(1)C(2) 129(2), N(1)C(6) 128(2); N(7)P(8)C(9) 102.6(7), N(7)P(8)C(15) 104.1(8), C(9)P(8)C(15) 102.5(7), C(2)N(7)P(8) 129.6(11), N(1)C(2)N(7) 121.4(13); planes N(1)C(2)C(3)/C(2)N(7)P(8) 3.7, C(15)P(8)C(9)/C(2)N(7)P(8) 88.9, C(10C(9)C(14)/C(16)C(15)C(20) 80.9.

nitrogen atom and the 2-pyridyl heteroaromatic system. Semiempirical calculations (AM1 [14]) of monomeric **2b** in the gas phase gave the bond angle C(2)N(7)P(8) = 130.9° (in good agreement with the experimental data; vide supra), and the dihedral angle N(1)C(2)N(7)P(8) = 17.7°. The calculated bond angles at the phosphorus atom are slightly larger than those determined by X-ray analysis.

NMR Spectroscopic Results

The ^{15}N and ^{31}P NMR data of **1–5** are given in Table 1, including coupling constants $J(^{31}P,^{15}N)$ and isotope induced chemical shifts $^{1}\Delta^{14/15}N(^{31}P)$. ^{13}C NMR data are given in Table 2, and ^{1}H NMR data are listed in the Experimental section. The assignment of all NMR signals was straightforward. The compounds are strictly monomeric in solution. With the exception of **2d**, all ^{15}N NMR spectra of the aminopyridines could be measured, and the ^{15}N resonance signals were extremely sharp ($h_{1/2} \leq 0.1$ Hz), indicating the absence of equilibria due to intermolecular association by hydrogen bonding. Furthermore, the NMR data of the amino-pyridine derivatives prove the absence of prototropic equilibria, in agreement with previous ^{1}H, ^{13}C, ^{15}N, and ^{31}P NMR studies of related (either two isopropyl groups at phosphorus or the phosphorus atom is linked to two oxygen atoms) 2-pyridylaminophosphanes [15].

The positive sign $^{1}J(^{31}P,^{15}N)$ [reduced coupling constant $^{1}K(^{31}P,^{15}N) < 0$; $K(A,X) = 4\pi^2 J(A,X)$ ($\gamma(A)$ $\gamma(X)$ h)$^{-1}$] has already been experimentally established for **5** [10], in agreement with literature data [6,7], and, in this work, also for $Ph_2PNHtBu$ (**1a**). In the latter case, selective heteronuclear ^{1}H $^{31}P\}$ double resonance experiments served for the comparison of $^{1}K(^{31}P,^{15}N)$ (<0) and $^{1}K(^{15}N,^{1}H)$ (>0 [16]; $^{1}J(^{15}N,^{1}H) = -77.0$ Hz). In this experiment ^{15}N is the passive spin, and since $\gamma(^{15}N) < 0$, it is advisable to use the notation of reduced coupling constants. The 2D

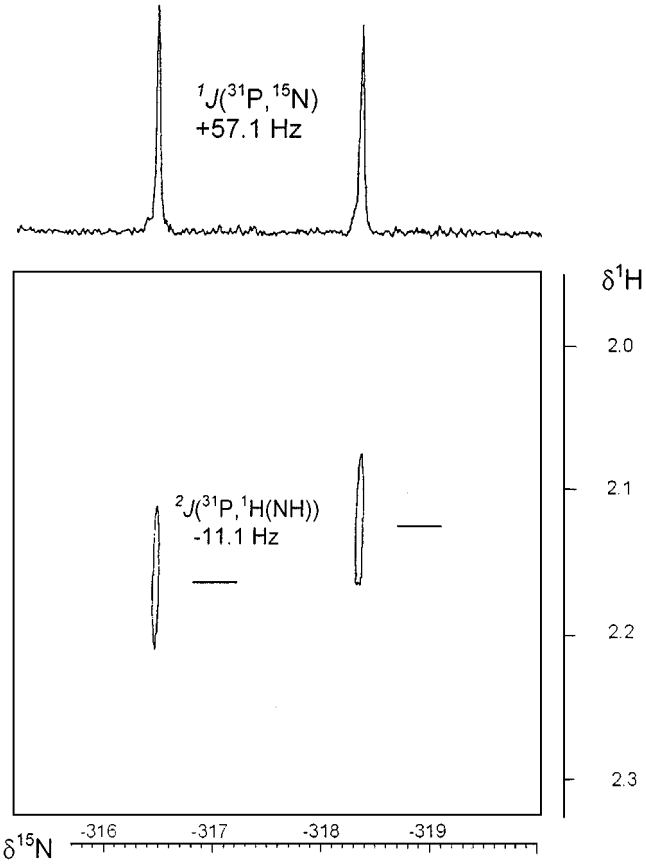


FIGURE 2 Contour plot of the 2D $^{15}N/^1H$ HETCOR experiment for **1a** (in C_6D_6 at 25°C; result of 64 scans and 32 experiments, with zero filling and Gaussian enhancement in both dimensions; 45 minutes of spectrometer time) showing a positive tilt for the cross peaks which arise from $^{31}P–^{15}N$ and $^{31}P–^1H(NH)$ coupling, indicating that the reduced coupling constants $^1K(^{31}P,^{15}N)$ (<0) and $^2K(^{31}P,^1H(NH))$ (<0) have identical signs.

$^{15}N/^1H$ HETCOR experiment (Figure 2) shows that $^2K(^{31}P,^1H(NH))$ (<0; $^2J(^{31}P,^1H(NH) = -11.9$ Hz) and $^1K(^{31}P,^{15}N)$ (<0) have the same sign (positive tilt of the cross peaks [17]). It can be assumed that all coupling constants $^1J(^{31}P,^{15}N)$ reported in this work possess a positive sign [$^1K(^{31}P, ^{15}N) < 0$], typical of the influence of the lone pair of electrons at the phosphorus atom [18]. The magnitude of $^1J(^{31}P, ^{15}N)$ (range from 50.3 to 63.5 Hz) changes very little, considering the different types of substituents at the nitrogen atom. This indicates that the influence of the phosphorus lone pair of electrons is dominating.

In contrast to the $^1J(^{31}P^{15}N)$ data, there is a fairly large range of the $\delta^{31}P$ data (23.8 to 62.5 ppm), and also of the $\delta^{15}N$ data (−226.5 to −344.7 ppm), as one would expect. The $\delta^{31}P$ data are not markedly affected if the phenyl (**2a**) is replaced by a pyridyl group (e.g., **2b–e**) at nitrogen, whereas the $\delta^{15}N$(amino) and $\delta^{15}N$(pyridine) values of the aminopyridine derivatives reflect increased (pp)π interactions when compared with the aniline derivative. This is in agreement with the results of previous NMR studies on aminopyridines [19,20]. The $\delta^{15}N$ data appear to be more sensitive than $\delta^{13}C$ data to changes in (pp)π interactions as a result of geometric constraints. Thus, the $\delta^{13}C$(pyridine) data of **2g** suggest that (pp)π bonding of the ring to the exocyclic nitrogen is hardly reduced as compared with **2b**, whereas the shift of the ^{15}N resonance of the amino nitrogen atom to lower frequencies (>20 ppm) and that of the pyridine nitrogen atom to higher frequencies (>20 ppm) clearly indicate reduced (pp)π interactions. This is also in agreement with the results of AM1 calculations [14] for **2g**, which give a dihedral angle N(1)C(2)NP = 66.4° (calculated for **2b**: 17.7°; **2e**: 8° and −172°). Another indication of potential (pp)π interactions is the magnitude of the coupling constants $^3J(^{31}P,^{13}C_{ar})$, which is substantial if a planar arrangement of the amino group and the aromatic ring is favorable and is close to zero (see **2g**) if this arrangement is unfavorable owing to steric hindrance. Both $\delta^{15}N$ and the $^3J(^{31}P,^{13}C_{pyr})$ values appear to be more reliable with regard to evaluation of the (pp)π bonding interactions than the changes in the $\delta^{13}C$ data.

A major contribution to the line widths of the ^{31}P resonance signals arises from scalar relaxation of the second kind owing to partially relaxed scalar $^{31}P–^{14}N$ coupling. Since this contribution is absent in the case of the $^{31}P–^{15}N$ isotopomers, the ^{15}N satellites owing to $^1J(^{31}P,^{15}N)$ are sharp signals, and their ^{31}P magnetization should decay more slowly than that of the respective $^{31}P–^{14}N$ isotopomer. Therefore, an appropriate delay (≈50 to 200 ms) in the Hahn-echo extension of the polarization transfer pulse sequence (INEPT-HEED) leads to reduced intensity of the parent ^{31}P signal, leaving the ^{15}N satellites almost unaffected; and by this allows for straightforward identification of the ^{15}N satellites as well as for fairly accurate (±1 ppb or better) determination of the isotope-induced chemical shifts $^1\Delta^{14/15}N(^{31}P)$ (Figure 3). The values $^1\Delta^{14/15}N(^{31}P)$ obtained in this work cover a range of ≈20 ppb and appear to be dependent on the type of substituent at the nitrogen atom (see Table 1). Isotope-induced chemical shifts can be understood to represent the combined influence of vibrational and electronic contributions, where the latter may be more important, in particular for heavy nuclei [21]. In the case of $^1\Delta^{12/13}C$ (^{119}Sn), many data have been collected, especially for methyltin compounds, and it was found that the magnitude and sign of the effect can be roughly correlated with the value of the coupling constants $^1J(^{119}Sn,^{13}C)$ [22,23], indicating the importance of the electronic contribution, which is reflected by the electron-mediated indirect nuclear spin–spin

TABLE 1 Chemical Shifts δ^{31}P, δ^{15}N, Isotope-Induced Chemical Shifts $^1\Delta^{14/15}$N(^{31}P)[a], and Coupling Constants $^1J(^{31}P,^{15}N)$ (±0.1 Hz) of the compounds **1–5**

Compound	$\delta^{31}P$	$\delta^{15}N$[b]	$^1\Delta^{14/15}N(^{31}P)$	$^1J(^{31}P,^{15}N)$
1a Ph_2P-NH-*t*Bu	23.8	−320.9	−36.4	57.1
1b Ph_2P-NEt_2[c]	62.5	−344.7	−29.5	61.3
1c Ph_2P-$NiPr_2$[d]	39.2	−324.8	−30.6	62.2
2a Ph_2P-NHPh	29.4	−313.2	−46.9	54.3
2b Ph_2P-NH-2-pyridyl	27.8	−298.4	−45.7	52.7
		−114.4 (py)		<0.5
2c Ph_2P-NH-3-pyridyl	30.2	−317.6	−48.0	55.7
		−68.0 (py)		5.9
2d Ph_2P-NH-4-pyridyl	28.3	n.m.	−48.0	51.4
2e Ph_2P-NH-2-pyrimidinyl	29.0	−290.6	−47.0	51.4
		−125.1 (pyrim.)		8.1
2f Ph_2P-NH-2,6-Me_2-C_6H_3	27.9	−302.2	−47.8	50.3
2g Ph_2P-NH-2-(3-Me)-py	37.0	−321.0	−45.0	58.7
		−93.6 (py)		2.0
3a Ph_2P-N(Me)Ph	56.8	n.m.	−40.0	60.7
3b Ph_2P-NPh_2	55.5	n.m.	−44.8	63.5
4 Ph_2P-NC_4H_4[e]	48.7	−226.5	−33.5	58.5
5 Ph_2P-NH-PPh_2[f]	44.2	n.m.	−40.0	57.3

[a]In ppb (±1 or better); negative sign denotes a shift to lower frequency with respect to the lighter isotopomer.
[b]n.m. means not measured; in the cases of **2d, 3a, 3b**, and experimental conditions for INEPT could not be established; data for **5** were taken from literature, and **5** was not measured again for ^{15}N NMR data.
[c]$^1J(^{31}P,^{13}C) = 15.2$ Hz; $^1\Delta^{12/13}C(^{31}P) = -7.0 \pm 2$ ppb (the lower accuracy is due to overlap with ^{13}C satellites arising from $^2J(^{31}PN^{13}C) = 15.8$ Hz); measured from the satellite spectrum of the $^{13}C-^{31}P-^{15}N$ isotopomer.
[d]For comparison: $[(C_5H_4)_2Fe]$P-N*i*Pr_2: 23.8 (δ^{31}P), −310.6 (δ^{15}N), −35.0 ($^1\Delta^{14/15}N(^{31}P)$, $^1J(^{31}P,^{15}N) = 64.7$ Hz [29].
[e]For comparison: Me_2P-NC_4H_4: 34.4 (δ^{31}P), −220.2 (δ^{15}N), −48.0 ($^1\Delta^{14/15}N(^{31}P)$), $^1J(^{31}P^{15}C) = 56.1$ Hz [25]; *t*Bu_2P-NC_4H_4: 91.6 (δ^{31}P), −218.5 (δ^{15}N), −45.6 ($^1\Delta^{14/15}N(^{31}P)$), $^1J(^{31}P^{15}N) = 63.2$ Hz [26]; $(Me_2N)_2$P-NC_4H_4: 112.9 (δ^{31}P), −204.2 ($\delta^{15}N_{pyrrole}$), −26.0 ($^1\Delta^{14/15}N(^{31}P)$), $^1J(^{31}P^{15}N) = 58.7$ Hz; $[CH_2N(Me)]_2$P-NC_4H_4: 104.8 (δ^{31}P), −187.9 ($\delta^{15}N_{pyrrole}$), −17.0 ($^1\Delta^{14/15}N(^{31}P)$), $^1J(^{31}P^{15}N) = 86.7$ Hz [25].
[f]Ref. [10].

coupling. Another recent study on $^1\Delta^{12/13}C(^{29}Si)$ values points toward a rather complex dependence of these parameters, not only on the coupling constants $^1J(^{29}Si,^{13}C)$ but also on the nature of the substituents [24]. This is more in agreement with the present results for $^1\Delta^{14/15}N(^{31}P)$ data, where there is no obvious relationship to changes in the magnitude of the coupling constants $^1J(^{31}P,^{15}N)$. Indeed, if both sign and magnitude of $^1J(^{31}P,^{15}N)$ are mainly governed by the influence of the lone pair of electrons at the phosphorus atom (vide supra), electronic effects contributing to $^1\Delta^{14/15}N(^{31}P)$ will not be well reflected by the changes in the magnitude of coupling constants $^1J(^{31}P,^{15}N)$.

This problem of relating $^1\Delta^{14/15}N(^{31}P)$ values directly to coupling constants $^1J(^{31}P,^{15}N)$ can be seen by comparing the data (vide infra) for various *N*-pyrrolylphosphanes available from this work and from the literature [25,26]. The principal structural features of all the pyrrole derivatives are the same as suggested by AM1 calculations [14], in agreement with low-temperature NMR studies on *t*Bu_2P-NC_4H_4 that show that the pyrrole group is oriented parallel to the assumed orientation of the lone pair of electrons at phosphorus [26]. It appears that an increase in the electronegativity of the other groups linked to phosphorus causes a decrease in the magnitude of $^1\Delta^{14/15}N(^{31}P)$ (see the similar $^1\Delta^{14/15}N(^{31}P)$ of the Me_2P and *t*Bu_2P derivatives in contrast to the $(Me_2N)_2$P compound, although the $^1J(^{31}P,^{15}N)$ values are all in a close range). The particular influence of the nature of the lone pair of electrons at the phosphorus atom is evident in the case of the cyclic diazaphospholidine derivative [25], where the value of $^1J(^{31}P,^{15}N)$ changes by 48% and the magnitude of $^1\Delta^{14/15}N(^{31}P)$ becomes smaller by 35% with respect to the noncyclic bis(dimethylamino) derivative [25].

	$Me_2P-NC_4H_4$	*t*$Bu_2P-NC_4H_4$	$Ph_2P-NC_4H_4$	$(Me_2N)_2P-NC_4H_4$	$[CH_2N(Me)]_2P-NC_4H_4$
			4		
$^1\Delta^{14/15}N(^{31}P)$	−48.0	−45.6	−33.5	−26.0	−17.0
$^1J(^{31}P,^{15}N)$	56.1	63.2	58.5	58.7	86.7

TABLE 2 ^{13}C NMR Data of the Compounds **1–4**[a]

Compound	$\delta^{13}C$ *(Ph_2P: i, o, m, p)*	$\delta^{13}C$ *(NR,R)*
1a Ph_2P-NH-*t*Bu[b]	141.1 [13.0], 131.2 [20.2], 128.1 [5.7], 128.3	51.1 [18.7], 32.1 [8.3]
1b Ph_2P-NEt_2	141.1 [15.2], 132.4 [20.1]. 128.37 [5.8], 128.36	44.6 [15.8], 14.6 [3.1]
1c Ph_2P-$NiPr_2$[c]	141.1 [14.0], 132.6 [20.8], 28.0 [4.2], 128.2	47.5 [9.3], 23.7 [6.8]
2a Ph_2P-NHPh	140.5 [12.5], 131.3 [20.8], 128.6 [6.8], 128.9	146.8 [17.1] (*i*), 116.3 [13.0] (o), 129.3 (*m*), 119.6 (*p*)
2b Ph_2P-NH-2-pyridyl	140.1 [11.9], 131.4 [20.8], 128.5 [6.2], 128.9	159.5 [22.3] (2), 108.7 [17.6] (3), 137.4 (4), 114.8 (5), 148.3 (6)
2c Ph_2P-NH-3-pyridyl	139.3 [10.2], 131.9 [20.6], 129.0 [6.5], 129.5	140.3 [11.6] (3), 144.7 [17.9] (2), 122.4 [17.9] (4), 124.2 (5), 140.3 (6)
2d Ph_2P-NH-4-pyridyl	139.3 [11.9], 131.5 [20.8], 128.6 [6.2], 129.2	150.4 (2,6), 111.1 [14.0] (3,5), 153.9 [19.2] (4)
2e Ph_2P-NH-2-pyrimidinyl	140.3 [16.6], 131.7 [21.8], 128.5 [6.2], 128.9	163.6 [16.6] (2), 157.8 [2.1] (4,6), 112.2 (5)
2f Ph_2P-NH-2,6-Me_2-C_6H_3	142.7 [15.5], 131.5 [21.5], 128.5 [5.5], 128.7	19.2 (Me), 143.3 [15.5] (*i*), 130.6 (*o*), 128.3 (*m*), 122.7 (*p*)
2g Ph_2P-NH-2-(3-Me)-py	141.5 [18.5], 131.6 [21.5], 128.5 [6.2], 128.8	16.4 (3-Me), 156.5 [11.5] (2), 117.4 [< 1.5] (3), 137.0 (4), 114.9 (5), 146.1 (6)
3a Ph_2P-N(Me)Ph	137.5 [16.9], 131.9 [20.0], 128.5 [6.2], 128.7	35.6 [9.2] (NMe), 151.6 [26.1] (*i*), 117.6 [15.4] (*o*), 128.9 (*m*), 119.9 (*p*)
3b Ph_2P-NPh_2	137.4 [16.9], 132.4 [21.5], 128.1 [6.2], 128.9	147.8 [7.7] (*i*), 124.3 [7.7] (*o*), 128.9 (*m*), 122.9 (*p*)
4 Ph_2P-NC_4H_4	137.4 [12.3], 132.0 [20.0], 128.6 [6.2], 129.6	125.5 [12.3] (2,5), 112.0 (3,4)

[a]Solutions in C_6D_6 (ca. 10–20%; w/v); $\delta^{13}C$ ±0.1 ppm; coupling constants $^nJ(^{31}P,^{13}C)$ in brackets ±0.5 Hz.
[b]In reasonable agreement with data from Ref. [35].
[c]Data for the N*i*Pr_2 group in agreement with Ref. [31e].

It is tempting to compare the isotope-induced chemical shifts $^1\Delta^{14/15}N(^{31}P)$ with $^1\Delta^{12/13}C(^{31}P)$ data. It appears that these values are small and negative for triorganophosphanes and related compounds [27,28], and much larger, also negative, for λ^3-phosphaalkynes and λ^3-phosphaalkenes [27]. We have determined $^1\Delta^{12/13}C(^{31}P) = -7.0$ ppb for **1b** in order to show that small values are also typical of aminodiphenylphosphanes. This was only possible by observing the satellites of the ^{13}C–^{31}P–^{15}N isotopomer, since otherwise the ^{13}C satellites are broad and unresolved (see Figure 3). Apparently, the trends are similar for both $^1\Delta^{14/15}N(^{31}P)$ and $^1\Delta^{12/13}C(^{31}P)$ values, considering the $^1\Delta^{14/15}N(^{31}P)$ values found in this work, and the larger $^1\Delta^{14/15}N(^{31}P)$ values for phosphazoles [9a] and of *t*BuP = N*t*Bu [9e], in which the phosphorus atoms are two coordinate.

CONCLUSIONS

A series of aminodiphenylphosphanes has been studied by NMR spectroscopy, mainly with respect to isotope-induced chemical shifts $^1\Delta^{14/15}N(^{31}P)$ by using the INEPT-HEED pulse sequence in order to obtain these parameters with ^{15}N at natural abundance. Although there is no obvious correlation of the $^1\Delta^{14/15}N(^{31}P)$ data with bond order, with the coupling constants $^1J(^{31}P,^{15}N)$, or with chemical shifts $\delta^{31}P$ or $\delta^{31}N$, the substituents at the nitrogen atom have a significant influence on $^1\Delta^{14/15}N(^{31}P)$: alkyl < H < aryl (increasingly negative values). The presence of the lone pair of electrons at phosphorus dominates the magnitude and sign of $^1J(^{31}P,^{15}N)$, and the same is true for $^1J(^{31}P,^{13}C)$, which also covers only a small range from 10.2 to 18.5 for the compounds studied. Thus, $^1\Delta^{14/15}N(^{31}P)$ (this work and [9]) and $^1\Delta^{12/13}C(^{31}P)$ values [27] show similar trends.

EXPERIMENTAL

All synthetic work and the handling of samples were carried out under an inert atmosphere (N_2 or Ar), using carefully dried glassware and dry solvents. Diphenylphosphorus chloride, all amines, pyrrole, BuLi (1.6 M in hexane), and **5** were commercially available. Diethylamine, *N*-methylaniline, pyrrole, *N*,*N*-diisopropylamine, and *tert*-butylamine

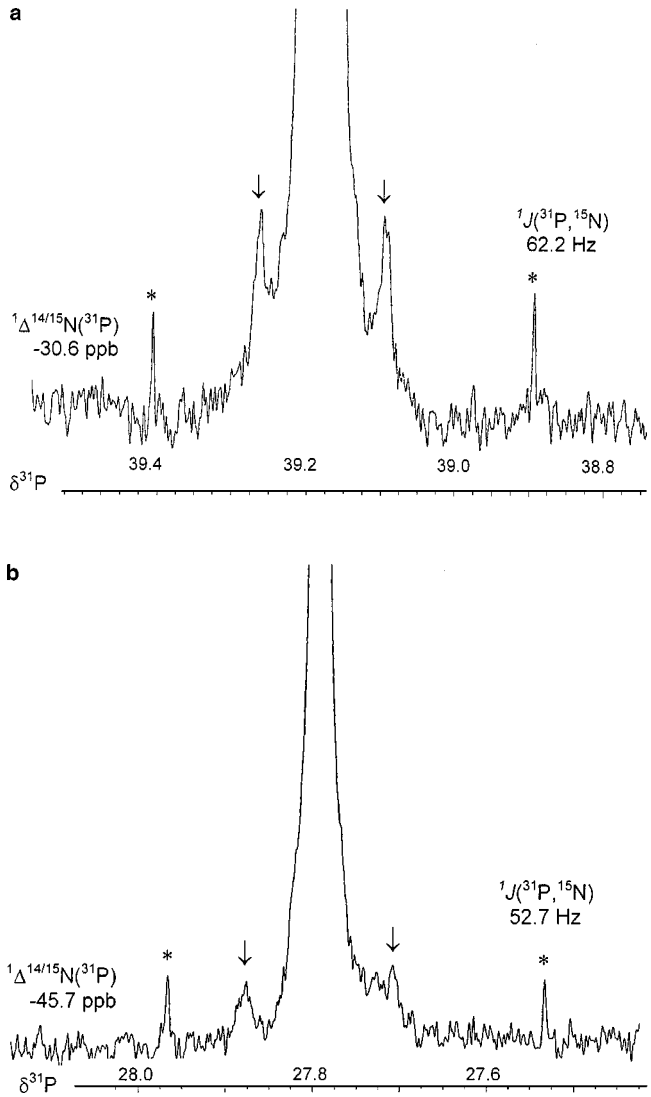


FIGURE 3 (a) Result of application of the INEPT-HEED pulse sequence (based on $J(^{31}P,^{1}H) = 10$ Hz and four hydrogen atoms; 16 transients; Hahn echo delay 100 ms) to Ph_2P-$NiPr_2$ **1c** (in C_6D_6 at 25°C; the ^{15}N satellites are marked by asterisks; note the appearance of the multitude of broad, badly resolved ^{13}C satellites; area is marked by arrows). (b) The same experiment as in part a) but for Ph_2P-NH-2-py **2b** (in C_6D_6 at 25°C; 16 transients; the Hahn echo delay (200 ms) has to be longer since the central line is more narrow owing to faster ^{14}N quadrupolar relaxation as compared to **1c**).

were dried according to established procedures and freshly distilled before use. N-Silylated amines were prepared according to reported procedures [30]. The preparation of the compounds **1a,b,c** [31], **2a** [30c], **2b** [11,32], **2e** [12], **3b** [31a], and **4** [33] has been reported previously. Progress of all reactions was monitored by NMR spectroscopy.

NMR spectra were recorded using a Bruker DPX 300 instrument, equipped with a multinuclear broadband probehead. Chemical shifts are given with respect to solvent signals [δ^1H (C_6D_5H) = 7.15; $\delta^{13}C$ (C_6D_6) = 128.0] and external references for $\delta^{31}P$ ($H_3PO_{4\ (aq)} = 0$ with $\Xi(^{31}P) = 40.480747$ MHz; $\delta^{15}N$ ($MeNO_2$, neat) = 0 with $\Xi(^{15}N) = 10.136767$ MHz; $^{15}N\{^1H\}$ NMR spectra were measured by the refocused INEPT pulse sequence [34], based either on $^1J(^{15}N,^1H)$ for the amino nitrogen or $^2J(^{15}N,^1H) \approx 10$ Hz for the pyridine nitrogen. ^{31}P NMR spectra for measuring isotope-induced chemical shifts $^1\Delta^{14/15}N(^{31}P)$ were recorded by the INEPT-HEED pulse sequence [8], and polarization transfer was based on a coupling constant $^3J(^{31}P,^1H_{ortho}) = 10$ Hz, using Hahn-echo delays between 50 and 200 ms, depending on the width of the ^{31}P NMR signal of the ^{31}P–^{14}N isotopomer (smaller line widths require longer Hahn-echo delays).

Synthesis of the Aminodiphenylphosphanes **1–3:** *General Procedures*

Diethylaminodiphenylphosphane **1b**. A solution of diethylamine (4.07 g; 55.7 mmol) in hexane (100 mL) was cooled to −78°C. Then a solution of diphenylphosphorus chloride (6.14 g, 27.8 mmol) in hexane (20 mL) was added under vigorous stirring, and the mixture was warmed to room temperature and kept stirring for 12 hours. After filtration and removal of the solvent, the product **1b** (7.08 g; 85%) was obtained by fractional distillation as a colorless liquid (b.p 110°C/0.18 Torr). ^1H NMR (300 MHz; C_6D_6): δ^1H [$J(^{31}P,^1H)$] = 7.50, 7.14 (m, 10H, Ph-H_o, $H_{m,p}$), 3.01 [9.5] (d,q, 4H, NCH_2), 0.85 (t, 6H, CH_3).

The compounds **1a** and **1c** were obtained in the same way.

Compound **1a:** Yellow liquid, b.p. 50–53°/0.1 Torr. ^1H NMR (300 MHz; C_6D_6): δ^1H [$J(^{31}P,^1H)$] = 7.45, 7.12 (m, 10H, Ph-H_o, $H_{m,p}$), 2.0 [11.9] (d, 1H, NH, $^1J(^{15}P,^1H) = 77.0$ Hz), 1.18 (s, 9H, *t*Bu).

1c: Colorless liquid, b.p.130–140°C/0.15 Torr; ^1H NMR (300 MHz; C_6D_6): δ^1H [$J(^{31}P,^1H)$] = 7.16, 7.14 (m, 10H, Ph-H_o, $H_{m,p}$), 3.29 [10.6] (d, sept, 2H, NCH), 1.04 [d, 12H, CH_3).

Anilinodiphenylphosphane **2a**. A solution of *N*-trimethylsilylaniline (1.0 g; 6.06 mmol) in benzene (50 mL) was cooled to 0°C. Diphenylphosphorus chloride (1.34 g; 6.06 mmol), dissolved in benzene (10 mL) was added under vigorous stirring. The mixture was warmed to room temperature and stirred continuously for 12 hours. The solvent and chlorotrimethylsilane were removed at low pressure, and the product **2a** was obtained as a viscous yellow liquid. ^1H NMR (300 MHz; C_6D_6): δ^1H [$J(^{31}P,^1H)$] = 4.18 [7.7] (d, 1H, NH, $^1J(^{15}N,^1H = 83.2$ Hz) 6.91–7.4

(m, 15H, PPh, NPh). The compounds **2b, 2c, 2d** and **2e** were prepared in the same way as **2a**.

Compound **2b:** Pale yellow solid (yield 85%); 1H NMR (300 MHz; C_6D_6): δ^1H [$J(^{31}P,^1H)$] = 5.60 [8.4] (s, 1H, NH), 7.09, 6.94, 6.27, 7.79 (m, 4H, pyr-$H^{3,4,5,6}$), 7.45, 7.00 (m, 10H, Ph-H_o, $H_{m,p}$).

Compound **2c:** White solid (yield 87%), ^{1}H NMR (300 MHz; C_6D_6): δ^1H [$J(^{31}P,^1H)$] = 6.32 [7.3] (d, 1H, NH); 8.53, 6.76, 7.46, 7.92 (m, 4H, pyr.-$H^{2,4,5,6}$), 7.54, 7.18 (m, 10H, Ph-H_o, $H_{m,p}$).

Compound **2d:** White solid (yield 90%); ^{1}H NMR (300 MHz; C_6D_6): δ^1H [$J(^{31}P,^1H)$] = 5.75 [7.7] (s, 1H, NH), 8.20, 6.75 (m, 4H, pyr.-$H^{2,6,3,5}$), 7.36, 7.04 (m, 10H, PPh-H_o, $H_{m,p}$).

In the case of **2e**, the reaction mixture was warmed and stirred for 7 days, and **2e** was isolated as a white solid (yield 80%); ^{1}H NMR (300 MHz; C_6D_6): δ^1H [$J(^{31}P,^1H)$] = 7.74, 5.85 (m, 3H, pyr.-$H^{4,6,5}$), 7.46, 7.00 (m, 10H, PPh-H_o, $H_{m,p}$).

N-Methylanilino-diphenylphosphane **3a**. A mixture of *N*-methylaniline (1.2 g; 11.1 mmol) and triethylamine (2.47 g; 11.2 mmol) was dissolved in hexane (150 mL) and cooled to −50°C. Diphenylphosphorus chloride (2.47 g; 11.2 mmol) was added under vigorous stirring. The mixture was warmed to room temperature and kept stirring for 2 hours. Then, insoluble material was filtered off, the solvent was removed in vacuo, and **3a** was obtained as a viscous yellow liquid (2.9 g, 90%). ^{1}H NMR (300 MHz; C_6D_6): δ^1H [$J(^{31}P,^1H)$] = 2.63 [1.5] (d, 3H, NMe), 7.33, 7.21, 6.88 (m, 5H, NPh-H_o, H_m, H_p), 7.39, 7.11 (m, 10H, PPh-H_o, $H_{m,p}$).

Compounds **2f** and **2g** were prepared in the same way as **3a**. **2f:** Colorless solid, ^{1}H NMR (300 MHz; C_6D_6): δ^1H [$J(^{31}P,^1H)$] = 1.96 (s, 6H, Me), 7.22 (m, 9H, N-Ph, PPh-$H_{m,p}$), 7.53 (m, 4H, PPh-H_o);

Compound **2g:** Colorless powder, mp 86-90°C ^{1}H NMR (300 MHz; C_6D_6): δ^1H [$J(^{31}P,^1H)$] = 4.60 [7.1] (s, 1H, NH, $^1J(^{15}N,^1H)$ = 84.3 Hz), 1.57 (s, 3H, CH_3), 7.10, 6.35, 8.09 (m, 3H, pyr.-$H^{4,5,6}$), 7.56, 7.09 (m, 10H, PPh-H_o, $H_{m,p}$).

N,N-Diphenylaminodiphenylphosphane **3b**. A solution of diphenylamine (1.65 g; 9.7 mmol) in hexane (50 mL) was cooled to −78°C, and a solution of ^{n}BuLi in hexane (3.5 mL; 2.5 M) was slowly added. The stirred reaction mixture was warmed to room temperature and then cooled again to −78°C before diphenylphosphorus chloride (2.15 g; 9.7 mmol) were added in one portion. This reaction mixture was warmed to room temperature and stirred continuously for 12 hours. Insoluble material was filtered off, and the solvent was removed in vacuo; product **3b** was left as a yellow oil (2.4 g; 70%). ^{1}H NMR (300 MHz; C_6D_6): δ^1H = 6.98, 7.02, 6.81 (m, 10H, NPh-H_o, H_m, H_p) 7.47, 7.16 (m, 10H, PPh-H_o, $H_{m,p}$).

Crystal Structure Analysis of **2b** *[13].* $C_{17}H_{15}N_2P$, colorless, rectangular crystal (mounted on a capillary) of dimensions $0.364 \times 0.168 \times 0.168$ mm, crystallizes monoclinically, space group *I*a; $a = 1433.2(3)$, $b = 828.2(2)$, $c = 2476.5(5)$ pm, $\beta = 96.79(3)^\circ$; Z = 8, $\mu = 0.179$ mm^{-1}; $F(000)$ 1168; radiation Mo Kα with $\lambda = 71.073$ pm; scan type $\omega/2\Theta$; temperature 183 K; 5721 reflections collected in the range 5.2 to 51.94° in 2Θ (index ranges $-17 \le h \le 17$, $0 \le k \le 10$, $-30 \le l \le 30$), 5721 reflections independent, 1994 reflections assigned to be observed ($F > 4\sigma(F)$); solution and refinement (SHELXS-93) with direct methods (hydrogen atoms: riding model, fixed isotropic U); full=matrix least squares on F^2; refinement with 369 parameters; $R1/wR2$ values 0.0452/0.1054; max./min. residual electron density 0.223/−0.221 e 10^{-6} pm^{-3}.

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