

NMR Studies of Organophosphorus Compounds

^{13}C — ^{31}P Spin-spin Coupling Constants in Some Heteroaromatic Phosphine Derivatives

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Magnitudes of the spin-spin coupling constants involving the aromatic ^{13}C atoms and ^{31}P in some heteroaromatic phosphines such as tri-2-furylphosphine, tri-(5-methyl-2-furyl)-phosphine, tri-2-thienylphosphine, and tri-3-thienylphosphine, and in two tetracoordinated phosphorus derivatives have been obtained from natural abundance, noise-modulated proton decoupled ^{13}C spectra. The assignments of ^{13}C chemical shifts, and thus of the ^{13}C — ^{31}P coupling constants, were based on established relationships and additivity rules of ^{13}C chemical shifts in furans and thiophenes, on the nuclear Overhauser enhancement effect, and for the two tetracoordinated compounds on single frequency, off resonance proton decoupling experiments. The one-bond ^{13}C — ^{31}P coupling constants in the phosphines are much smaller than in the tetracoordinated compounds. This may be explained in terms of the changes in phosphorus hybridization. Furthermore, in the phosphines, the magnitude of this coupling constants is smaller than the two-bond ^{13}C — C — ^{31}P coupling, and is smaller than any of the long-range ^{13}C — ^{31}P couplings in some of the compounds.

Measurements of spin-spin coupling constants between ^{13}C and directly bonded nuclei are of special importance for the testing of qualitative ¹ and quantitative ² theories on chemical bonding. A change in the sign of the reduced coupling constant, $^1K_{\text{CX}}$, from positive to negative across the Periodic Table (e.g. from $^1K_{\text{CH}}$ to $^1K_{\text{CF}}$) has been predicted,³ and it has recently been stated that the borderline region, where the change is expected, is in the Groups V and VI.¹ Indeed recent INDO molecular orbital calculations on one-bond ^{13}C — ^{14}N coupling constants ² show that these couplings are small in magnitude, in agreement with experimental values, and furthermore, exhibit a variation in sign for different molecules. Thus a knowledge of ^{13}C — ^{31}P coupling constants in different organophosphorus compounds would be of interest, since this might throw light on deficiencies in the theoretical methods in comparison to

cases such as ¹³C-¹H and ¹³C-¹⁹F, where all couplings are positive and negative, respectively, and rather large. Furthermore, with the use of ¹³C resonance spectroscopy becoming increasingly widespread in organic chemistry, a knowledge of ¹³C-³¹P coupling constants would be of importance in the determination of structures of organophosphorus compounds.

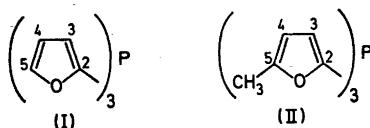
Determinations of the signs and magnitudes of ¹³C-³¹P coupling constants involving sp³ hybridized carbon atoms and tri- and tetracoordinated phosphorus atoms have been obtained from heteronuclear double resonance experiments utilizing observations of ¹³C proton satellites.⁴ Further data on ¹³C-³¹P couplings have been obtained by direct observation of ¹³C spectra⁵ and from ¹³C-¹H decoupled spectra.⁶

In connection with a study on ¹H-³¹P coupling constants of ring protons and ring methyl-protons with phosphorus, and their sensitivity to phosphorus hybridization in a series of aromatic and heteroaromatic phosphine derivatives⁷ it was of interest to obtain information on ¹³C-³¹P couplings involving aromatic carbons and phosphorus in these systems. A recent communication⁶ on similar couplings in triphenylphosphine and its methylphosphonium salt prompts us to report data obtained for the direct and long-range ¹³C-³¹P couplings in some heteroaromatic phosphine derivatives utilizing noise-modulated proton decoupled ¹³C spectra.⁸

RESULTS AND DISCUSSION

The complete proton decoupled ¹³C spectra of the furyl- and thienyl-phosphine derivatives reported here generally consist of four doublets for the aromatic carbons due to splitting by the spin- $\frac{1}{2}$ phosphorus nuclei (Fig. 1); the chemical shifts and coupling constants involving these carbons are given in Table 1. Assignments of the doublets to the individual ring carbons were deduced from nuclear Overhauser enhancement effects,⁹ single-frequency, off-resonance proton decoupling,^{8c} and finally, in cases where off-resonance decoupled spectra were not obtained, from substituent effects on ¹³C-chemical shifts. Additivity of these substituent effects¹⁰ was found very useful as shown in the assignments of the spectra of tri-2-furylphosphine (I) and tri-(5-methyl-2-furyl)-phosphine (II).

Tri-2-furylphosphine (I) and tri-(5-methyl-2-furyl)-phosphine (II). The earlier established additivity of methyl group substituent effects in 2-methylfuran and 2,5-dimethylfuran¹⁰ allowed determination of a convincing set of assignments for all resonances encountered in the spectra of (I) and (II).



The four ring carbon resonances for both (I) and (II) fall in two well-separated groups (Fig. 1): one to low field (C-2 and C-5), and one to high field (C-3 and C-4) from neat benzene (external reference) as do the two resonances

Table I. ^{13}C Chemical shifts, phosphorus substituent effects, and ^{13}C — ^{31}P spin-spin coupling constants in some heteroaromatic phosphine derivatives.

Compound	Conc. (% w/w)	^{13}C Chemical shifts ^e			Substituent effects ^b				^{13}C — ^{31}P Coupling constants ^c			
		$\delta_{\text{C}(s)}$	$\delta_{\text{C}(s)}$	$\delta_{\text{C}(s)}$	C(2)	C(3)	C(4)	C(5)	$J_{\text{P-C}(s)}$	$J_{\text{P-C}(s)}$	$J_{\text{P-C}(s)}$	
Tri-2-Fu-P (I)	45 CS ₂	-21.44	+ 6.09	+16.16	- 6.44	-12.01	-1.94	- 4.66	2.9	23.5	6.4	3.1
Tri-(5-Me-2-Fu)-P (II) ^d	25 CS ₂	-19.99	+ 5.53	+19.93	- 6.49	-11.27	-1.57	- 4.13	<1.3	22.5	5.6	3.2
Tri-Ph-P (III)	45 CS ₂	- 9.64	- 6.04	- 0.80	- 9.64	- 6.02	- 0.80	- 0.89	12.3	19.9	6.1	<1.3
Tri-2-Th-P (IV)	70 CS ₂	-11.19	- 7.91	- 0.55	-14.29	- 9.51	-2.15	- 7.59	12.4 ^e	19.55 ^e	6.7 ^e	0 ^e
Tri-3-Th-P (V)	45 CS ₂	- 3.23/ - 3.32 ^f	-10.03	- 3.59/ - 3.49 ^f	- 6.33/ - 6.42 ^f	-11.63	- 5.19/ - 5.09 ^f	- 2.27	23.3 ^f	14.0	18.3 ^f	6.4
Di-Me-2-Th-PS (VI)	26 dioxane	-71.34 (-16.34)	-67.22 (-12.22)	-61.38 (- 6.38)	-66.10 (-11.10)	-19.44	-13.82	-7.98	-14.20	85.1	9.8	13.1
Tri-3-Th-PO (VII)	16 dioxane	-66.89 (-11.89)	-69.51 (-14.51)	-61.79 (- 6.79)	-59.99 (- 4.99)	-14.99	-16.11	-8.39	- 8.09	14.3	112.9	15.6

^a In ppm relative to neat benzene as external reference (compounds (I)–(V)) and relative to dioxane as internal reference (compounds (VI)–(VII)). Values in parentheses are relative to benzene; the chemical shift of dioxane relative to external benzene is taken to be +55 ppm. Errors are estimated to ± 0.02 – 0.04 ppm. (Note: The ^{13}C chemical shift scale is positive in the high field direction.)

^b Differences in chemical shifts (ppm) between the parent compounds (taken from Ref. 10) and the phosphorus substituted compounds. (Thio- $\delta_{\text{C}(s)\text{C}(s)} = 3.1$ and $\delta_{\text{C}(s)\text{C}(s)} = +1.6$ ppm; furan: $\delta_{\text{C}(s)\text{C}(s)} = +18.1$ ppm; 5-methylfuran: $\delta_{\text{C}(s)} = -13.5$, $\delta_{\text{C}(s)} = 16.8$ ppm; $\delta_{\text{C}(s)} = +21.5$, and $\delta_{\text{C}(s)} = -24.5$ ppm.)

^c In Hz with errors estimated to ± 0.2 – 0.5 Hz.

^d The methyl ^{13}C resonance is a singlet ($J_{\text{P-CH}_3} < 1.3$ Hz) at $\delta_{\text{CH}_3} = +12.41$ ppm from neat cyclohexane as external reference.

^e Values reported by Weigert and Roberts.³

^f Definite assignment not possible (see text).

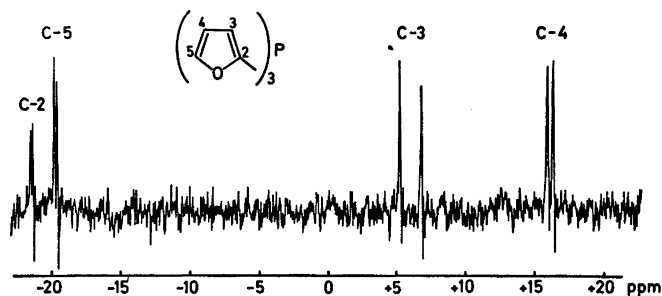


Fig. 1. 15.09 MHz single scan, proton decoupled natural abundance ¹³C NMR spectrum of tri-2-furylphosphine (I) (45 % w/w solution in CS₂). The ppm scale is positive upfield from neat benzene used as external reference.

(C-2,5 and C-3,4) in furan.¹⁰ The assignment of the two low field resonances, C-2 and C-5, in tri-2-furylphosphine (I) was straightforward, as the lowest field resonance shows a much less pronounced Overhauser enhancement than all other resonances (Fig. 1), thus corresponding to C-2. The two high field chemical shifts (C-3 and C-4) can readily be assigned by comparison with the four ring carbon resonances, still remaining undetermined, in tri-(5-methyl-2-furyl)-phosphine (II), using the methyl substituent parameters of Grant *et al.*¹⁰ and assuming additivity of substituent effects. This also allowed a complete chemical shift assignment for (II), all low field peaks of which exhibit decreased Overhauser enhancement. With the C-3 and C-4 resonances being unassigned for (I) there were two possible sets of chemical shift substituent effects which in turn led to two sets of additivity calculated chemical shifts for (II), as shown in Table 2. A comparison between the observed shifts for (II) and the two calculated sets (Table 2) shows that only one of these is consistent with the experimental values, thus allowing the remaining assignment of C-3 and C-4 in (I) and of the resonances in (II).

Table 2. ¹³C Chemical shifts (ppm) in tri-(5-methyl-2-furyl)-phosphine (II) calculated from substituent effects.

Position	Substituent effects (ppm) in furans ^a			Calc. chem. shifts (II)		Obs. chem. shifts (II)
	5-methyl-furan ^b	(I)				
C-2	+1.83	- 6.44	- 6.44	-19.61	-19.61	- 19.99
C-3	-0.74	-12.01	- 1.94	+ 5.35	+15.42	+ 5.53
C-4	+4.06	- 1.94	-12.01	+20.22	+10.15	+19.93
C-5	-9.18	- 4.66	- 4.66	-28.84	-28.84	-28.63

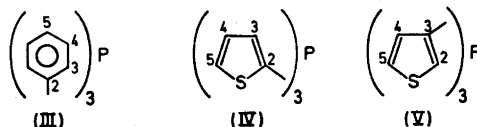
^a Chemical shifts of C-2,5 and C-3,4 in furan are taken to be -15.0 and +18.1 ppm, respectively, from neat benzene as external reference.¹⁰

^b From Table III in Ref. 10.

Furthermore, the assumed additivity of substituent effects appears to be borne out extremely well.

The values of the two sets of $^{13}\text{C}-^{31}\text{P}$ coupling constants in (I) and (II) obtained from the above assignments are in good mutual agreement, the magnitudes of the couplings for the methyl derivative being slightly smaller than for (I). A similar trend may be noted for the analogous $^{13}\text{C}-^1\text{H}$ long-range couplings determined for furan and 2-methylfuran.¹¹ The one-bond $^{13}\text{C}-^{31}\text{P}$ couplings are remarkably small, the magnitudes being smaller than any of the long-range couplings in (I) and (II). In the spectrum of (II), the C-2 resonance could not be resolved into a doublet, thus showing $^1J(^{13}\text{C}-^{31}\text{P})$ to be less than the half-width (1.3 Hz) of the resonance peak. To our knowledge, this is the smallest reported one-bond $^{13}\text{C}-^{31}\text{P}$ coupling, if not the smallest one-bond coupling, observed between any spin nuclei, although some $^{13}\text{C}-^{15}\text{N}$ couplings appear to be of similar small magnitude.¹²

Tri-2-thienylphosphine (IV) and tri-3-thienylphosphine (V). The four doublet ^{13}C -resonances observed for tri-2 and 3-thienylphosphine, (VI) and (V), respectively, were assigned on the basis of the phosphorus substituent effects obtained for (I) and (II) and for triphenylphosphine (III), as no off-resonance decoupling experiments and no studies of methyl derivatives of these two compounds have been performed so far.



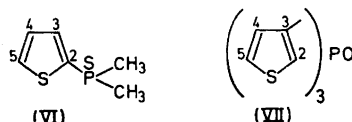
$^{13}\text{C}-^{31}\text{P}$ couplings in (III) were recently reported by Weigert and Roberts.⁶ However, the results obtained for (III) in this study are included in Table 1, especially for purposes of comparison with the phosphorus substituent effects on the ^{13}C chemical shifts. The results from 15 and 25 MHz spectra⁶ immediately gave the correct assignment of the three closely spaced lines for the carbons C-4 and C-5, and as seen from Table 1, the $^{13}\text{C}-^{31}\text{P}$ couplings agree well with those earlier reported.⁶

For the two compounds (IV) and (V), the four ring carbon resonances are shifted to lower field as compared to the respective carbons of the parent aromatic ring (in thiophene $\delta_{\text{C}(2,5)} = +3.1$, and $\delta_{\text{C}(3,4)} = +1.6$ ppm relative to external benzene¹⁰) in agreement with the results for (I), (II), and (III). From decreased Overhauser enhancement the carbons directly attached to phosphorus, C-2 in (IV) and C-3 in (V), were easily assigned as the lowest field resonances in both spectra. For (I), (II), and (III), a large downfield shift may also be noted for this carbon (*ca.* 6–14 ppm).

The smallest downfield shift in (I), (II), and (III), caused by phosphorus substitution (*ca.* 1–2 ppm), was clearly experienced by the C-4 carbons. This could be utilized in the assignments of the resonances for C-4 in (IV) and C-5 in (V), both of which are shifted *ca.* 2 ppm downfield from their respective resonances in thiophene.

The relative larger phosphorus substituent effects on the C-3 carbons, as compared to the effects on the C-5 carbons in (I), (II), and (III), served as an aid in the assignments of the two remaining resonances in (IV). The resulting values of the ¹³C–³¹P coupling constants for (IV) roughly follow those obtained for (I), (II), and (III), the two-bond couplings being the largest of the sets in all cases. From the present data a definite assignment of the C-2 and C-4 carbon resonances in (V) was not possible due to small differences in chemical shifts and ¹³C–³¹P coupling constants for the two carbons. In Table 1, two tentative assignments for the two overlapping doublets are given, which are based on the anticipated values of the two-bond ¹³C–³¹P coupling constants, however, the correct one is not obvious. As for thiophene,¹⁰ the C-2 resonance is observed at slightly higher field than the C-4 resonance in both cases.

Dimethyl-2-thienylphosphine sulfide (VI) and tri-3-thienylphosphine oxide (VII). The 25.15 MHz spectra of the tetracoordinated derivatives (VI) and (VII) were obtained using dioxane as solvent. The chemical shifts are referred to the natural abundance ¹³C-resonance used as internal lock. The carbons directly bonded to phosphorus were easily identified from decreased Overhauser enhancement as the lowest field resonance in both spectra.



Single frequency, off resonance proton decoupled spectra, in which the sample is strongly irradiated at a frequency several hundred Hz off the aromatic proton frequencies (*i.e.* at the dioxane proton resonance as in Figs. 2 and 3), were found very useful in the ¹³C chemical shift assignments. In such spectra, no long-range ¹³C–¹H couplings¹¹ are observed, and the direct ¹³C–¹H couplings are reduced to about 30–40 Hz. Comparison of the observed residual ¹J_{C–H} splittings, *J*_{C–H}^r, obtained from the doublet of doublets for each C–H bonded carbon, with the residual splittings calculated using the expression

Table 3. Calculated and observed residual splittings, *J*_{C–H}^r = Δω*J*_{C–H}/γ*H*₂,^a from the single-frequency, off resonance proton decoupling experiments (Figs. 2 and 3).

Residual splittings	Compound (VI)		Compound (VII)	
	Calc.	Obs.	Calc.	Obs.
<i>J</i> _{C(2)–H(2)} ^r	—	—	40.9	40.0
<i>J</i> _{C(3)–H(3)} ^r	33.7	32.2	—	—
<i>J</i> _{C(4)–H(4)} ^r	30.2	30.4	31.7	32.4
<i>J</i> _{C(5)–H(5)} ^r	39.1	37.8	37.6	38.2

^a In Hz. The magnitudes of the ¹J_{C–H} coupling constants used for the calculation of *J*_{C–H}^r were those observed in thiophene¹⁷: ¹J_{C(2)–H(2)} = ¹J_{C(5)–H(5)} = 185 Hz and ¹J_{C(3)–H(3)} = ¹J_{C(4)–H(4)} = 167 Hz. For compound (VI): γ*H*₂/2π = 2000 Hz; and for compound (VII): γ*H*₂/2π = 1950 Hz

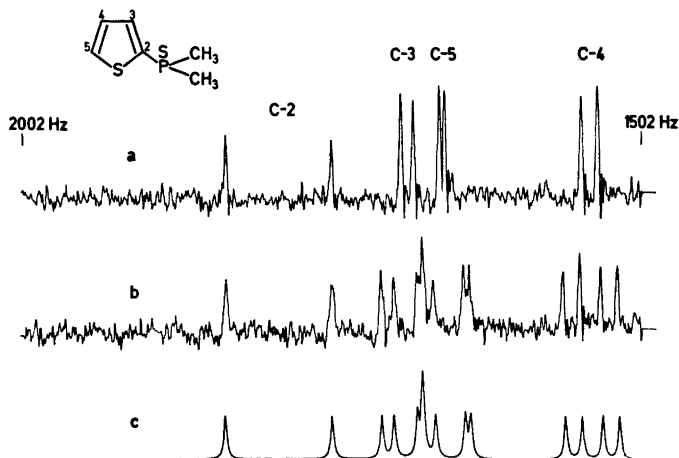


Fig. 2. (a) 25.15 MHz proton noise-decoupled, natural abundance ¹³C NMR spectrum (69 scans) of dimethyl 2-thienylphosphine sulfide (VI) (26 % w/w solution in dioxane). The frequency scale is downfield from natural abundance ¹³C-dioxane used as internal lock. (b) Single frequency, off resonance proton decoupled ¹³C spectrum (100 scans) obtained by strong irradiation at the dioxane proton frequency. The computer simulated double resonance ¹³C spectrum (c), and the residual splittings J_{C-H}^r (see Table 3) were calculated using the experimental parameters of Table I; $\gamma H_2/2\pi = 2000$ Hz; $\nu_{H(3)} = 404$ Hz, $\nu_{H(4)} = 362$ Hz, and $\nu_{H(5)} = 423$ Hz (at 100 MHz relative to internal dioxane); the $^1J_{C-H}$ values are those for thiophene.¹⁷

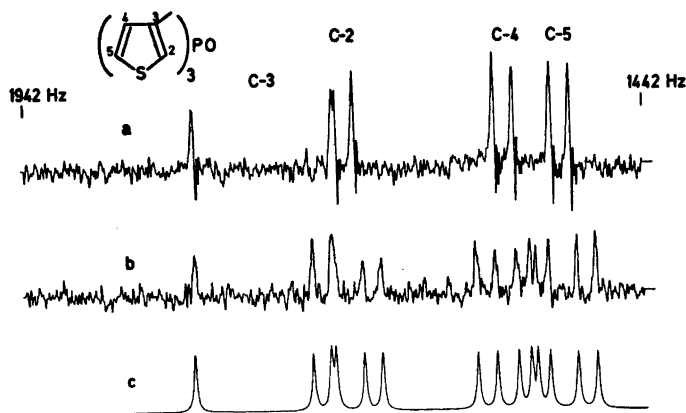


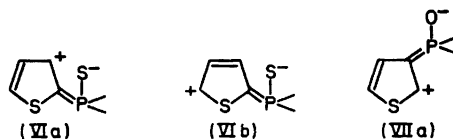
Fig. 3. (a) 25.15 MHz proton noise-decoupled, natural abundance ¹³C NMR spectrum (80 scans) of tri-3-thienylphosphine oxide (VII) (16 % w/w solution in dioxane). Frequencies are downfield from dioxane, used as internal lock. (b) Observed (100 scans) and (c) computer simulated single frequency, off resonance proton decoupled ¹³C spectrum. The parameters used in the calculations of spectrum (c) and the residual splittings in Table 3 are those of Table I; $\gamma H_2/2\pi = 1950$ Hz; $\nu_{H(2)} = 431$ Hz, $\nu_{H(4)} = 370$ Hz, and $\nu_{H(5)} = 396$ Hz (at 100 MHz relative to internal dioxane); $^1J_{C-H}$ values are taken from thiophene.¹⁷

$J_{\text{C-H}}^r = \Delta\omega J_{\text{C-H}}/\gamma H_2$ ($\Delta\omega = 2\pi\Delta\nu$ is the frequency offset of the irradiating field H_2) given by Ernst ^{8a} (see Table 3) or with calculated double resonance spectra,¹³ allows an unambiguous assignment of C-5 in (VI) and C-4 in (VII).

Finally, as observed for the corresponding ^1H chemical shifts,^{7c} it is assumed that C-3 will be more deshielded than C-4 in (VI), and C-2 more deshielded than C-5 in (VII), which is in accordance with the order of observed and calculated residual splittings $J_{\text{C-H}}^r$ (Table 3).

^{13}C Chemical shifts. From the above study of phosphine derivatives and from the data presented in Table 1 it is noted that phosphorus substitution causes downfield shifts of all aromatic carbon atoms. The largest shifts are observed for the directly phosphorus bonded carbons and for the carbons C-3, C-5 in the 2-substituted derivatives, and C-2, C-4 in the 3-substituted derivatives, whereas the effects on the carbons C-4 (or C-5 in (V)) are smaller and of comparable magnitudes for all classes of compounds. Taking into account the reverse order of ^{13}C and ^1H chemical shifts in thiophene,¹⁰ a comparison of the ^{13}C chemical shifts obtained in this study with the corresponding ^1H shifts ^{7c} shows that the same shielding effects are roughly operative for both nuclei, although no perfect correlation exists. However, the ^{13}C shifts are several times greater than the proton shifts.

Consideration of the ^{13}C chemical shifts for the tetracoordinated derivatives (VI) and (VII) reflects the presence of $d\pi - p\pi$ interactions in these compounds, as indicated by the canonical structures (VIa and b) and (VIIa). Contributions



of such structures to the hybrids would result in substantial deshielding of C-3 and C-5 in (VI), and C-2 in (VII), in agreement with the experimental observations. However, since little is known regarding the magnetic and electric field effects of the phosphoryl and thiophosphoryl groups, any conclusion based on the chemical shifts must be qualitative.

$^{13}\text{C} - ^{31}\text{P}$ Spin-spin coupling constants. From the $^{13}\text{C} - ^{31}\text{P}$ coupling constants (Table 1), obtained from the assigned ^{13}C resonance doublets, it is noted that for the trivalent phosphorus compounds, the magnitudes of the one-bond $^{13}\text{C} - ^{31}\text{P}$ couplings are considerably smaller than previously reported one-bond couplings involving aromatic carbon atoms (*e.g.* $^{13}\text{C} - ^1\text{H}$ and $^{13}\text{C} - ^{19}\text{F}$ couplings). Extremely small one-bond couplings, smaller than any of the long-range $^{13}\text{C} - ^{31}\text{P}$ couplings, were observed in the two furylphosphines and, as mentioned above, this coupling was even not resolvable in the spectrum of tri-(5-methyl-2-furyl)-phosphine (II). In any of the phosphines, the magnitude of the one-bond coupling constant does not exceed that of the two-bond coupling.

The magnitudes of the long-range $^{13}\text{C} - ^{31}\text{P}$ couplings in the phosphines decrease with increasing number of intervening bonds between the coupling nuclei and thus parallels the behaviour of the related $^1\text{H} - ^{31}\text{P}$ couplings in heteroaromatic and triphenylphosphine derivatives.^{7c} Opposite trends may

be noted for the analogous $^{13}\text{C}-^1\text{H}$ long-range couplings in benzene,¹⁴ thiophene, and furan,¹¹ as these couplings vary in an oscillating manner with increasing number of bonds. The vicinal, three-bond $^{13}\text{C}-^{31}\text{P}$ couplings are all of similar magnitude and show the same constancy as observed for the corresponding $^{13}\text{C}-^1\text{H}$ couplings.¹⁴ The magnitudes of these three-bond $^{13}\text{C}-^1\text{H}$ couplings have been explained with reference to the *trans* $^1\text{H}-^1\text{H}$ couplings in substituted ethylenes and the Karabatsos relationship¹⁵ for sp^2 carbon atoms, $^3J_{\text{CH}} = 0.4$ $^3J_{\text{HH}}$.^{6,11,14} On the other hand, the three-bond $^{13}\text{C}-^{31}\text{P}$ couplings in heteroaromatic phosphines and triphenylphosphine correlate well with $^3J(^{13}\text{C}-^{31}\text{P}) = 1/4$ $^3J(^1\text{H}-^{31}\text{P})$, where $^3J(^1\text{H}-^{31}\text{P})$ is the analogous *trans* $^1\text{H}-^{31}\text{P}$ coupling in trivinylphosphine.¹⁶

Tetracoordination of phosphorus causes a large increase in the magnitude of the one-bond $^{13}\text{C}-^{31}\text{P}$ coupling, as observed for the compounds (VI) and (VII); minor changes also occur for the long-range couplings. A similar change has been observed for $^1J(^{13}\text{C}-^{31}\text{P})$ in alkylphosphine derivatives^{1,4-6} in which $^1J(^{13}\text{C}-^{31}\text{P})$ is small and negative for the trivalent phosphorus compounds, becoming large and positive on tetracoordination of phosphorus, and increasingly positive as more electronegative groups or atoms are bonded to phosphorus. Although the signs of the coupling constants in Table 1 have not been determined, it is thus assumed that $^1J(^{13}\text{C}-^{31}\text{P})$ in (VI) and (VII) is positive, whereas the sign of this coupling in the phosphines (I)–(V) is unknown. However, assuming a dependence of $^1J(^{13}\text{C}-^{31}\text{P})$ in tri-2-furylphosphine (I) and tri-2-thienylphosphine (IV) on the ring heteroatom electronegativity by analogy with the effect of substituent electronegativity on $^1J(^{13}\text{C}-^1\text{H})$ couplings (increase of $^1J(^{13}\text{C}-^1\text{H})$ with the X electronegativity in the system $\text{X}-^{13}\text{C}-\text{H}$) suggests a lower value for $^1J(^{13}\text{C}-^{31}\text{P})$ in (IV) as compared to that in (I). This involves a negative sign for $^1J(^{13}\text{C}-^{31}\text{P})$ in tri-2-thienylphosphine (IV), while no conclusion regarding the sign for the small one-bond coupling in (I) may be drawn so far. Further evidence for a negative one-bond $^{13}\text{C}-^{31}\text{P}$ coupling in (IV) has recently been obtained from a study on long-range ring methyl proton-phosphorus couplings in tri-(methylthienyl)-phosphines.^{7f} With a negative sign for $^1J(^{13}\text{C}-^{31}\text{P})$ in (IV), this coupling is about 20 Hz below that in (I), a difference also obtained between the corresponding $^1J(^{13}\text{C}-\text{H})$ couplings in thiophene and furan (in thiophene $^1J_{\text{C}(2)-\text{H}(2)} = 185$ Hz; in furan $^1J_{\text{C}(2)-\text{H}(2)} = 201$ Hz¹⁷).

The increase observed for $^1J(^{13}\text{C}-^{31}\text{P})$ on tetracoordination of phosphorus is in qualitative agreement with both experimental and theoretical results for other one-bond $^{13}\text{C}-\text{X}$ coupling constants² and with the model proposed for such couplings.^{1,3} According to this model, one-bond couplings are mostly dependent on the *s*-character of the orbital used by the X atom in forming the C–X bond (*e.g.*, $^1J(^{13}\text{C}-^1\text{H})$ large positive, and $^1J(^{13}\text{C}-^{19}\text{F})$ large negative).² Phosphorus in phosphines uses nearly pure *p* orbitals to form bonds to carbon,^{1,18} as does fluorine, whereas hybrid orbitals are used in the tetracoordinated phosphorus compounds. Thus the changes in phosphorus hybridization on tetracoordination are reflected by the observed increase in $^1J(^{13}\text{C}-^{31}\text{P})$. The larger magnitude of $^1J(^{13}\text{C}-^{31}\text{P})$ in (VII) as compared to that in (VI) may in part be rationalized by using the Walsh rule^{1,19} that the *s*-character of a phosphorus atom tends to concentrate in the bonds towards the more

electropositive groups or atoms.^{1,19} Finally, the long-range $^{13}\text{C}-^{31}\text{P}$ couplings in the tetracoordinated compounds show more resemblance with the analogous $^{13}\text{C}-^1\text{H}$ long-range couplings than those in the phosphines, a trend that is probably also related to the increased s -character in the P-C bonds. It may be noted that the three-bond couplings in (VI), (VII), and methyl triphenylphosphonium bromide⁶ are all of similar magnitude and correlate well with the Karabatsos relation $^3J(^{13}\text{C}-^{31}\text{P}) = 0.4 ^3J(^1\text{H}-^{31}\text{P})$.

EXPERIMENTAL

Materials. The compounds used in this study are those of earlier studies on $^1\text{H}-^{31}\text{P}$ coupling constants.^{7a-c,e}

^{13}C Spectra. Spectra of the phosphines were obtained on a JEOL C-60HL spectrometer, operating at 15.09 MHz. The spectra were generally obtained as single scan spectra with complete proton decoupling. However, in a few cases, time averaging technique was used in order to increase the signal-to-noise ratio. The ^{13}C resonance of neat benzene was used as external reference; ^{13}C chemical shifts and $^{13}\text{C}-^{31}\text{P}$ coupling constants were read off from spectra recorded with a sweep width of 0.5 ppm/cm and a sweep time of 0.12 ppm/s. Spectra of the two tetracoordinated phosphine derivatives were obtained on a Varian HA-100 spectrometer, operating at a frequency of 25.15 MHz. Both noise-modulated proton decoupled, and single frequency, off resonance proton decoupled spectra were recorded. The ^{13}C resonance of solvent dioxane was used as internal lock, and the chemical shifts are referred to the lock signal. The Varian C-1024 CAT was used for time averaging of the 50-100 scans necessary for acceptable signal-to-noise ratios, using a sweep width of 10 Hz/cm and a sweep time of 10 Hz/sec. Sample solutions were contained in 8 mm sample tubes for both spectrometers.

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