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

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Z. Naturforsch. **47b,** 437–438 (1992);
received September 17, 1991

Phosphaalkynes, Coupling Constants, NMR-$^1H\{^{31}P\}$ Hetronuclear Double Resonance, Two-dimensional (2D) $^{13}C/^1H$ Heteronuclear Shift Correlations

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

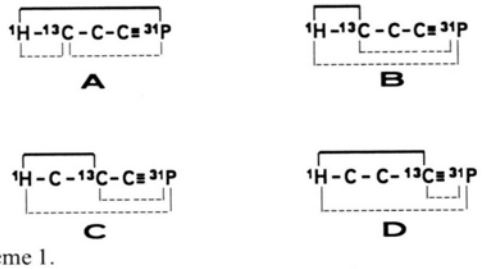
The convenient synthesis of kinetically stabilized phosphaalkynes such as the *tert*-butylphosphaalkyne (**1**) [1] has played a major role in the development of an enormously rich chemistry [2].

$$(CH_3)_3C-C{\equiv}P$$
1

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 $^1J(^{15}N{\equiv}^{13}C)$ and $^1J(^{31}P{\equiv}^{13}C)$, that the sign of $^1J(^{31}P{\equiv}^{13}C)$ should be positive [4]. Here, we confirm this assumption by the experimental sign-determination of $^1J(^{31}P{\equiv}^{13}C)$ 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 constant has to be known. In the case of compound **1,** it can be safely assumed that $^1J(^{13}C^1H) > O$ [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 $^1H\{^{31}P\}$ experiment, observing the ^{13}C satellites of the *tert*-butyl protons in **1** (**A**). Since ^{13}C is the passive nucleus, the signs of $^1J(^{13}C^1H)$ (> O [6]) and $^3J(^{31}P^{13}C)$ are compared and shown to be alike. Furthermore, three $^{13}C\{^1H\}$ or $^1H\{^{13}C\}$ experiments are necessary. These experiments are most readily conducted as two-dimensional (2D) $^{13}C/^1H$ heteronuclear shift correlations [7], based on $^1J(^{13}C^1H)$ (**B**), $^2J(^{13}C^1H)$ (**C**) and $^3J(\equiv^{13}C^1H)$ (**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 $^nJ(^{13}C^1H)$ (see **C, D**), than one-dimensional selective $^{13}C\{^1H\}$ or $^1H\{^{13}C\}$ experiments. Taking into account the result of experiment **A,** it follows from **B** that $^4J(^{31}P^1H) > O$. This can be used in **C** and **D** to obtain the absolute positive signs of the coupling constants $^2J(^{31}P^{13}C)$ and $^1J(^{31}P{\equiv}^{13}C)$, respectively.



Scheme 1.

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: $^1J(^{13}C^1H)/^3J(^{31}P^{13}C) > O$; since $^1J(^{13}C^1H) > O$, it follows that $^3J(^{31}P^{13}C) > O$ (+6.0 Hz).
B: $^3J(^{31}P^{13}C)/^4J(^{31}P^1H) > O$; it follows from **A** that $^4J(^{31}P^1H) > O$ (+0.9 Hz).
C: $^4J(^{31}P^1H)/^2J(^{31}P^{13}C) > O$; it follows from **B** that $^2J(^{31}P^{13}C) > O$ (+ 18.2 Hz).
D: $^4J(^{31}P^1H)/^1J(^{31}P{\equiv}^{13}C) > O$; it follows from **B** that $^1J(^{31}P{\equiv}^{13}C) > O$ (+38.5 Hz).

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Verlag der Zeitschrift für Naturforschung,
D-W-7400 Tübingen
0932–0776/92/0300–0437/$ 01.00/0

Clearly, these results provide a firm basis for the discussion of changes in the magnitude of $^1J(^{31}P{\equiv}^{13}C)$ in phosphaalkynes. The previous conclusions [4] are shown to be correct. The knowledge of the positive sign of $^1J(^{31}P{\equiv}^{13}C)$ 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 ± 1 °C. The $^1H\{^{31}P\}$ experiments have been carried out using a BRUKER WP 200 spectrometer, equipped with a second frequency synthesizer and a selective amplifier. The correct power level for ^{31}P irradiation was checked for the main signal ($^4J(^{31}P^1H)$ = 0.9 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 $^{13}C/^1H$ 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 6 s) 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 $^nJ(^{13}C^1H)$ serving for polarization transfer in the 2D experiments were 130 Hz (n = 1), 4.4 Hz (n = 2) and 4.8 Hz (n = 3).

Support of this work by Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie is gratefully acknowledged.

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