

## On the Signs and Magnitudes of $^{13}\text{C}-^{31}\text{P}$ Spin-Spin Coupling Constants in Triphenylphosphine

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In a discussion<sup>1</sup> on experimentally determined one-bond  $^{13}\text{C}-^{31}\text{P}$  coupling constants in terms of the Fermi contact interaction mechanism, a literature value<sup>2</sup> of 21 Hz was used for  $^1J(^{13}\text{C}-^{31}\text{P})$  in triphenylphosphine and furthermore, its sign was assumed *positive*. The magnitude of this coupling constant has earlier been reported by us<sup>3</sup> and others<sup>4</sup> to be *ca.*

12 Hz. However, from the discussion in the paper of Gansow and Kimura<sup>2</sup> it is concluded that their value is not merely an erratum, but more likely originates from an erroneous measurement as judged from the published spectrum. Thus, in order to throw light on this discrepancy and to contribute to the understanding of  $^{13}\text{C}-^{31}\text{P}$  spin coupling mechanisms, this note reports on the signs and accurate magnitudes ( $\pm 0.03$  Hz) of the  $^{13}\text{C}-^{31}\text{P}$  coupling constants in triphenylphosphine revealing that  $^1J(\text{C}-\text{P})$  is *negative*.

The magnitudes of the  $^{13}\text{C}-^{31}\text{P}$  couplings (Table 1) were obtained from single scan natural abundance  $^{13}\text{C}$  spectra (Figs. 1 and 2, Varian XL-100-15 spectrometer, 25.2 MHz) using complete proton decoupling, a sweep width of 0.5 Hz/cm, and a sweep rate of 0.025 Hz/sec. Under these conditions, a value of 0.33 Hz was obtained

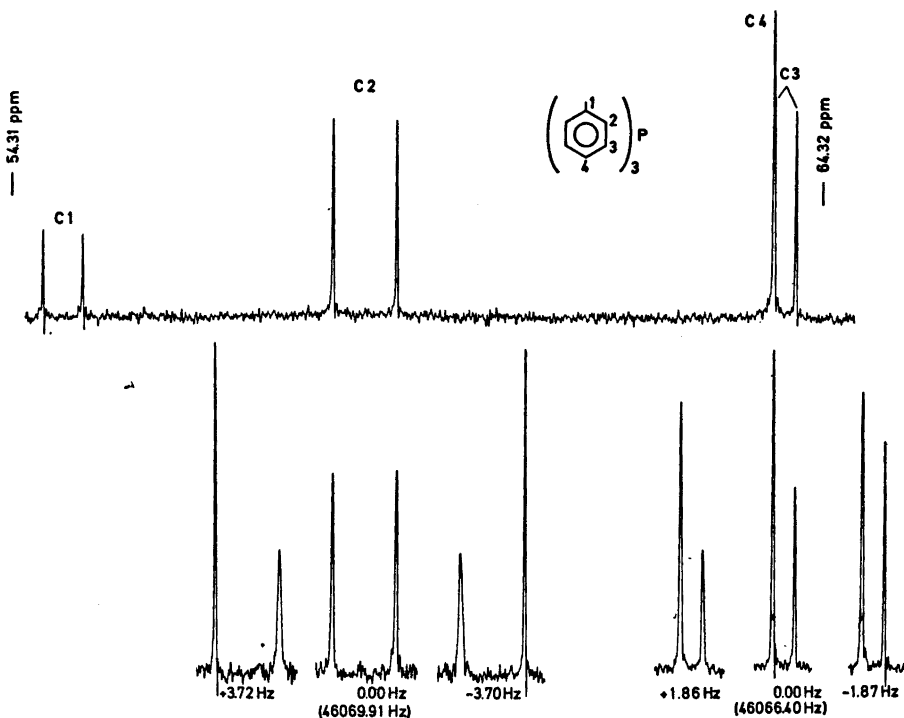


Fig. 1. (Upper) Natural abundance  $^{13}\text{C}$  NMR spectrum (single scan;  $^1\text{H}$  noise-decoupled) of triphenylphosphine. (Lower) Selective  $^1\text{H}$  decoupled C(2) and C(3) spectra with offsets (Hz) in the decoupling frequencies for H(2) and H(3) (frequencies on the Varian Cycrocode decoupler offset scale are in parentheses). The ppm scale is upfield from internal  $\text{CS}_2$ .

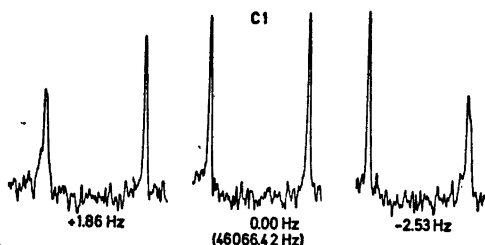


Fig. 2. Selective  $^1\text{H}$  decoupled C(1) spectra in triphenylphosphine for relative sign determination of  $^1J(^{13}\text{C}-^{31}\text{P})$ . Decoupling offsets (Hz) indicated as in Fig. 1. Sweep frequency increases from right to left.

Table 1.  $^{13}\text{C}$  chemical shifts and  $^{13}\text{C}-^{31}\text{P}$  coupling constants,  $J(^{13}\text{C}-^{31}\text{P})$ , in triphenylphosphine.<sup>a</sup>

Carbon	Chemical shifts <sup>b</sup>	$J(^{13}\text{C}-^{31}\text{P})$ <sup>c</sup>
C(1)	54.97	-12.51
C(2)	58.65	+19.65
C(3)	63.85	+6.80
C(4)	63.71	0.33

<sup>a</sup> As a (36 % w/w) solution in  $\text{CS}_2$  (52 % w/w) and  $(\text{CD}_3)_2\text{CO}$  (12 % w/w);  $(\text{CD}_3)_2\text{CO}$  is used as internal lock signal source ( $^2\text{H}$  lock mode).

<sup>b</sup> In ppm upfield from internal  $\text{CS}_2$  with errors  $\pm 0.01$  ppm.

<sup>c</sup> In Hz with errors  $\pm 0.03$  Hz.

for  $^4J(\text{C}(4)-\text{P})$ , a coupling not previously resolved.

Signs of the  $^{13}\text{C}-^{31}\text{P}$  coupling constants could be obtained for the one-, two-, and three-bond couplings using off-resonance or selective proton decoupling techniques.<sup>5</sup> As can be seen from the peak heights in the decoupled spectra of Fig. 1, the signs of  $^2J(\text{C}(2)-\text{P})$  and  $^3J(\text{C}(3)-\text{P})$  are the same as  $^3J(\text{H}(2)-\text{P})$  and  $^4J(\text{H}(3)-\text{P})$ , respectively, *i.e.* positive.<sup>6</sup> The sign of  $^1J(\text{C}(1)-\text{P})$  was determined by selective decoupling of the long-range  $^3J(\text{C}(1)-\text{H}(3))$  coupling (*ca.* 7 Hz<sup>7</sup>) in the H(3) proton spectrum for the two phosphorus spin states while observing the effect on the lines of the C(1) doublet. From the

observed spectra (Fig. 2) it is concluded that  $^1J(\text{C}(1)-\text{P})$  is of opposite sign to  $^4J(\text{H}(3)-\text{P})$ , *i.e.* negative.

The positive sign obtained for the two- and three-bond  $^{13}\text{C}-^{31}\text{P}$  couplings has been observed for the corresponding  $^{13}\text{C}-^1\text{H}$  and  $^{13}\text{C}-^{19}\text{F}$  couplings in benzene<sup>7</sup> and monofluorobenzene.<sup>8</sup> Negative one-bond  $^{13}\text{C}-^{31}\text{P}$  couplings in aromatic phosphines have been reported for tri-2- and 3-thienylphosphine.<sup>5</sup>

The results for  $^1J(\text{C}-\text{P})$  obviously tend to make the plot<sup>1</sup> of  $^1J(\text{C}-\text{P})/s_{\text{C}}$  versus  $s_{\text{P}}$  non-linear. Thus any conclusions based on this plot (*e.g.* estimation of C-P-C bond angles) should be made with reference to the results reported here.

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