Remarkably Large $^{15}$N, $^{13}$C and $^{18}$O Isotope NMR Shifts of the Mono-coordinate Phosphorus Atoms in the Compounds (Me$_3$Si)$_2$PrNCP, K+[PrNCP]$^-$ and KOCP $\cdot$ 2 DME (DME = 1,2-Dimethoxyethane)

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Dedicated to Professor Ekkehard Fluck on the occasion of his 70th birthday

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Aminomethylidyne phosphane, Phosphantriylmethyamide, Isotope Shifts

The $^{31}$P and $^{13}$C NMR spectra of the heteroatom-substituted $\lambda^3$-phosphaalkynes (Me$_3$Si)$_2$PrNCP (1), K+[PrNCP]$^-$ (2) and KOCP $\cdot$ 2 DME (3) are described (Me = methyl; Pr = isopropyl). In addition, $^{15}$N NMR data of 1 and 2 as well as further NMR results of all accessible nuclei of 1 to 3 are reported. The absolute values of the coupling constants $^{1}J(3^{13}P^{15}C)$ of 1, 2 and 3, 16.2, 45.7 and 57.2 Hz, respectively, are considerably different; the geminal coupling constants $^{2}J(3^{13}P^{15}N)$ of the first two compounds show a decrease in the reverse order, 15.1 and 3.3 Hz, $^{13}$C, $^{31}$P, $^{15}$N, and $^{18}$O isotope effects on the nuclear shielding of the $^{31}$P nucleus in the non isotope-enriched compounds 1, 2 or 3 are presented and discussed. The [mono-$^{13}$C]isotopomers of 1, 2 and 3 exhibit extremely negative $^{31}$P--$^{13}$C one-bond isotope shifts varying from $-211$ to $-223$ ppb. Remarkably, for 1 and 2 large two-bond $^{31}$P$^{15}$N isotope shifts of $-32$ and $-84$ ppb, respectively, are observed. An unexpectedly large two-bond $^{31}$P$^{18}$O isotope effect of $-124$ ppb was assigned to the [mono-$^{18}$O]isotopomer of compound 3. A three-bond $^{31}$P$^{13}$C isotope shift of $-27$ ppb was found in 2.

Introduction

The influence of isotope effects on the shielding of the $^{31}$P nucleus in compounds with phosphorus in oxidation states three or five has been summarized in two review articles [1, 2]. However, compounds containing low-coordinate phosphorus atom have been published [1, 2, 9, 10]. In contrast, unusually large $^{31}$P$^{13}$C isotope effects over two bonds in both of the $\lambda^3$-phosphaalkynes Pr$_3$Si-O-C≡P and (dme)$_2$Li-O-C≡P were observed without $^{18}$O enrichment [3]; the values exceed those previously known over one bond substantially.

With this in mind, an investigation of further $^{31}$P isotope shifts in compounds containing low-coordinate phosphorus was initiated in order to better understand the sometimes strongly differing heteroatom-induced $^{31}$P isotope effects. The isotope effect caused by the $^{15}$N nucleus in amino-$\lambda^3$-phosphaalkynes is to our knowledge unknown. A comparative quantumchemical $ab$ initio calculation of the shielding of the phosphorus nucleus in isotopomeric $\lambda^3$-phosphoralkylene molecules can only be reasonably performed with access to a large number of such nmr data. Here we report the $^{31}$PX isotope shifts observed in the heteroatom-substituted $\lambda^3$-phosphoralkynes (Me$_3$Si)$_2$PrNCP (1) [11],...
Results and Discussion

The NMR data for the $\lambda^3$-phosphoralkyne 1 as well as for the ionic compounds 2 and 3 are summarized in Table 1 along with the atom labelling which is also used in the following discussion. Most of the NMR data already published for compound 1 [11] have been confirmed; in addition we have determined the chemical shifts and related coupling constants for the $^{15}$N and $^{29}$Si nuclei as well as for the vicinal $^1$H-$^3$C coupling constants; the latter lies within the expected range. A small $^{2}J(^{15}$NH$_{1}$) value is to be expected due to the coupling path over the sp$^3$ hybridised carbon C$_2$ [12]. Only four geminal $^{31}$P$^{15}$N coupling constants are known to date [12 - 14]; however, for the five-membered rings in 1,2,3- and 1,2,4- $\alpha^2\lambda^3$-diaza phospholes absolute values varying between 2.0 and 8.8 Hz have been measured [8, 13].

Strikingly, the geminal $^{31}$P$^{15}$N coupling constant for the NC$_3$P fragment of compound 1 (15.1 Hz) exceeds that of 2 (3.3 Hz) by approximately a factor of five (see Table 1). By contrast, the $^{1}J$(PC$_1$) coupling in 1 (18.2 Hz) is smaller than that of 2 (45.7 Hz) by a factor of 2.5, the latter being in the range of $\lambda^3$-phosphaalkynes containing a C$_3$C=C=1P fragment (cf. [3]). Further, a ca. 90 ppm decrease in shielding of the phosphorus nucleus in 1 with respect to 2 (−137.59 vs. −226.10 ppm), but a ca. 40 ppm increase in shielding of the nitrogen atom (−288.4 vs. −248.1 ppm) as well as of the carbon atom C$_1$ (153.87 vs. 178.79 ppm) of about 25 ppm are observed. This strongly indicates a change in the charge distribution of the $\pi$ system going from molecule 1 to the anion of 2 and suggests the following mesomerism [15]:

$$\text{K}^{+}[\text{PrNCP}]^{-} \quad \text{and KOCP} \cdot 2 \text{DME (3)}$$

with the X-nuclei (X = $\text{C}_{13}$, $\text{N}^{15}$, $\text{O}^{18}$, $\text{Si}^{29}$) up to four bonds away from the phosphorus atom.

$\delta$ [ppm] $^{13}$C $^{15}$N $^{18}$O

Table 1. Chemical shifts and coupling constants for $\lambda^3$-phosphoralkyne 1 in C$_6$D$_6$, potassium phosphonatriylmethylamide (2) dissolved in THF-d$_8$ with an equimolar amount of 1,4,7,10,13,16-hexaoxacyclooctadecane ([18]crown-6), and potassium phosphonatriylmethoxide (3) in DME-d$_{10}$ at 300 K.

<table>
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$^{\alpha}$ The chemical shifts $\delta^{13}$C and $\delta^{1}$H determined for 1 differ from those given in [11] by less than 0.1 ppm; for $\delta^{31}$P a value of −140 ppm was published; $^{\gamma}$ the coupling constants $^{1}J$(PC$_1$), $^{1}J$(PC$_2$) and $^{2}J$(H$_2$H$_2$) published in [11] agree to within 0.1 Hz with values given here, however, $^{2}J$(HH)$_{1}$ should read $^{2}J$(HH)$_{1}$; $^{\gamma}$ too dilute for $^{15}$N NMR spectra; $^{\gamma}$ from the $^{15}$N projection of $^{13}$H$^{30}$H$^{6}$ $\gamma$-2D HMBC experiment (measuring time 17 min.) [31]; $^{\gamma}$ in [11] the line of C$_3$ is described as a singlet; $^{\gamma}$ from the doublet of the $^{1}$H coupled $^{31}$P NMR spectrum with $\Delta

K$^{+}[C(H$_{3}^{1}$)$_{2}$C(H$_{2}$)-N-C=]=P(1)$^{\gamma}$

K-O-C$_{3}$=P(3)
Fig. 1. $^{13}$C, $^{29}$Si and $^{15}$N satellites in the $161.978$ MHz $^{31}$P{¹H} NMR spectrum of [N-trimethylsilyl-isopropylamino]-methylidynephosphane (1) in $C_6D_6$ at 300 K. The satellite signals for [mono-$^{13}$C], [mono-$^{29}$Si] and [mono-$^{15}$N] isotopomers are indicated with "*" (i = 1), "<" (i = 2), "-", and "*", respectively (see Table 1 for atom numbering; digital resolution 0.03 Hz per point, 10 320 scans, total measurement time 19.5 h, Gaussian filtering). The $40.561$ MHz $^{15}$N{¹H} NMR spectrum of a concentrated solution at 300 K is shown as (a) (90% in $C_6D_6$, digital resolution 0.06 Hz per point, 20 180 scans).

Table 2. Isotope Shifts $^n\Delta^{31}P(X)$ ($n = 1 - 4$, $X = ^{15}$N, $^{13}$C (i = 1 - 3), $^{18}$O, $^{29}$Si) of the [mono-X]isotopomers of $\lambda^3$-phosphaalkyne 1 in $C_6D_6$, compound 2 dissolved in THF-$d_8$ with an equimolar amount of [18]crown-6, and potassium phosphanetriylmethoxide (3) in DME-$d_{10}$ at 300 K.

<table>
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<td>$^{29}$Si</td>
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The $^{31}P${¹H} spectrum of potassium N-isopropyl-N-(phosphanetriylmethyl)amide (2) dissolved
Fig. 2. (a) 202.429 MHz $^{31}P\{^{1}H\}$ NMR spectrum of $\lambda^{3}$-phosphaalkyne 1 with both P=C satellite signals ("\*"), and the high-field line of the $^{15}N$ satellite doublet ("\*\*\*\*"). (b) 202.429 MHz $^{31}P\{^{1}H,^{15}N\}$ triple-resonance NMR spectrum of 1; the $^{15}N$ singlet lies within the main peak. The frequency scale bar is valid for both spectra (digital resolution 0.3 Hz per point, 4096 scans, total measurement time 3.3 h).

Fig. 3. $^{13}C$ and $^{15}N$ satellites in the 81.016 MHz $^{31}P\{^{1}H\}$ NMR spectrum of compound 2 dissolved in THF-d$_8$ with an equimolar amount of [18]crown-6 at 300 K. The satellite doublets belonging to [mono-$_{^{13}C}$] and [mono-$_{^{15}N}$]isotopomers are indicated by "\Rightarrow \Leftarrow" (i = 1), "\*\*\*\*\*\*" (i = 2), and "\*\*\*" respectively (see Table 2 for atom numbering; digital resolution 0.02 Hz per point, 22 140 scans, total measurement time 66.9 h). (a) shows the 202.411 MHz $^{31}P,^{15}N$ 1D ge-HMBC spectrum discussed in the text (digital resolution 0.1 Hz per point, 8192 scans, total measurement time 7 hours) [21]. The $\delta^{31}P$ regions cover the same range in both spectra (0.69 ppm).

in THF-d$_8$ shows, apart from the expected very broad singlet ($\Delta\nu_{1/2} = 7$ Hz), only the high-field line of the $^{31}P=^{13}C$ doublet. Since the base of the main peak at the top of this satellite line is 75 Hz, no further isotopomer signals could be identified. However, when an equimolar amount of 1,4,7,10,13,16-hexaoxacyclooctadecane ([18]crown-6) was added to this solution, the linewidth $\Delta\nu_{1/2}$ of the main
peak was diminished to 0.4 Hz and the aforementioned base thereby decreased to only 4 Hz (see Fig. 3). We believe the previously mentioned line broadening to be a consequence of a nuclear quadrupole interaction between the NCP fragment and the $^{39}\text{K}$ isotope (natural abundance 93.1%) [18]; an increase in the spatial distance between the cation (encapsulated in [18]crown-6) and anion in 2 could explain the observed line narrowing (cf. [15, 19, 20]). It should be noted that the [18]crown-6 complex of 2 was isolated from a tetrahydrofuran solution and structurally characterized [15].

A doublet in the $^{31}\text{P}^1\text{H}$ NMR spectrum of compound 2 can be assigned to the [mono-$^{15}\text{N}$]-isotopomer by performing a $^{31}\text{P}$-$^{15}\text{N}$ 1D HMBC experiment with pulsed field gradients [21]. Because the related pulse sequence excites only those $^{31}\text{P}$ nuclei that are coupled to neighbouring $^{15}\text{N}$ nuclei (all other $^{31}\text{P}$ signals including the main peak being suppressed), the existence and position of $^{15}\text{N}$ satellites are unambiguously confirmed (see Fig. 3a).

Comparison of the data collected for $^{3}\text{P}$-phosphaalkynes 1 to 3 in Table 2 reveals unusually large isotope shifts $\Delta^{31}\text{P}^{13}\text{C}$ of the [mono-$^{13}\text{C}$]isotopomers, which exceed the previous maximum value of $-209$ ppb for the trisopropylsiloxy derivative $^{1}\text{Pr}_{3}\text{Si}-\text{O}-\text{C}=\text{P}$ (5) [3]. The shift value for the N-isopropyl-N-(phosphanetriylmethyl)amide anion of 2 ($-223$ ppb) is larger than those of compounds 1 and 3 ($-211$ and $-212$ ppb) by 11 ppb. Remarkably, the three-bond effect $2\Delta^{31}\text{P}^{12}\text{C}$ in the anion of 2 ($-27$ ppb) is larger than those induced by $^{13}\text{C}$ nuclei over two bonds in trans-ethene-1,2-bis(dialkylphosphonates) [22], bis(diphenylphosphanyl)ethyne [23] and a four-membered $\sigma^{3}\lambda^{1}$-phosphorusheterocycle [4]; these values fall in a narrow range of $-4$ to $+4$ ppb. Further, $3\Delta^{31}\text{P}^{13}\text{C}$ of this last compound ($+2$ ppb) [4] differs little from that measured for $^{3}\text{P}$-phosphaalkyne 1 ($-1$ ppb; see Table 2).

For the oxygen substituted $^{3}\text{P}$-phosphaalkynes R-O-C≡P, singlets of the [mono-$^{18}\text{O}$]isotopomers with intensities of 0.2% relative to the $^{31}\text{P}$ main peak appear at similarly high fields, namely $-124$ (R = K$_{\text{solv}}$, 3) and $-117$ ppb (R = (dme)$_{2}$Li, 4); by contrast, the shift $2\Delta^{31}\text{P}^{18}\text{O}$ for compound 5 (R = $^{1}\text{Pr}_{3}\text{Si}$) of $-94$ ppb differs by approximately 30 ppb [3]. Compared with these values the $^{15}\text{N}$ induced shifts $2\Delta^{31}\text{P}^{15}\text{N}$ of the NCP fragments in the [mono-$^{15}\text{N}$]isotopomers of compounds 1 and 2 are clearly smaller. In this context one should mention that the influence of the $^{15}\text{N}$ nucleus on the $^{31}\text{P}$ shielding in the anion of 2 is about 2.5 times stronger than in the related neutral compound 1 ($-84$ vs. $-32$ ppb; see Table 2). Both these values [24] are clearly larger than $^{15}\text{N}$ isotope effects reported for only one bond of a 1,1-bis(dimethylamino)-4-bis(dimethylamino)thiophosphoryl substituted 2,3-dihydro-$\lambda^{5}$-phosphete ($-17$ to $-21$ ppb) [4] and of 2-phenylamino-$\lambda^{3}$-1,3,2-dioxaphosphorinanes ($-9$ to $-15$ ppb) [25], but differ from values obtained for di-$\text{t}$-butylaminophosphonophanes and ($^1\text{Bu}_2\text{PN=})_2\text{S}$ ($-42$ to $-58$ ppb) [26]. D- and triazaphospholes with two-coordinate phosphorus, however, tend to have $1\Delta^{31}\text{P}^{15}\text{N}$ absolute values ($-72$ to $-114$ ppb) [8] partially larger than the $2\Delta^{31}\text{P}^{15}\text{N}$ shifts of the $\lambda^{3}$-phosphaalkynes 1 and 2.

**Experimental Section**

[N-Trimethylsilyl-isopropylamino]methylidynephosphophane (1) was prepared according to the method of Appel and Poppe from tris(trimethylsilyl)phosphane and isopropylsiliconate [11]. This compound reacts with potassium tert-butanolate in tetrahydrofuran to yield potassium N-isopropyl-N-(phosphanetriylmethyl)amide (2). After isolation of the solvent-free yellow powder, tetrahydrofuran-$d_8$ solutions of 2 with and without one equivalent of 1,4,7,10,13,16-hexaoxacyclooctadecane ([18]crown-6) were used to obtain NMR spectra. Potassium bis(trimethylsilyl)phosphanide [27], synthesized from tris(trimethylsilyl)phosphane and potassium tert-butanolate, reacts with carbonic acid diethylester in 1,2-dimethoxyethane to give potassium phosphoranylmethoxide. The pale yellow solid (3) was characterized as containing two molecules of 1,2-dimethoxyethane per formula unit; 1,2-dimethoxyethane-$d_{10}$ solutions were used for NMR spectroscopic studies. Details of the synthesis and characterization of the $^{3}\text{P}$-phosphaalkynes 2 and 3, and the crystal structures of the [18]crown-6 complexes will be reported elsewhere [15, 28].

The NMR spectra were recorded on AM 200, AM 400, Avance™ 400 and Avance™ 500 (with three channel equipment) spectrometers from Bruker Analytik GmbH, D-76287 Rheinstetten. Due to air and moisture sensitivity of the compounds the sample tubes (5 mm i.d.) were sealed under argon. Sample concentration was approximately 2.5 mol L$^{-1}$ unless otherwise stated. Chemical shifts $^{31}\text{P}$ were referenced to 85% H$_3$PO$_4$ as external standard, $^{13}\text{C}$ and $^1\text{H}$ via the deuterated solvent to TMS; $^{31}\text{P}$ was also referred to TMS, $^{15}\text{N}$ to CH$_3$NO$_2$ and $^{18}\text{O}$ to D$_2$O. Low frequency shifts are taken negative with respect to stan-
The programs Bruker WIN1D-NMR, version 6.0 and WIN2D-NMR version 6.01 were available for spectra interpretation. Isotope shifts $\Delta^{131\text{P}}(X)$ over $n$ bonds, $X = ^{13}\text{C, }^{15}\text{N, }^{18}\text{O and }^{29}\text{Si}$, are defined as usual [3, 29]; the measurement accuracy is $< \pm 1$ ppb (cf. [3, 25, 30]).

Acknowledgements

We wish to thank the Deutschen Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

[24] To the best of our knowledge no $^2\Delta^{131\text{P}}(^{15}\text{N})$ values of phosphorus nitrogen compounds are given in the literature.