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Aminophosphanes with Bulky Amino Groups: Molecular Structure, Coupling Constants $^1J(^{31}P, ^{15}N)$ and $^2J(^{31}P, ^{29}Si)$, and Isotope-Induced Chemical Shifts $^1\Delta^{14/15}N(^{31}P)$

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ABSTRACT: *The preferred conformation of aminophosphanes with bulky amino groups (***1–20***) was determined by NMR spectroscopy in solution, in two cases in the solid state (***11,17***) and in one case (***11***) by X-ray crystallography. Trimethylsilylaminodiphenylphosphanes $Ph_2PN(R)SiMe_3$ (R = Bu (**1**), Ph (**2**), 2-pyridyl (**3**), 2-pyrimidyl (**4**), Me_3Si (**5**)), amino(chloro)phenylphosphanes Ph(Cl)PNRR′ (R = Bz, R′ = Me (**6**), R = Bz, R′ = ^{t}Bu (**7**), R = Et, R′ = Ph (**8**)), amino(chloro)*tert-*butylphosphanes ^{t}Bu(Cl)PNRR′ (R = R′ = ^{i}Pr (**9**), R = Me, R′ = ^{t}Bu (**10**), R = Bz, R′ = ^{t}Bu (**11**), R = H, R′ = ^{t}Bu (**12**), R = Et, R′ = Ph (**13**), R = ^{i}Pr, R′ = Ph (**14**), R = Bu, R′ = Ph (**15**), R = Bz, R′ = Ph (**16**), R = R′ = Ph (**17**), R = R′ = Me_3Si (**18**)), 3-*tert-butyl-2-chloro-1,3,2-oxazaphospholane (**19**) and benzyl(*tert-*butyl)aminodichlorophosphane (**20**) were studied by ^1H, ^{13}C, ^{15}N, ^{29}Si, and ^{31}P NMR spectroscopy. In all cases, the more bulky substituent at the nitrogen atom prefers the* syn-*position with respect to the assumed orientation of the phosphorus lone pair of electrons. Many of the derivatives studied adopt this preferred conformation even at room temperature. Numerous signs of coupling constants $^1J(^{31}P, ^{15}N)$, $^2J(^{31}P, ^{13}C)$, and $^2J(^{31}P, ^{29}Si)$ were determined. Low temperature NMR spectra were measured for derivatives for which rotation about the P—N bond at room temperature is fast, showing the presence of two rotamers at low temperature. The respective conformation of these rotamers could be assigned by ^{13}C, ^{15}N, and ^{31}P NMR spectroscopy. Isotope-induced chemical shifts $^1\Delta^{15/14}N(^{31}P)$ were determined for all compounds at natural abundance of ^{15}N by using Hahn-echo extended polarization transfer experiments. The molecular structure of* **11** *in the solid state*

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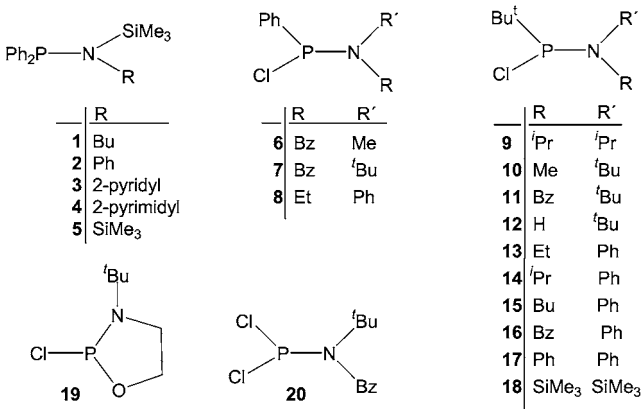
reveals pyramidal surroundings of the nitrogen atom and mutual trans*-positions of the* tert*-butyl groups at phosphorus and nitrogen.* © 2002 Wiley Periodicals, Inc. Heteroatom Chem 13:667–676, 2002; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10084

INTRODUCTION

Aminophosphanes with bulky amino groups are of interest in the synthesis of compounds which require kinetic stabilization [1–4]. With regard to the structure of aminophosphanes, the bulkiness of the amino group may enforce a preferred conformation of the aminophosphane, which otherwise would be less populated. If one or two trimethylsilyl groups are linked to the nitrogen atom, important electronic properties of the amino group are affected [5,6]. Effects exerted by the bulky amino groups should be reflected by NMR parameters. Very few systematic studies on such aminophosphanes have been reported. Trimethylsilylaminophosphanes have been studied focusing on ^{1}H, ^{13}C, ^{29}Si, ^{31}P NMR data and on coupling constants $^{2}J(^{31}P, ^{29}Si)$ [7], and a second report has dealt with similar topics together with ^{15}N NMR parameters and isotope-induced chemical shifts $^{1}\Delta^{14/15}N(^{31}P)$, with emphasis on $(Me_3Si)_2N\text{-}PMe_2$ and derivatives [8]. Recently we determined $^{1}\Delta^{14/15}N(^{31}P)$ values and ^{15}N NMR parameters for a series of aminodiphenylphosphanes [9]. The present work covers similar aspects of some analogous *N*-trimethylsilyl derivatives **1–5**. Amino(phenyl)chlorophosphanes **6–8**, amino(*tert*-butyl)chlorophosphanes **9–18**, a heterocyclic amino(chloro)phosphane **19**, and an aminodichlorophosphane **20** were studied in order to show the general relevance of the NMR data. In the case of **11**, an X-ray structural analysis was carried out, and solid state ^{13}C and ^{31}P MAS spectra were measured to compare the main structural features in the solid and liquid state (see Scheme 1).



SCHEME 1 Aminophosphanes studied.

RESULTS AND DISCUSSION

Synthesis of the Aminophosphanes

Compounds **1–5** were prepared by the reaction of the respective freshly prepared *N*-lithiotrimethylsilylamine with Ph_2PCl [10,11]. The same types of reaction, using $PhPCl_2$, $^{t}BuPCl_2$, or PCl_3 and 1 equiv of the respective lithium amide, afforded the chlorophosphanes **6–18** and **20** either as colorless oils or as colorless solids. The heterocyclic compound **19** was obtained in moderate yield (35%) as a colorless oil from the reaction of PCl_3 in hexane with *N*-*tert*-butyl ethanolamine, $^{t}BuNH\text{-}CH_2CH_2\text{-}OH$, in the presence of 2 equiv of triethylamine. All compounds are sensitive to moisture, can be kept for a prolonged time under an inert atmosphere, and are readily soluble in benzene, toluene or dichloromethane, and chloroform. Slow decomposition takes place in chloroform.

*Molecular Structure of Benzyl(tert-butyl)amino-tert-butyl(chloro)phosphane (**11**)*

The molecular structure of **11** is shown in Fig. 1 together with selected structural data given in the

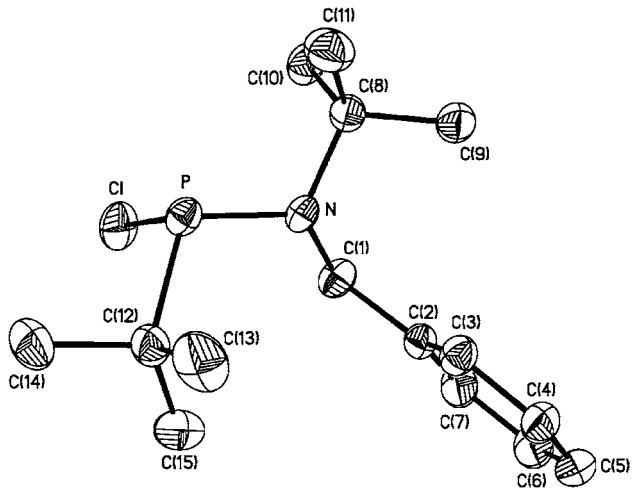


FIGURE 1 ORTEP view of the molecular structure of **11** (50% probability level). Selected bond lengths (pm) and angles (degrees): P—N 168.9(2), P—Cl 216.46(11), P—C(12) 189.0(3), N—C(1) 148.7(3), N—C(8) 154.4(3), C(1)—C(2) 153.6(3), C(8)—C(9) 153.4(4), C(12)—C(13) 154.0(4); N—P—Cl 103.92(8), Cl—P—C(12) 97.94(9), P—N—C(1) 120.98(16), P—N—C(8) 114.8(2), C(1)—N—C(8) 115.14(18), N—C(1)—C(2) 115.8(2); dihedral angles: C(8)NPC(12) 157.2, C(1)PNC(12) 57.4, C(8)PNCl 99.3, C(1)NPCl 46.1.

legend [12]. To the best of our knowledge, this is the first example of a molecular structure of an aminophosphane bearing a chloro function and an alkyl group at the phosphorus atom. The P—N bond (168.8(2) pm) is significantly elongated when compared with that in $F_2P—NMe_2$(162.8 pm [13]), and it is only slightly shorter than that in $^tBu_2P—NEt_2$ (169.1 pm [14]). Other noteworthy features of the molecular structure of **11** are the *gauche* conformation with a maximum distance between the two *tert*-butyl groups (torsion angle C(12)PNC(8) 156.9°) and the nonplanar, i.e. pyramidal surroundings of the nitrogen atom (sum of bond angles at nitrogen 351.1°). The latter is remarkable since the surroundings of the nitrogen atom in $^tBu_2P—NEt_2$ are close to trigonal planar (sum of bond angles 358.5° [14]). The particular conformation of **11** in the solid state means that the N—C(^{t}Bu) bond is almost exactly syn and the N—C(Bz) bond is almost exactly anti with respect to the assumed orientation of the lone pair of electrons at the phosphorus atom.

NMR Spectroscopic Results

Selected NMR data of the compounds studied are listed in Tables 1 (**1–5**), 2 (**6–8**), 3 (**9–18**), and 4 (**19, 20**). The assignment of all NMR data was straightforward, routine 1D and 2D methods being used. The particular structural attraction of the phosphanes studied is the question of their conformation in solution and in the solid state, and in which way this property is reflected by NMR parameters. Furthermore, all phosphanes studied here possess only one P—N bond, which makes them suitable candidates for the determination of isotope induced chemical shifts $^1\Delta^{14/15}N(^{31}P)$ at natural abundance of the isotopes using Hahn-echo extended (HEED) NMR experiments [15], based on polarization transfer [16] from ^1H to ^{31}P.

Conformation of the Aminophosphanes

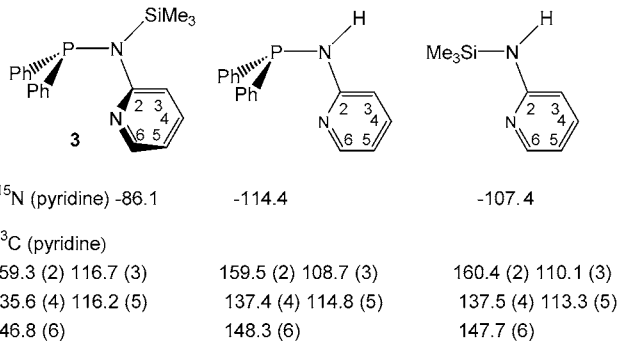
Typical of the conformation with syn and anti orientation of the N—C bond with respect to the assumed orientation of the lone pair of electrons at the phosphorus atom, the sign of $^2J(^{31}P, N, ^{13}C)$ is positive and the magnitude of the coupling constant is large (syn) or the coupling constant is small and of either (frequently negative) sign [17,18]. This is true for most of the phosphanes studied, even at room temperature, and points clearly towards hindered rotation about the P—N bond and the presence of a preferred conformation. In the case of the *N*-silylaminophosphanes **1–4**, the magnitude of $^2J(^{31}P, N, ^{29}Si)$ is large and the sign is negative [7,8] (reduced coupling constant $^2K(^{31}P, N, ^{29}Si) > 0$ because of $\gamma(^{29}Si) < 0$), which indicates that the N—Si bond is in the syn position and the N—C bond in the anti position. Because of the presence of an *N*-trimethylsilyl group in **2, 3**, and presumably also in **4** a coplanar arrangement of the amino group and the respective aromatic ring (phenyl, 2-pyridyl, and 2-pyrimidyl) is energetically unfavorable, and, therefore, (pp)π interactions between the amino-nitrogen atom and the pyridine ring will not be efficient, as indicated by the nitrogen and carbon NMR data shown in Scheme 2 (note the reduced shielding of the pyridine nitrogen and the $^{13}C(3)$ nuclei in **3**).

In the case of **5**, the ^{29}Si NMR spectrum at low temperature reveals a large and a small value of $^2J(^{31}P, N, ^{29}Si)$, which correspond to the mean value at room temperature only if the signs are opposite.

TABLE 1 Selected NMR Data[a] of Trimethylsilylaminodiphenylphosphanes, $Ph_2P—N(R)\ SiMe_3$, (**1–5**), in C_6D_6 at (23 ± 1)°C

No.	$\delta^{31}P$	$\delta^{15}N$	$\delta^{13}C(P)$	$\delta^{13}C(NR)$	$\delta^{29}Si(N)$	$^1\Delta^{14/15}N(^{31}P)$
1	49.2	−349.2 [+65.6]	140.9 [−17.9]	48.2 [−5.5]	11.1 [−31.8][b]	−35.1
2	52.2	−322.1 [70.6]	139.9 [−17.9]	145.6 [±8.2]	11.5 [−31.6]	−46.0
3	42.9	−305.9 [+71.1] −86.1 [0.7]	138.0 [−22.6]	159.3 [±6.9]	11.5 [−30.0]	−46.8
4	46.3	−289.5 [+73.7] −125.5 [<0.5]	139.1 [19.0]	164.1 [5.8]	12.7 [−27.9]	−46.5
4Se	59.0[c]	[+21.8][d]	[+90.7][d]		17.1 [5.7]	−32.5
5	50.2	−351.4 [+65.8]	140.8 [−24.6]	4.2 [6.1]	10.3 [−6.9][e,f]	−34.9

[a]Coupling constants $J(^{31}P, ^{13}C)$, $J(^{31}P, ^{15}N)$, and $J(^{31}P, ^{29}Si)$ are given in brackets (±0.1 Hz). Isotope-induced chemical shifts $^1\Delta^{14/15}N(^{31}P)$ are given in ppb (±1 or less), and a negative sign denotes that the resonance signal of the heavy isotopomer is shifted to lower frequency.
[b]$^1J(^{29}Si,^{15}N) = 15.1$ Hz.
[c]$^1J(^{31}P, ^{77}Se) = 778.2$ Hz.
[d]Data measured from ^{31}P NMR spectra.
[e]$^1J(^{29}Si,^{15}N) = 7.9$ Hz.
[f]Coalescence temperature in ^{29}Si NMR spectra: −20°C; energy of activation about the P—N bond: $\Delta G^* = 53.3 \pm 2$ kJ/mol. At −40°C, the ^{29}Si NMR spectrum shows two doublets at $\delta^{29}Si$ 12.4 [10.0] and 9.05 [24.7].



SCHEME 2 Proposed preferred conformation of **3**. Comparison of ^{15}N and ^{13}C NMR data of **3** with related 2-aminopyridine derivatives [9,36].

It is important to use ^{29}Si NMR to study the dynamic behavior of **5**, since the hindered rotation about the P—N bond (ΔG^* (253 K) = 53.3 ± 2 kJ/mol) is not readily apparent from ^1H and ^{13}C NMR spectra: The expected ^1H and ^{13}C NMR signals for nonequivalent $NSiMe_3$ groups are not resolved. If the groups at the nitrogen atom become less bulky, rotation about the P—N bond becomes fast on the NMR time scale. For example, in the case of **17**, the low temperature ^{13}C NMR spectrum is required to show the presence of two different N—Ph groups, in agreement with the solid-state ^{13}C MAS spectrum. Since the $\delta^{31}P$ and $\delta^{13}C$ NMR data for the solid state and for the solution of **17** at −65°C are rather similar, it can be assumed that the solid-state structure is retained in solution at low temperature. The same situation applies for solid-state and solution-state NMR data of **11** (even at room temperature), where the solid-state structure was determined by X-ray analysis (vide supra). The activation energies ΔG^* for rotation about the P—N bond are in a small range for those aminophosphanes which do not give separate signals of the conformers at room temperature (at coalescence: $\Delta G^* = 49.7$ (**6**, see Ref. [18a] for similar phosphanes), 48.3 (**13**), 46.6 (**15**), 41.7 (**16**), 42.0 (**17**) all ±2 kJ/mol). In all cases studied here, the conformation with the more bulky group at the nitrogen atom in the syn-position with respect to the assumed orientation of the phosphorus lone pair of electrons is preferred.

Coupling Constants $^1J(^{31}P, ^{15}N)$

The application of polarization transfer, based on small long-range scalar $^{15}N—^1H$ coupling [$^3J(^{15}N, ^1H)$], proved successful for measuring the ^{15}N NMR spectra of **1–20** at natural abundance. The $^1J(^{31}P, ^{15}N)$ data thus obtained confirm the assignment of ^{15}N satellites in the HEED experiments (vide infra). The sign of $^1J(^{31}P, ^{15}N)$ can be assumed as positive ($^1K(^{31}P, ^{15}N) < 0$ because $\gamma(^{15}N) < 0$) for all the phosphanes studied. This was checked by a series of appropriate 2D HETCOR experiments (mainly correlations of the type $^{13}C/^1H$ and $^{15}N/^1H$) for some representative examples (**1, 7, 12, 19, 20**) in the same way as has been shown for other aminophosphanes [8,9,19,20]. The lone pair of electrons at the phosphorus atom is mainly responsible for the negative contributions to $^1K(^{31}P, ^{15}N)$ [21].

In some cases, for less bulky amino groups, the ^{15}N NMR spectra were also measured at low temperature, in order to find out whether different conformations have a significant influence on the magnitude of $^1J(^{31}P, ^{15}N)$. As expected, the room temperature ^{15}N NMR spectra of **6, 13, 15**, and **16** show a doublet corresponding to the mean value of $^1J(^{31}P, ^{15}N)$, whereas the low temperature ^{15}N NMR spectra show two doublets, proving the presence of two rotamers in solution (see Fig. 2). This is also evident from two ^{31}P NMR signals at low temperature. The similar magnitude of the $^1J(^{31}P, ^{15}N)$ values for each pair of rotamers (Tables 2 and 3) indicates that this parameter is not very sensitive to the conformation: This again proves that both the sign and range of

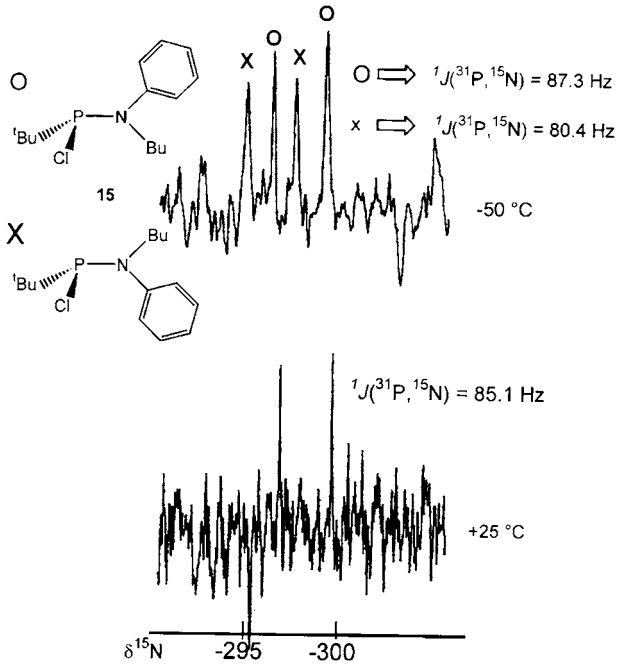


FIGURE 2 30.4 MHz ^{15}N NMR spectra (^1H inverse gated decoupled) of **15** in CD_2Cl_2 at room temperature (lower trace) and at −50°C upper trace. The two rotamers are present in almost equal amounts. The one with the larger coupling constant $^1J(^{31}P, ^{15}N)$ is slightly in excess as can be seen by comparison with the mean value of $^1J(^{31}P, ^{15}N)$. The $\delta^{15}N$ values change slightly with temperature.

TABLE 2 Selected NMR Data[a] of Amino(phenyl)chlorophosphanes, Ph(Cl)P—NRR′ (**6–8**), in C_6D_6 at (23 ± 1)°C

No.	$\delta^{31}P$	$\delta^{15}N$	$\delta^{13}C(P)$	$\delta^{13}C(N)$	$^1\Delta^{14/15}N(^{31}P)$
6[b]	139.7	−320.1 [+77.6]	139.9 [−28.9]	58.7 [+24.0] (R) 36.0 [<1] (R′)	−37.0
7	134.0	−290.6 [+86.5]	138.4 [−31.1]	49.1 [−9.8] (R) 59.0 [+18.0] (R′)	−38.3
8	134.0	−289.9 [+80.9]	138.7 [−30.6]	46.1 [<1] (R) 145.2 [13.6] (R′)	−39.5

[a]Coupling constants $J(^{31}P, ^{13}C)$ and $J(^{31}P, ^{15}N)$ are given in brackets (±0.1 Hz). Isotope-induced chemical shifts $^1\Delta^{14/15}N(^{31}P)$ are given in ppb (±1 or less), and a negative sign denotes that the resonance signal of the heavy isotopomer is shifted to lower frequency.
[b]NMR spectra measured at −60°C in CD_2Cl_2: $\delta^{13}C$ 34.0 [−11.4] (N—Me_{anti}), 60.2 [+38.2] (N—$CH_{2\ syn}$) (70%), 38.9 [+33.2] (N—Me_{syn}), 54.5 [−10.5] (N—$CH_{2\ anti}$) (30%); $\delta^{15}N$ −319.1 [76.7] (30%), −318.9 [78.0] (70%); $\delta^{31}P$ 142.5 (30%), 144.4 (70%).

$^1J(^{31}P, ^{15}N)$ are dominated by the presence and the nature of the lone pair of electrons at the phosphorus atom.

Isotope-Induced Chemical Shifts $^1\Delta^{14/15}N(^{31}P)$

Recently isotope-induced chemical shifts in phosphorus compounds have attracted considerable interest, in particular the fairly large $^1\Delta^{12/13}C(^{31}P)$ data for phosphaalkenes and phosphaalkynes have been noted [22]. In aminophosphanes containing only one P—N bond, the $^{31}P/^{14}N$ and $^{31}P/^{15}N$ isotopomers differ significantly with respect to the relaxation rate of the ^{31}P nuclei. In the $^{31}P/^{14}N$ isotopomer the transversal relaxation time $T_2(^{31}P)$ is governed by the mechanism ascribed to the scalar relaxation of the second kind [23] owing to unresolved $^{31}P—^{14}N$ scalar coupling (^{14}N: $I = 1$), and this is reflected by broadened

TABLE 3 Selected NMR Data[a] of Amino(*tert*-butyl)chlorophosphanes, ^{t}Bu(Cl)P—NRR′ (**9–18**), in C_6D_6 at (23 ± 1)°C

No.	$\delta^{31}P$	$\delta^{15}N$	$\delta^{13}C(P)$	$\delta^{13}C(N)$	$^1\Delta^{14/15}N(^{31}P)$
9	143.1	−296.9 [+82.6]	37.8 [−33.3]	48.0 (broad) (R, R′)[b]	−35.7
10	151.6	−309.4 (+86.3]	37.5 [−34.9]	31.5 [−7.6] (R) 57.6 [+20.2] (R′)	−28.9
11	161.0	−297.0 [+85.9]	37.7 [−40.0]	49.8 [−7.1] (R) 59.2 [+20.2] (R′)	−29.5
12[c]	136.8	−289.5 [+76.4]	34.5 [−22.9]	– 52.2 [+10.4] (R′)	−42.3
13[d]	153.3	−297.0 [+81.9]	38.1 [−34.9]	50.2 [±4.4] (R) 146.6 [+18.5] (R′)	−39.0
14	151.9	−287.5 [+87.3]	37.3 [−33.8]	58.8 [+21.8] (R) 142.7 [<1] (R′)	−25.9
15[e]	154.6	−298.5 [+85.1]	38.1 [−34.3]	55.1 [+19.1] (R) 146.6 [±2.7] (R′)	−31.4
16[f]	153.3	−298.1 [+85.7]	38.3 [−34.9]	59.4 [+20.2] (R) 146.5 [±2.7] (R′)	−36.7
17[g]	145.8	–	37.6 [−33.2]	147.4 [±6.0] (R, R′)	−39.1
18[h]	161.5	−324.8	38.5 [−50.4]	10.0 [−32,4](^{29}Si; R) 10.0 [+5.8] (^{29}Si; R′)	−28.8

[a]Coupling constants $J(^{31}P, ^{13}C)$, $J(^{31}P, ^{15}N)$, and $J(^{31}P, ^{29}Si)$ are given in brackets (±0.1 Hz). Isotope-induced chemical shifts $^1\Delta^{14/15}N(^{31}P)$ are given in ppb (±1 or less), and a negative sign denotes that the resonance signal of the heavy isotopomer is shifted to lower frequency.
[b]Rotation about the P—N bond is slow on the NMR time scale. ^{13}C NMR spectrum measured at −40°C in CD_2Cl_2: $\delta^{13}C$ 45.1 [+27.4] (N—CH_{syn}), 49.0 [−8.4] (N—CH_{anti}).
[c]Solid-state ^{13}C and ^{31}P MAS spectra: $\delta^{13}C$ 51.0, 142.3 (N—CH_2Ph), 60.0, 30.6 (N—^{t}Bu), 39.1, 27.3 (P—^{t}Bu); $\delta^{31}P$ 167.1.
[d]NMR spectra measured at −60°C in CD_2Cl_2: $\delta^{13}C$ 41.7 [−7.1] (N—$CH_{2\ anti}$), 146.4 [+23.4] (N—Ph_{syn}) (50%), 55.6 [+39.8] (N—$CH_{2\ syn}$), 144.2 [−13.6] (N—Ph_{anti}) (50%); $\delta^{15}N$ −298.6 [75.7] (50%), −298.9 [91.9] (50%); $\delta^{31}P$ 157.1 (50%), 152.8 (50%).
[e]NMR spectra measured at −60°C in CD_2Cl_2: $\delta^{13}C$ 47.8 [broad] ($CH_{2\ anti}$), 147.2 [+25.6] (N—Ph_{syn}) (55%), 60.4 [+40.3] (N—$CH_{2\ syn}$), 144.9 [−12.7] (N—Ph_{anti}) (45%); $\delta^{15}N$ −296.5 [80.4] (45%), −298.0 [87.3] (55%); $\delta^{31}P$ 157.7 (45%), 152.9 (55%).
[f]NMR spectra measured at −60°C in CD_2Cl_2: $\delta^{13}C$ 50.3 [broad] (N—$CH_{2\ anti}$), 146.9 [+22.9] (N—Ph_{syn}) (50%), 64.7 [+43.1] (N—$CH_{2\ syn}$), 144.4 [−13.1] (N—Ph_{anti}) (50%); $\delta^{15}N$ −302.7 [78.3] (50%), −298.8 [84.2] (50%); $\delta^{31}P$ 161.1 (50%), 156.3 (50%).
[g]NMR spectra measured at −65°C in CD_2Cl_2: $\delta^{13}C$ 149.3 [+23.4] (N—Ph_{syn}), 144.5 [−8.2] (N—Ph_{anti}); solid-state ^{13}C and ^{31}P MAS spectra: $\delta^{13}C$ 150.3, 145.3 (N—Ph), 38.2, 27.0 (P—^{t}Bu); $\delta^{31}P$ 157.0.
[h]Data from Ref. [8].

^{31}P NMR signals. Such interactions are absent in the ^{31}P/^{15}N isotopomer (^{15}N: $I = \frac{1}{2}$) and, therefore, the induced ^{31}P magnetization of this isotopomer decays more slowly, giving rise to sharper signals. The ^{15}N satellites because of $^{1}J(^{31}\mathrm{P}, ^{15}\mathrm{N})$ can be readily detected (in spite of the low natural abundance of ^{15}N: 0.37%), since the ^{31}P NMR signal of the ^{31}P/^{14}N isotopomer is suppressed to a large extent [15] (see Fig. 3). These experiments are carried out most conveniently by extension of polarization transfer pulse sequences such as INEPT [16]. They allow us to measure $^{1}J(^{31}\mathrm{P}, ^{15}\mathrm{N})$ and at the same time the isotope-induced chemical shifts $^{1}\Delta^{14/15}\mathrm{N}(^{31}\mathrm{P})$ with high precision at natural abundance of ^{15}N [8,9,15,24]. Because of the high NMR sensitivity of the ^{31}P nucleus, this information is available even after some minutes, in general within less than 1 h of instrument time, even for moderately concentrated samples (10–20 mg in 0.6 ml of solvent).

The smallest (negative) values $^{1}\Delta^{14/15}\mathrm{N}(^{31}\mathrm{P})$ are found for compounds with two Me_3Si groups at the nitrogen atom, followed by the combinations alkyl/Me_3Si and alkyl/alkyl. The presence of *N*-aryl groups gives rise to larger negative values. The influence of substituents at the phosphorus atom is rather small. Thus, the $^{1}\Delta^{14/15}\mathrm{N}(^{31}\mathrm{P})$ value for **20** is somewhat more negative than that for the corresponding compounds **7** and **11**. By changing the phosphorus oxidation state from P(III) to P(V) as in **4** and **4Se** the values $^{1}\Delta^{14/15}\mathrm{N}(^{31}\mathrm{P})$ become less negative as observed previously for other examples [8,20a,25]. Although the isotope-induced chemical shifts $^{1}\Delta^{14/15}\mathrm{N}(^{31}\mathrm{P})$ must be regarded mainly as a consequence of electron-mediated effects [26] (unlike effects arising from $^{1/2}$H substitution), in the cases studied here and in similar phosphorus-nitrogen compounds, a straightforward correlation with changes in the coupling constants $^{1}J(^{31}\mathrm{P}, ^{15}\mathrm{N})$, also an electron-mediated quantity, is not obvious. This is in contrast to the situation for $^{1}\Delta^{12/13}\mathrm{C}(^{29}\mathrm{Si})$ [27] or $^{1}\Delta^{12/13}\mathrm{C}(^{119}\mathrm{Sn})$ [28] where such correlations exist. Since the magnitude of the coupling constants $^{1}J(^{31}\mathrm{P}, ^{15}\mathrm{N})$ depends in a complex way on the nature of the phosphorus lone pair, crude correlations with the $^{1}\Delta^{14/15}\mathrm{N}(^{31}\mathrm{P})$ may just indicate different phosphorus coordination numbers and oxidation states.

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. Phosphorus halides (Ph_2PCl, $PhPCl_2$, $^{t}BuPCl_2$, PCl_3), all amines, chlorotrimethylsilane, and BuLi (1.6 M in hexane) were commercially available. The amines were dried according to established procedures, and

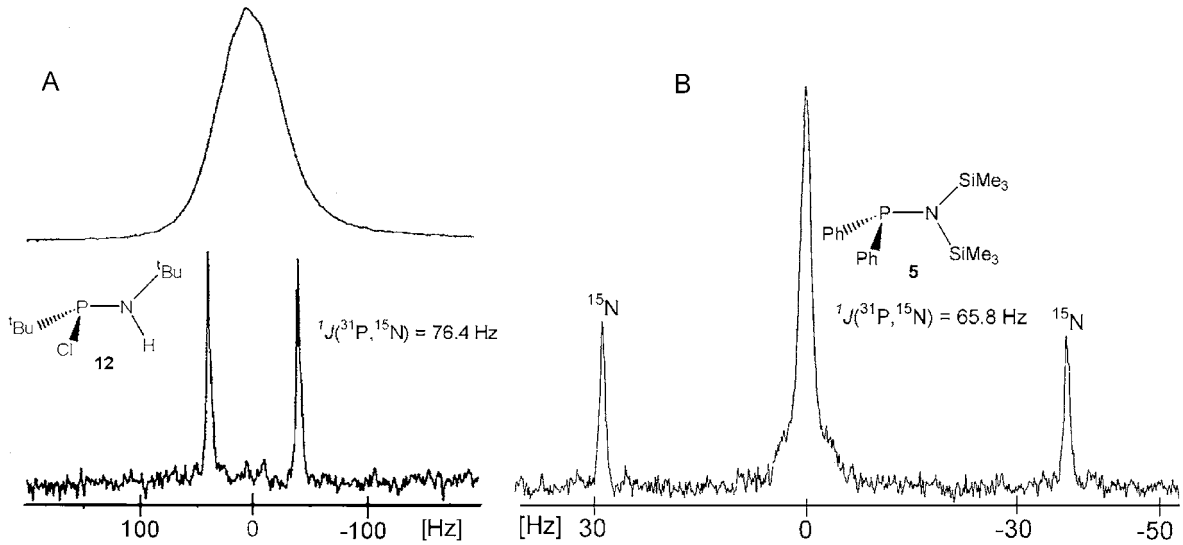


FIGURE 3 121.5 MHz ^{31}P HEED NMR experiments (based on refocused INEPT with ^{1}H decoupling) shown for the (A) compounds **12** in C_6D_6 (3%) and (B) **5** in C_6D_6 (25%), both samples in 5-mm tubes. Conditions for A: 320 transients; acquisition time 3 s; Hahn-echo delay 0.1 s; repetition delay 10 s. Conditions for B: 32 transients; acquisition time 4 s; Hahn-echo delay 0.6 s; repetition delay 5 s. In the case of **12**, the ^{14}N quadrupolar relaxation rate is rather slow, giving rise to a markedly broad ^{31}P NMR signal (upper trace of A), which is readily suppressed completely by a short Hahn-echo delay (0.1 s). In the case of **5**, the ^{14}N quadrupolar relaxation rate is fast and therefore, the ^{31}P NMR signal of the ^{31}P/^{14}N isotopomer is much less broadened when compared with **12**. As a consequence, a much longer Hahn-echo delay (0.6 s) is required in order to suppress at least partly the signal of the ^{31}P/^{14}N isotopomer.

TABLE 4 Selected NMR Data[a] of 3-*tert*-Butyl-2-chloro-1,3,2-oxazaphospholane **19** and Benzyl(*tert*-Butyl)aminodichlorophosphane **20** in C_6D_6 at (23 ± 1)°C

No.	$\delta^{31}P$	$\delta^{15}N$	$\delta^{13}C(N)$	$^{1}\Delta^{14/15}N(^{31}P)$
19	155.1	−274.8 [+78.1]	53.3 [6.5] (NCH_2) 41.9 [8.2] (NC) 70.5 [8.2] (OCH_2)	−33.2
20	177.7	−277.0 [+100.4]	48.6 [−6.5] (NCH_2) 60.2 [+24.0] (NC)	−37.4

[a]Coupling constants $J(^{31}P, ^{13}C)$, $J(^{31}P, ^{15}N)$, and $J(^{31}P, ^{29}Si)$ are given in brackets (±0.1 Hz). Isotope-induced chemical shifts $^{1}\Delta^{14/15}N(^{31}P)$ are given in ppb (±1 or less), and a negative sign denotes that the resonance signal of the heavy isotopomer is shifted to lower frequency.

freshly distilled before use. *N*-Silylated amines were prepared according to reported procedures [29]. The preparation of some of the compounds by using slightly different routes has been reported previously (**1** [11a,b], **2** [11c], **5** [10], **6** [17d,30], **8** [30], **9** [10c], **12** [31], **17** [32], **18** [10c], and **19** [33]). The selenide **4Se** was prepared only on NMR scale from **4** and an excess of selenium. Progress of all reactions was monitored by NMR spectroscopy.

NMR spectra were recorded from samples in C_6D_6 at (23 ± 1)°C (if not stated otherwise), using Bruker DPX 300, AC 300, DRX 500, JEOL 270, and JEOL 400 instruments, equipped with multinuclear broad band probeheads. Chemical shifts are given with respect to solvent signals [$\delta^{1}H$ (C_6D_5H) = 7.15; $\delta^{13}C$ (C_6D_6) = 128.0, 53.8 (CD_2Cl_2)] 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; $^{15}N\{^{1}H\}$ NMR spectra were measured by the refocused INEPT pulse sequence [16], based either on $^{1}J(^{15}N, ^{1}H)$ for the amino nitrogen or $^{2}J(^{15}N, ^{1}H) \approx 10$ Hz for the pyridine-nitrogen or directly by using inverse gated ^{1}H decoupling. ^{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 [15], and polarization transfer was based on a coupling constant $^{3}J(^{31}P, ^{1}H_{ortho}) = 10$ Hz for phenylphosphorus derivatives and $^{3}J(^{31}P, ^{1}H) = 14.5$ Hz for *tert*-butylphosphorus compounds, using Hahn-echo delays between 0.05 s and 1.5 s, depending on the width of the ^{31}P NMR signal of the $^{31}P/^{14}N$ isotopomer (see Fig. 3). Solid-state ^{13}C (75.5 MHz) and ^{31}P (121.5 MHz) MAS NMR spectra (conventional Hartmann–Hahn cross-polarization (CP) conditions) were measured from samples packed into air-tight inserts fitting into 5 mm ZrO_2 rotors, using a Bruker MSL 300 spectrometer.

Electron impact (EI) mass spectra at 70 eV were recorded using a VARIAN MAT CH7 instrument with direct inlet. Mass data are given for the isotopes ^{1}H, ^{12}C, ^{14}N, ^{28}Si, ^{31}P, and ^{35}Cl. Melting points (uncorrected) were measured using a Büchi 510 apparatus.

Synthesis of the N-trimethylsilyl-aminodiphenylphosphanes **1–5**. *General Procedures*

Trimethylsilyl(butyl)aminodiphenylphosphane **1**. A solution of butylaminodiphenylphosphane [34] (2.03 g, 7.9 mmol) in hexane (50 ml) was cooled to −78°C, and a solution of ^{n}BuLi in hexane (4.9 ml, 1.6 M) was slowly added. The stirred reaction mixture was warmed to room temperature, and then cooled again to −78°C. Chlorotrimethylsilane (0.86 g, 7.9 mmol) was slowly added under vigorous stirring. This mixture was warmed to room temperature and kept stirring for 0.5 h. Insoluble material was filtered off, and the solvent was removed in vacuo; product **1** was left as a yellow oil (2.52 g, 97%). ^{1}H NMR (300 MHz; C_6D_6): $\delta^{1}H$ = 7.50–7.05 (m, 10H, PPh_2), 3.36, 1.37, 1.23, 0.88 (m, m, m, t, 9H, N—Bu), 0.45 [1.4] (d, 9H, N—$SiMe_3$).

Trimethylsilyl(phenyl)aminodiphenylphosphane **2**. A suspension of freshly prepared *N*-lithio-trimethylsilylaniline (8 mmol) in hexane (50 ml) was cooled to −78°C and diphenylphosphorus chloride (0.86 g, 7.9 mmol) was slowly added. This mixture was warmed to room temperature and kept stirring for 0.5 h. Insoluble material was filtered off, and the solvent was removed in vacuo; the product **2** (1.97 g, 93%) was obtained as a colorless liquid.

^{1}H NMR (400 MHz): δ = 7.49–6.67 (m, 15H, N—Ph, PPh_2), 0.33 [1.8] (d, 9H, N—$SiMe_3$); ^{13}C NMR (67.9 MHz): δ [$J(^{31}P, ^{13}C)$] = 145.5 [7.8], 124.6, 130.2, 128.2 (N—Ph—$C^{1,2,6,3,5,4}$), 139.7 [17.6], 133.3 [20.7], 127.9 [6.2], 128.5 (Ph—C_i, C_o, C_m, C_p), 1.4 [8.3] (N—$SiMe_3$).

Compounds **3, 4** (similar compounds have been reported [35]), and **5** were prepared in the same way as **2** after *N*-lithiation of the respective amines.

3: yield 87% (1.89 g), yellow solid. ^{1}H NMR: δ [$J(^{31}P, ^{1}H)$] = 6.42, 6.71, 6.28, 7.96 (m, m, m, 4H, pyr.-$H^{3,4,5,6}$), 7.44, 7.06 (m, 4H, m, 6H, PPh_2); 0.55 [1.6] (d, 9H, N—$SiMe_3$); ^{13}C NMR: δ [$J(^{31}P, ^{13}C)$] = 159.3 [6.9], 116.7 [4.5], 135.6, 116.2, 146.8 (pyr.-$C^{2,3,4,5,6}$), 138.0

[22.6], 131.2 [19.6], 128.3 [4.8], 128.1 (PPh—C_i, C_o, C_m, C_p), 2.5 [10.3] (N—$SiMe_3$).

4: yield 63% (1.0 g), yellow liquid. ^{1}H NMR: δ [J(^{31}P, ^{1}H)] = 7.82, 5.93 (m, 2H, m, 1H, pyr.-$H^{4,6,5}$), 7.79, 7.21 (m, 4H, m, 6H, PPh_2); 0.75 [1.9] (d, N—$SiMe_3$); ^{13}C NMR: δ [J(^{31}P, ^{13}C)] = 164.1 [5.8], 156.8, 113.7, (pyr.-$C^{2,4,6,5}$), 139.1 [19.0], 132.6 [21.4], 128.3 [5.7], 128.6 (PPh—C_i, C_o, C_m, C_p), 3.0 [10.9] (N—$SiMe_3$).

5: yield 92% (1.5 g), viscous, colorless liquid. ^{1}H NMR (400 MHz; C_7D_8): δ = 7.54, 7.09 (m, 4H, m, 6H, PPh_2), 0.20 (s, 18H, N—$(SiMe_3)_2$); ^{13}C NMR (100.5 MHz): δ^{13}C [J(^{31}P, ^{13}C)] = 140.8 [24.6], 130.7 [19.6], 127.8 [4.9], 127.7 (PPh—C_i, C_o, C_m, C_p), 4.1 [7.4] (N—$SiMe_3$).

Synthesis of the Amino(chloro)phenylphosphanes **6–8** *and of the Amino(chloro)tert-butylphosphanes* **9–18**. *General Procedures*

A solution of the respective amine (21.0 mmol) in hexane (100 ml) was cooled to −78°C and a solution of BuLi (20 mmol) in hexane (12.5 ml, 1.6 M) was added under vigorous stirring. The mixture was warmed to room temperature and heated at reflux for 3 h. Then a solution of $PhPCl_2$ (3.6 g, 20 mmol) or ^{t}BuPCl$_2$ (3.2 g, 20 mmol) in hexane (50 ml) was added dropwise at room temperature, and the reaction mixture was kept stirring for 24 h. Insoluble material was filtered off, hexane was removed in vacuo, and samples of the residue were checked for purity by NMR spectroscopy. In general the products could be used for reactions [3,4] without further purification. In most cases the residues were purified either by distillation or recrystallization.

6: b.p. 101–106°C (10^{-2} Torr); yield 53%, colorless oil. ^{1}H NMR [^nJ(^{31}P, ^{1}H)]: δ = 8.0–7.5 (m, 10H, Ph, P—Ph), 4.50, 4.34 (m, m, 2H, NCH_2), 2.64 [10.2] (d, 3H, NMe).

7: m.p. 53–55°C; yield 60%, colorless crystals from pentane at −78°C. ^{1}H NMR [^nJ(^{31}P, ^{1}H)]: δ = 7.8–6.8 (m, 10H, Ph, P—Ph), 4.52 [5.6], 4.14 [3.8] (m, m, 2H, NCH_2), 1.45 [1.5] (d, 9H, N^{t}Bu). $C_{17}H_{21}ClNP$ (305.77) calc./found (%): C 64.7/66.8 H 8.9/8.9 N 6.75/5.6

8: b.p. 110°C (10^{-2} Torr); yield 43%, colorless oil. ^{1}H NMR [^nJ(^{31}P, ^{1}H)]: δ = 8.0–7.3 (m, 10H, N—Ph, P—Ph), 3.6, 1.13 (m, t, 2H, 3H, N—Et).

9: b.p. 45–48°C (10^{-2} Torr); yield 52%, colorless liquid. ^{1}H NMR (CD_2Cl_2; −40°C) [^nJ(^{31}P, ^{1}H)]: δ = 3.68, 2.72, 1.17, 0.92, 0.90, 0.74 (m, m, d, d, 1H, 1H, 3H, 3H, 3H, 3H, N^{I}Pr$_2$)1.04 [14.9] (d, 9H, P—^{t}Bu).

10: b.p. 100–105°C (10^{-2} Torr); yield 68%, colorless liquid. ^{1}H NMR [^nJ(^{31}P, ^{1}H)]: δ = 2.46 [4.1] (d, 3H, N—Me), 1.12 [2.1] (d, 9H, N—^{t}Bu), 1.04 [14.7] (d, 9H, P—^{t}Bu).

11: m.p. 78–79°C; yield 58%, colorless crystals from pentane at −78°C. ^{1}H NMR [^nJ(^{31}P, ^{1}H)]: δ = 7.3–7.1 (m, 5H, Ph), 4.57, 4.07 (m, 2H, NCH_2), 1.31 [1.0] (d, 9H, N—^{t}Bu), 1.07 [14.8] (d, 9H, P—^{t}Bu); EIMS: 286 (2%, M^+), 252 (15%, $MH^+ - Cl$), 210 (29%, $MH^+ - Ph$), 91 (100%, $PhCH_2^+$).

12: colorless liquid; decomposes during attempted distillation. ^{1}H NMR [^nJ(^{31}P, ^{1}H)]: δ = 2.75 [12.0] (d, broad, 1H, NH), 1.12 [1.1] (d, 9H, N—^{t}Bu), 0.99 [13.4] (d, 9H, P—^{t}Bu).

13: b.p. 112–113°C (10^{-2} Torr); yield 51%, colorless liquid. ^{1}H NMR [^nJ(^{31}P, ^{1}H)]: δ = 7.2–7.0 (m, 5H, N—Ph), 3.4, 0.88 (m, t, 2H, 3H, N—Et), 0.98 [14.5] (d, 9H, P—^{t}Bu). $C_{12}H_{19}ClNP$ (243.70) calc./found (%): C 59.1/59.3 H 7.9/8.0 N 5.75/5.8.

14: b.p. 114–115°C (10^{-2} Torr); yield 64%, colorless liquid. ^{1}H NMR [^nJ(^{31}P, ^{1}H)]: δ = 7.2–6.9 (m, 5H, N—Ph), 3.78, 0.99, 0.91 (m, d, d, 1H, 3H, 3H, N—^{I}Pr), 0.85 [14.3] (d, 9H, P—^{t}Bu); EIMS: 257 (10%, M^+), 222 (18%, $M^+ - Cl$), 200 (76%, $M^+ - Bu$), 122 (100%, $M^+ - Ph$). $C_{13}H_{21}ClNP$ (257.73) calc./found: C 60.6/60.4 H 8.2/8.3 N 5.4/5.7.

15: b.p. 140–150°C (10^{-2} Torr) partial decomposition; yield 22%, colorless oil. ^{1}H NMR [^nJ(^{31}P, ^{1}H)]: δ = 7.3–7.1 (m, 5H, N—Ph), 3.45, 1.39, 1.25, 0.85 (m, m, m, t, 9H, N—Bu), 1.00 [14.7] (d, 9H, P—^{t}Bu).

16: yellowish, oily liquid; decomposes during attempted distillation. ^{1}H NMR [^nJ(^{31}P, ^{1}H)]: δ = 7.1–6.8 (m, 5H, Ph), 4.51 (m, 2H, NCH_2), 0.94 [14.5] (d, 9H, P—^{t}Bu).

17: m.p. 51–53°C; yield 41%, colorless crystals from pentane at −30°C. ^{1}H NMR [^nJ(^{31}P, ^{1}H)]: δ = 7.1–6.8 (m, 10H, NPh_2), 1.04 [15.2] (d, 9H, P—^{t}Bu).

Synthesis of Benzyl(tert-butyl)amino-dichlorophosphane **20**

Phosphorus trichloride (16.5 g, 120 mmol) was dissolved in ether (100 ml) and added dropwise at 0°C to a solution of benzyl(*tert*-butyl)amine (19.6 g, 120 mmol) and triethylamine (12.1 g, 120 mmol) in ether (200 ml). After stirring for 24 h at room temperature, insoluble material was filtered off, and the solvent was removed in vacuo. A slightly yellowish oily liquid was left which was identified as pure **20** (yield 86%), ready for further reactions. ^{1}H NMR [^nJ(^{31}P, ^{1}H)]: δ = 7.4–7.1 (m, 5H, Ph), 4.76 [3.8] (d, 2H, NCH_2), 1.44 [3.4] (d, 9H, N—^{t}Bu).

X-Ray Structural Analysis of **11** *[12]*

Intensity data collection was carried out on a Siemens P4 diffractometer with Mo Kα-radiation

($\lambda = 71.073$ pm, graphite monochromator) at 173 K. All hydrogen atoms were on calculated positions and were refined with isotropic thermal parameters (1.2 times the equivalent temperature factor of the atom to which they are attached). All non-hydrogen atoms have been refined anisotropically. Compound **11**, a colourless isometrical crystal of dimensions $0.35 \times 0.30 \times 0.30$ mm, crystallizes orthorhombically, space group $P2_12_12_1$; $a = 886.8(2), b = 1069.8(2), c = 1753.4(4)$ pm, $Z = 4$, $\mu = 0.312$ mm^{-1}; 2232 reflections collected in the range (2–24.8)° in ϑ, 2061 reflections independent, 1907 reflections assigned to be observed ($I > 2\sigma(I)$); full matrix least squares refinement on F^2 with 164 parameters, $R1/wR2$-values 0.0300:0.0742, no absorption correction, max/min residual electron density 0.34/−0.22 e 10^{-6} pm^{-3}.

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