

^{31}P - ^{77}Se Spin-Spin Coupling in Ter- and Quinque-valent Phosphorus Compounds

By W. McFARLANE* and J. A. NASH

(Chemistry Department, Sir John Cass College, Jewry Street, London, E.C.3)

Summary $^1J(^{31}\text{P}$ - $^{77}\text{Se}) = -205$ and -341 Hz. in $\text{Me}_2\text{-PSeMe}$ and $\text{Me}_2\text{P(S)SeMe}$, respectively.

MEASUREMENTS of nuclear spin coupling constants between pairs of directly bound elements are important for testing quantitative theories of chemical bonding.¹ For valid comparisons the signs of the coupling constants must be known, and these are also essential for a proper interpretation of empirical trends. Couplings involving phosphorus are of special interest because of the ease with which changes in hybridization and effective nuclear charge can be brought about by altering the substituents and valency of the phosphorus atom,² and we now report the determination of the sign and magnitude of the P-Se coupling

constant in P^{III} and P^{V} compounds. $^1\text{H}\cdots\{^{13}\text{C}\}$, $^1\text{H}\cdots\{^{31}\text{P}\}$, and $^1\text{H}\cdots\{^{77}\text{Se}\}$ heteronuclear double resonance experiments were performed³ on methyl dimethylphosphino-selenoite and Se-methyl dimethylphosphinoselenoithioate using a modified JEOL C-60-H spectrometer, with the results listed in the Table. The samples contained the isotopes ^{13}C and ^{77}Se in natural abundance (*ca.* 1.1 and 7.5%, respectively), and all signs of coupling constants are related to a positive sign for $^1J(^{13}\text{C}$ -H) in a methyl group.⁴ Previously the magnitudes of the two ^{31}P - ^{77}Se couplings in P_4Se_3 have been measured by direct ^{31}P magnetic resonance.⁵

The reduced¹ coupling constants $^1K(\text{P-Se})$ in the P^{III} and P^{V} compounds are thus -211 and -369×10^{20} cm.⁻³ respectively. An important feature is that the transformation $\text{P}^{\text{III}} \rightarrow \text{P}^{\text{V}}$ makes $^1K(\text{P-Se})$ more negative. This is the opposite direction to the changes of $^1K(\text{P-H})$, $^1K(\text{P-C})$, $^1K(\text{P-F})$, and $^1K(\text{P}^{\text{III}}\text{-P}^{\text{V}})$ which accompany this transformation in many other compounds.^{1,2} However, $^1K(\text{P-P})$ does become *slightly* more negative in going from Me_2PPMe_2 to $\text{Me}_2\text{P(S)PMe}_2$. Negative coupling constants between directly bound atoms arise when one of the coupled nuclei has valence *s*-electrons of low energy, so that the overlap integral between the *s*-orbitals of the two atoms is small. Changes in the coupling constants will depend additionally on $|\Psi_{3s(\text{P})}|^2$ and α_{P}^2 , and the several P-H and P-C coupling constants show that these are normal.⁶ In the P^{III} compound there will be a contribution from the structure $\text{Me}_2\text{P}^+:\text{Se-Me}$, whilst in the P^{V} compound $\text{Me}_2\text{P(S)}^-:\text{Se}^+\text{Me}$ may be significant, and the change in $^1K(\text{P-Se})$ may depend on changes at the selenium atom. This view is supported by the large (138 p.p.m.) ^{77}Se chemical shift difference between the two compounds.

We thank the S. R. C. for funds for the spectrometer and ancillary equipment, and the Governors of Sir John Cass College for a research assistantship (to J.A.N.).

(Received, June 25th, 1969; Com. 918.)

TABLE
N.m.r. parameters of molecules with a P-Se bond

		$\text{Me}_2\text{PSeMe}^{\text{a}}$	$\text{Me}_2\text{P(S)SeMe}^{\text{b}}$
		Hz.	Hz.
$^1J(^{13}\text{C}$ -H)	(P)	$+129.0 \pm 0.2$	$+131.2 \pm 0.2$
$^1J(^{13}\text{C}$ -H)	(Se)	$+140.0 \pm 0.2$	$+145.0 \pm 0.2$
$^1J(^{13}\text{C}$ - ^{31}P)		-25 ± 2	$+50 \pm 4$
$^1J(^{31}\text{P}$ - $^{77}\text{Se})$		-205 ± 6	-341 ± 4
$^2J(^{31}\text{P} \cdots \text{H})$		$+7.0 \pm 0.2$	-12.7 ± 0.2
$^2J(^{31}\text{P} \cdots ^{13}\text{C})$		$+19.5 \pm 1$	-5 ± 2
$^2J(^{77}\text{Se} \cdots \text{H})$		$+10.7 \pm 0.2$	$+10.8 \pm 0.2$
$^3J(^{31}\text{P} \cdots \text{H})$		$+7.0 \pm 0.2$	$+12.2 \pm 0.2$
$^3J(^{77}\text{Se} \cdots \text{H})$		$+8.1 \pm 0.2$	$+3.9 \pm 0.2$
$\tau(\text{CH}_3)$	(P)	8.66 ± 0.01 p.p.m.	7.98 ± 0.01 p.p.m.
$\tau(\text{CH}_3)$	(Se)	8.13 ± 0.01 p.p.m.	7.85 ± 0.01 p.p.m.
$\Xi(^{13}\text{C})$	(P) ^c	$25,145,440 \pm 4$	$25,145,713 \pm 6$
$\Xi(^{13}\text{C})$	(Se)	$25,145,070 \pm 1$	$25,145,197 \pm 3$
$\Xi(^{31}\text{P})$		$40,480,780 \pm 5$	$40,482,405 \pm 8$
$\Xi(^{77}\text{Se})$		$19,072,631 \pm 8$	$19,075,258 \pm 3$

^a Containing *ca.* 5% CH_2Cl_2 to actuate the field-frequency locking circuits of the spectrometer.

^b Saturated solution in CH_2Cl_2 .

^c $\Xi(\text{X})$ is the resonant frequency of X corrected³ to a field strength at which Me_4Si would give a proton resonance of exactly 100 MHz.

¹ J. A. Pople and D. P. Santry, *Mol. Phys.*, 1964, **8**, 1; W. McFarlane, *Quart. Rev.*, 1969, **23**, 187.

² R. K. Harris and E. G. Finer, *Chem. Comm.*, 1968, 110.

³ W. McFarlane, *Ann. Rev. N. M. R. Spectroscopy*, 1968, **1**, 131.

⁴ A. Saupe and G. Englert, *Phys. Rev. Letters*, 1963, **11**, 462; E. L. Mackor and C. McLean, *J. Chem. Phys.*, 1966, **44**, 64.

⁵ R. A. Dwek, R. E. Richards, D. Taylor, G. J. Penney, and G. M. Sheldrick, *J. Chem. Soc. (A)*, 1969, 935.

⁶ W. McFarlane, *Proc. Roy. Soc.*, 1968, **A**, 306, 185.