Sign-Determination of Spin-Spin Coupling Constants in *tert*-Butylphosphaalkyne

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The signs of the coupling constants $^1J(^{31}\text{P}\equiv^{13}\text{C})$ ($> \text{O}$), $^2J(^{31}\text{P}^{13}\text{C})$ ($> \text{O}$), $^3J(^{31}\text{P}^{13}\text{C})$ ($> \text{O}$) and $^4J(^{31}\text{P}^1\text{H})$ ($> \text{O}$) in *tert*-butyl-phosphaalkyne (**1**) were determined by selective $^1\text{H}\{^{31}\text{P}\}$ NMR experiments and two-dimensional (2D) $^{13}\text{C}/^1\text{H}$ heteronuclear shift correlations based on $^nJ(^{13}\text{C}^1\text{H})$ ($n = 1, 2, 3$), confirming the previously assumed positive sign of $^1J(^{31}\text{P}\equiv^{13}\text{C})$ in phosphaalkynes.

The convenient synthesis of kinetically stabilized phosphaalkynes such as the *tert*-butylphosphaalkyne (**1**) [1] has played a major role in the development of an enormously rich chemistry [2].

Among other physical methods, ^1H , ^{13}C and ^{31}P NMR measurements have served from the beginning for the characterization of phosphaalkynes and, consequently, a wealth of data is available now [1–3]. Recently, ^{13}C and ^{31}P NMR data of phosphaalkynes were correlated with corresponding ^{13}C and ^{15}N NMR parameters of nitriles [4]. As one of the results, it was concluded, on the basis of the linear correlation between coupling constants $^1J(^{15}\text{N}\equiv^{13}\text{C})$ and $^1J(^{31}\text{P}\equiv^{13}\text{C})$, that the sign of $^1J(^{31}\text{P}\equiv^{13}\text{C})$ should be positive [4]. Here, we confirm this assumption by the experimental sign-determination of $^1J(^{31}\text{P}\equiv^{13}\text{C})$ in compound **1**.

Relative signs of coupling constants are determined most conveniently by applying various double resonance techniques. The spin system under consideration must contain at least three spins, e.g., ^{31}P , ^{13}C and ^1H (see Scheme I), of which one functions as the so-called passive spin while resonances of the other two spins are either observed or irradiated [5]. In order to obtain the absolute signs, one absolute sign of a “key” coupling con-

stant has to be known. In the case of compound **1**, it can be safely assumed that $^1J(^{13}\text{C}^1\text{H}) > \text{O}$ [6] and the absolute signs of all coupling constants involving the ^{31}P nucleus can be determined by four different heteronuclear double resonance experiments as shown in Scheme I.

The starting point is provided by a selective $^1\text{H}\{^{31}\text{P}\}$ experiment, observing the ^{13}C satellites of the *tert*-butyl protons in **1** (**A**). Since ^{13}C is the passive nucleus, the signs of $^1J(^{13}\text{C}^1\text{H})$ ($> \text{O}$ [6]) and $^3J(^{31}\text{P}^{13}\text{C})$ are compared and shown to be alike. Furthermore, three $^{13}\text{C}\{^1\text{H}\}$ or $^1\text{H}\{^{13}\text{C}\}$ experiments are necessary. These experiments are most readily conducted as two-dimensional (2D) $^{13}\text{C}/^1\text{H}$ heteronuclear shift correlations [7], based on $^1J(^{13}\text{C}^1\text{H})$ (**B**), $^2J(^{13}\text{C}^1\text{H})$ (**C**) and $^3J(^{13}\text{C}^1\text{H})$ (**D**). This type of experiment has already proved extremely helpful for determining signs of coupling constants [8]. It is very fast (ca. 5 to 10 minutes) because of the small sweep width usually required in F_1 (^1H) (see experimental part), and it is much more efficient, particularly in the case of small long range couplings $^nJ(^{13}\text{C}^1\text{H})$ (see **C**, **D**), than one-dimensional selective $^{13}\text{C}\{^1\text{H}\}$ or $^1\text{H}\{^{13}\text{C}\}$ experiments. Taking into account the result of experiment **A**, it follows from **B** that $^4J(^{31}\text{P}^1\text{H}) > \text{O}$. This can be used in **C** and **D** to obtain the absolute positive signs of the coupling constants $^2J(^{31}\text{P}^{13}\text{C})$ and $^1J(^{31}\text{P}\equiv^{13}\text{C})$, respectively.

Scheme I.

Relevant spin systems of the phosphaalkyne **1**; bold drawn lines connect nuclei which are either irradiated or observed and thin broken lines show which coupling constants are to be compared with respect to their sign.

A: $^1J(^{13}\text{C}^1\text{H})/^3J(^{31}\text{P}^{13}\text{C}) > \text{O}$; since $^1J(^{13}\text{C}^1\text{H}) > \text{O}$, it follows that $^3J(^{31}\text{P}^{13}\text{C}) > \text{O}$ (+6.0 Hz).

B: $^3J(^{31}\text{P}^{13}\text{C})/^4J(^{31}\text{P}^1\text{H}) > \text{O}$; it follows from **A** that $^4J(^{31}\text{P}^1\text{H}) > \text{O}$ (+0.9 Hz).

C: $^4J(^{31}\text{P}^1\text{H})/^2J(^{31}\text{P}^{13}\text{C}) > \text{O}$; it follows from **B** that $^2J(^{31}\text{P}^{13}\text{C}) > \text{O}$ (+18.2 Hz).

D: $^4J(^{31}\text{P}^1\text{H})/^1J(^{31}\text{P}\equiv^{13}\text{C}) > \text{O}$; it follows from **B** that $^1J(^{31}\text{P}\equiv^{13}\text{C}) > \text{O}$ (+38.5 Hz).

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Clearly, these results provide a firm basis for the discussion of changes in the magnitude of $^1J(^{31}\text{P}\equiv^{13}\text{C})$ in phosphalkynes. The previous conclusions [4] are shown to be correct. The knowledge of the positive sign of $^1J(^{31}\text{P}\equiv^{13}\text{C})$ in **1** should also stimulate to test computational schemes [9] with respect to the respective contributions of mechanisms of spin-spin coupling.

Experimental

Compound **1** was prepared as described [1, 3d, 10], dissolved in C_6D_6 (ca. 10% V/V) in a 5 mm (o.d.) tube, degassed by several pump freeze/thaw cycles and sealed. All measurements were carried out at $27 \pm 1^\circ\text{C}$. The $^1\text{H}\{^{31}\text{P}\}$ experiments have been carried out using a BRUKER WP 200 spectrometer, equipped with a second frequency synthesizer and a selective amplifier. The correct pow-

er level for ^{31}P irradiation was checked for the main signal ($^4J(^{31}\text{P}^1\text{H}) = 0.9\text{ Hz}$) before the ^{13}C satellites were recorded with simultaneous ^{31}P irradiation at higher or lower frequency with respect to the central ^{31}P resonance. The 2D $^{13}\text{C}/^1\text{H}$ heteronuclear shift correlations were performed using a BRUKER AC 300 instrument. The spectral widths were 2 Hz (F_1) and 200 Hz/1 K data points (F_2); 8 experiments of 8 scans (recycle time 6s) each gave a sufficient signal-to-noise ratio after zero-filling and Gaussian multiplication in both dimensions (ca. 12 minutes of spectrometer time). The coupling constants $^nJ(^{13}\text{C}^1\text{H})$ serving for polarization transfer in the 2D experiments were 130 Hz ($n = 1$), 4.4 Hz ($n = 2$) and 4.8 Hz ($n = 3$).

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