Magnetic Double Resonance Studies of Trimethylstannylphosphines and their Complexes

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The reduced coupling constant ^1K(PSn) has substantial negative values in the compounds $(Me_3Sn)_{3-n}Ph_nP$ (n = 0—2) and increases algebraically to values close to zero in transition metal carbonyl complexes $(Me_3Sn)_{3-n}Ph_nPM(CO)_5$ (M = Cr, Mo, or W). This behaviour parallels that of ^1K(PC) in analogous compounds but there is a substantial negative contribution in the tin-containing compounds which is attributed to a larger energy gap between the phosphorus and tin valence atomic orbitals. In contrast with the behaviour of triorganophosphines the phosphorus chemical shifts do not vary linearly with n, and the changes in phosphorus shielding which accompany complex formation are discussed.

It is now well established that a change in the co-ordination number of phosphorus leads to substantial changes in spin coupling constants involving the ^{31}P nucleus.[1] In many cases for nuclei which are directly bound to phosphorus the changes are in magnitude only, but with ^{13}C quaternisation of phosphorus is normally accompanied by a change in the sign of $^1J(^{31}P-^{13}C)$ from negative in P^{III} compounds to positive in species with higher-valent phosphorus.[1] This behaviour can be attributed to a change in the sign of the mutual polarisability of the valence *s* orbitals of phosphorus and carbon, and is related to the value of β, the *s* orbital overlap integral for the P–C bond.[2] Only for a relatively small range of values of β is the change in the valency of the phosphorus atom likely to produce a sign inversion, and it is therefore of interest to determine for which other elements directly bound to phosphorus such a change is observed.

Published data show that a sign inversion of $^1J(^{31}P-X)$ may accompany the transformation $P^{III} \longrightarrow P^{IV}$ or P^{V} for X = $^{31}P^{V}$, but not for X = ^{1}H, ^{19}F, $^{31}P^{III}$, or ^{77}Se, and results for other X are not yet available.[3,4] We have therefore studied the behaviour of $^1J(^{31}P-^{119}Sn)$ in some organostannylphosphines when the phosphorus atom is quaternised by co-ordination to a zero-valent transition metal system.[5] The resulting complexes are not ideal for our purpose because the oxidation state of phosphorus can be regarded as being intermediate between three and five, but attempts to quaternise organostannylphosphines by reacting them with oxygen or sulphur lead to rupture of the weak phosphorus–tin bond. An advantage of having a transition metal (M) co-ordinated to phosphorus is that if its nucleus has a suitable spin (preferably $I = \frac{1}{2}$, *e.g.* ^{103}Rh, ^{183}W, or ^{195}Pt) the size of $^1J(^{31}P-M)$ can be used to assess the hybridisation of phosphorus.[6,7]

Previously $^1J(^{31}P-^{119}Sn)$ has been found to have values of +590 and +550 Hz in Me_3SnPPh_2 and $Me_3SnP(H)Ph$ respectively [8,9] (note that ^{119}Sn has a negative magnetic moment), and to have a magnitude of *ca.* 2200 Hz in organophosphine complexes of tin tetrachloride, although the sign has not been determined in these.[6]

EXPERIMENTAL

Me_3SnPPh_2, $(Me_3Sn)_2PPh$, and $(Me_3Sn)_3P$ were prepared by standard methods; they were reacted with tetrahydrofuran–$M(CO)_5$ (M = Cr or W) in anhydrous tetrahydrofuran to give complexes which were purified by recrystallisation.[5,10]

The samples contained the isotopes ^{13}C, ^{119}Sn, and ^{183}W in natural abundance (*ca.* 1·1, 8·6, and 14·3% respectively) and were examined as neat liquids or concentrated solutions at 24 °C on a spectrometer operating at a proton frequency of 60 MHz. $^1H-\{^{13}C\}$, $^1H-\{^{31}P\}$, and $^1H-\{^{119}Sn\}$ double resonance experiments showed that $^2J(^{119}Sn \cdots H)$ is positive in

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[1] W. McFarlane, *Proc. Roy. Soc.*, 1968, **306*A***, 185.

[2] J. A. Pople and D. P. Santry, *Mol. Phys.*, 1964, **8**, 1.

[3] W. McFarlane, *Quart. Rev.*, 1969, **23**, 187.

[4] C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, 1969, **51**, 2790.

[5] H. Schumann, O. Stelzer, J. Kuhlmey, and V. Niederreuter, *Chem. Ber.*, 1971, **104**, 993.

[6] G. S. Mather, G. M. McLaughlin, and A. Pidcock, *J.C.S. Dalton*, 1973, 1823.

[7] J. F. Nixon and A. Pidcock, *Ann. Rep. N.M.R. Spectroscopy*, 1969, **2**, 345.

[8] H. Elser and H. Dreeskamp, *Ber. Bunsengesellschaft Phys. Chem.*, 1969, **73**, 619.

[9] P. G. Harrison, S. E. Ulrich, and J. J. Zuckerman, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 865.

[10] H. Nöth and S. N. Sze, *J. Organometallic Chem.*, 1972, **43**, 249.

$(Me_3Sn)_2PPh$ [relative to $^1J(^{13}C-H) > 0$] in agreement with expectation,[11] and this sign is assumed in the other compounds. Standard heteronuclear double resonance techniques were then used to obtain the data listed in the Table, and all spectra were calibrated.

RESULTS AND DISCUSSION

The isotope ^{119}Sn has a negative magnetogyric ratio and it is therefore convenient to discuss the results in terms of reduced coupling constants K (defined[2] by $K(XY) = 2\pi . J(XY)/\hbar\gamma_X\gamma_Y$) in order to avoid dependence upon individual nuclear properties. The results in the Table thus show that $^1K(PSn)$ is negative in both the free organostannylphosphines and their metal carbonyl complexes. This is in apparent contrast to the behaviour of $^1K(PC)$ which is normally negative in an organophosphine but becomes positive when the phosphorus atom is quaternised;[1] however, the *change* in the coupling constant is in the same direction in each case. Furthermore, the state of hybridisation of phosphorus in the two types of complex may be different, and the tendency for $^1K(PSn)$ to become less negative as the number of tin atoms bound to phosphorus decreases suggests that this is actually so. This effect can be allowed for as follows. A plot of $^1J(^{31}P-^{119}Sn)$ against $^1J(^{31}P-^{183}W)$ in these compounds is linear, and extrapolation to the value of $^1J(^{31}P-^{183}W)$ in $Ph_3PW(CO)_5$ gives a value of -125 Hz for $^1J(^{31}P-^{119}Sn)$ when the bonding situation at phosphorus is similar to that in a triarylphosphine complex. A similar result is predicted from a plot of $^1J(^{31}P-^{119}Sn)$ against n in the series $(Me_3Sn)_{3-n}Ph_nPW(CO)_5$. This figure would correspond to a positive $^1K(PSn)$ in the metal complexes and the changes in $^1K(PC)$ and $^1K(PSn)$ can be regarded as being strictly analogous, although as will emerge later there is a significant additional negative contribution to the reduced coupling constants when tin is one of the coupled nuclei.

N.m.r. parameters of organostannylphosphines and their complexes

Compound[a]	$^1J(^{31}P-^{119}Sn)$ /Hz	$^2J(^{119}Sn\cdots H)$ /Hz	$^3J(^{31}P\cdots H)$ /Hz	$^1J(^{31}P-^{183}W)$ /Hz	$\delta(Me)$[b]/p.p.m.	$\delta(^{119}Sn)$[c]/p.p.m.	$\delta(^{31}P)$[d]/p.p.m.
$(Me_3Sn)_3P$ (1)[e]	$+832.5 \pm 0.5$	$+52.5 \pm 0.2$	$+1.8 \pm 0.1$		$+0.28$	$+36.3 \pm 0.1$	-329.6 ± 0.1
$(Me_3Sn)_3PCr(CO)_5$ (2)[h]	$+409.5 \pm 1.0$	$+52.9 \pm 0.2$	$+3.1 \pm 0.1$		$+0.32$	$+64.2 \pm 0.1$	-303.1 ± 0.1
$(Me_3Sn)_3PW(CO)_5$ (3)[h]	$+375.5 \pm 1.0$	$+53.0 \pm 0.2$	$+3.4 \pm 0.1$	$+143 \pm 3$	$+0.30$	$+63.4 \pm 0.1$	-346.6 ± 0.1
$(Me_3Sn)_2PhP$ (4)[f]	$+724 \pm 3$	$+52.1 \pm 0.2$	$+2.1 \pm 0.1$		$+0.28$	$+14.2 \pm 0.1$	-165.2 ± 0.1
$(Me_3Sn)_2PhPCr(CO)_5$ (5)[h]	$+253 \pm 3$	$+52.9 \pm 0.2$	$+3.3 \pm 0.1$		$+0.35$	$+39.7 \pm 0.1$	-129.1 ± 0.1
$(Me_3Sn)_3PhPW(CO)_5$ (6)[h]	$+216 \pm 3$	$+53.1 \pm 0.2$	$+3.5 \pm 0.1$	$+173 \pm 10$	$+0.31$	$+41.6 \pm 1.0$	-172.6 ± 0.1
Me_3SnPh_2P (7)[e,g]	$+596 \pm 2$	$+51.9 \pm 0.2$	$+2.1 \pm 0.1$		$+0.14$	-2.3 ± 0.1	-58.3 ± 0.1
$Me_3SnPh_2PW(CO)_5$ (8)[h]	$+50 \pm 5$	$+53.4 \pm 0.2$	$+3.6 \pm 0.1$	$+200 \pm 5$	$+0.21$	$+33.7 \pm 0.2$	-52.6 ± 0.1
$Ph_3PW(CO)_5$ (9)[i]				$+245 \pm 10$			-19.3 ± 0.1

[a] All samples contained tetramethylsilane. [b] The Ξ value is the resonant frequency corrected to a magnetic field in which the protons of tetramethylsilane resonate at exactly 100 MHz. [c] Positive downfield from Me_4Sn, for which Ξ (^{119}Sn) is taken to be 37,290,665 Hz. [d] Positive downfield from 85% aq.H_3PO_4, for which Ξ (^{31}P) is taken to be 40,480,790 Hz. The ^{31}P chemical shifts of compounds (1)—(3) and (7)—(9) are in agreement with those in refs. 5, 8—10, and 17. [e] The sample contained *ca.* 35% benzene. [f] The sample contained *ca.* 10% CH_2Cl_2. $^1H-\{^{13}C\}$ and $^1H-\{^{31}P\}$ double resonance experiments gave the following parameters: $^1J(^{13}C-^1H) = +129.6 \pm 0.2$; $^2J(^{31}P\cdots{}^{13}C) = +8 \pm 2$; Ξ (^{13}C) = 25,144,868 ± 2; $^3J(^{31}P\cdots{}^1H) = +2.1 \pm 0.1$ Hz. [g] The parameters given here agree well with those in refs. 8 and 9. [h] Benzene solution. [i] Concentrated CH_2Cl_2 solution. The value of $^1J(^{31}P-^{183}W)$ differs from that given in ref. 18 but has been remeasured and is believed to be correct.

The molecular orbital treatment by Pople and Santry suggests that the Fermi contact contribution normally dominates the spin coupling mechanism for directly bound elements and is given by expression (1) where

$$K \propto \psi_{ns}^2(0)A.\psi_{ns}^2(0)B.\pi_{AB} \qquad (1)$$

$\psi_{ns}^2(0)$ is the ns electron density at the parent nucleus and π_{AB} is the mutual polarisability of the valence s orbitals of A and B and depends upon α^2 (the s character of the hybrids used to form the A–B bond) and upon orbital energy differences.

In many cases the variations of π_{AB} in this expression may be discussed in simple terms, particularly when K_{AB} is large as for $K(CH)$, $K(CC)$, $K(SnC)$, $K(SnH)$, $K(PH)$, $K(PF)$, $K(CF)$, $K(PW)$, *etc.*: the changes in the coupling constants can then be discussed in terms of changes in $\psi_{ns}^2(0)$ and α^2, and simple relations between different coupling constants can be written down. In particular relation (2) appears to hold to ±15% in a range of

$$^1K(SnX) = 8.5\,{}^1K(CX) \qquad (2)$$

compounds for X = H, C, Sn, or F. For example $^1K(CH) = ca.\ 4$, $^1K(SnH) = ca.\ 40$, $^1K(CC) = 4.4$, $^1K(SnC) = ca.\ 30$, $^1K(SnSn) = ca.\ 270$, $^1K(CF) = ca.\ 5.5$, $^1K(SnF) = ca.\ 55\ nm^{-3}$ in comparable molecules. However our results show that for X = P this is not so: in Me_3P $^1K(PC)$ is -1.2 and in compound (1) $^1K(PSn)$ is $-46\ nm^{-3}$ whereas equation (2) predicts $-10\ nm^{-3}$. Similar discrepancies are found for the transition metal carbonyl complexes, and in all cases there is a significant additional negative contribution to the phosphorus–tin reduced coupling constant. However, the *changes* in $^1K(PC)$ and $^1K(PSn)$ (*ca.* 3·5 and 28 nm^{-3} respectively) which accompany complex formation are in accord with equation (2), although this may be fortuitous. It is clear that a change in the sign of K cannot arise unless π_{AB} also changes sign, and the foregoing results are consistent with π_{PC} and π_{PSn} having significantly different values in both the free phosphines and their complexes.

π_{AB} Is related to the valence s overlap integral β between A and B and is negative when β is very small and positive when β is large.[12] Thus negative reduced coupling constants arise when β is small, *i.e.* when the s valence orbital of one of the atoms is of significantly different energy from the other orbitals. As the energy difference decreases π_{AB} will pass through zero and will eventually

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[11] W. McFarlane, *J. Chem. Soc.* (*A*), **1967**, 528.

[12] E. G. Finer and R. K. Harris, *Progr. N.M.R. Spectroscopy*, 1971, **6**, 61.

adopt a large positive value when the mean excitation energy approximation for the contact interaction becomes valid. In either of these extreme situations small changes in β arising from changes in the orbital energies will have comparatively little effect upon π_{AB} and the simple treatment outlined above will suffice.

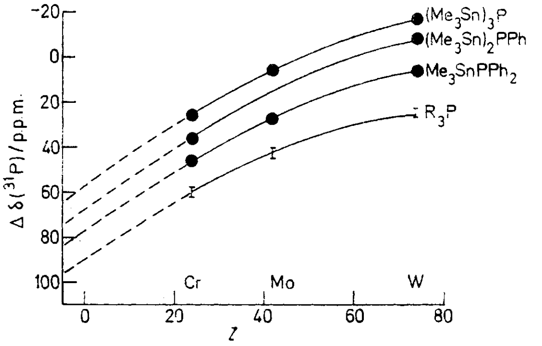
Our results show that for both the P–C and the P–Sn bonds variations of π_{AB} have an important effect upon the coupling constant and hence that β is of *moderate* size. That is, in the P^{III} compounds in particular, the phosphorus 3*s* electrons are quite tightly bound and are of significantly lower energy than the carbon 2*s* or the tin 5*s* electrons. The greater negative value of π_{AB} in the tin case can be attributed to the lower electronegativity of tin compared to carbon, which will lead to greater orbital energy differences. When the phosphorus is quaternised the energy of the phosphorus 3*s* electrons becomes higher, and so π_{AB} and the reduced coupling constant become less negative.

It is to be expected that the behaviour of silicon in this respect would be intermediate between that of carbon and tin, but at present very few data are available on this point. In $(SiH_3)_3P$ and $(Me_3Si)_3P$, ${}^1K$(PSi) has values of $-4{\cdot}4$ and $\pm 2{\cdot}8$ nm^{-3} resepctively,[13,14] indicating considerable sensitivity to the effects of substituents as would be expected, and we would predict that in P^{V} compounds this coupling constant will have relatively small positive values.

The ^{119}Sn chemical shift of each of the P^{III} compounds changes *ca.* 30 p.p.m. to lower field on complex formation, and this can be ascribed to the increase in the effective electronegativity of the phosphorus atom. It has been shown that in species Me_3SnX the tin chemical shift changes to lower field as the electronegativity of X increases.[15] The small increases in ${}^2J(^{119}Sn \cdots H)$ which accompany complex formation can be attributed to this cause also. However, the changes in these two parameters as the number of tin atoms bound to phosphorus is altered are not in the directions expected from simple considerations of inductive effects, and it may be that the foregoing agreement is fortuitous.

The ^{31}P chemical shifts for the three stannylphosphines show that it is not possible to assign a unique 'group contribution to the phosphorus shielding' to the trimethylstannyl group.[16] In fact for compounds (1), (4), and (7) the required contributions are −110, −81, and −52 p.p.m. respectively (note that the sign convention used here is the opposite of that in ref. 17) in marked contrast to the position with alkyl groups for which a single group contribution per group can predict ^{31}P chemical shifts to closer than 2 p.p.m. This could indicate that there are large differences in the inter-bond angles at phosphorus in compounds (1), (4), and (7). Alternatively, the anomalous phosphorus chemical shifts might arise from the changing number of polarisable (*i.e.* tin) atoms attached to phosphorus since this kind of effect is known to occur with other nuclei.[18]

The co-ordination chemical shift parameter [*i.e.* the change in δ(^{31}P) on complex formation] is sometimes used, but this concept must be applied with caution if metals in different rows of the Periodic Table are involved. Thus for triorganophosphines the co-ordination shifts are *ca.* 60, 40, and 25 p.p.m. to low field for pentacarbonylchromium, -molybdenum, and -tungsten groups respectively,[17] while for the organostannylphosphines they are much more variable and of opposite signs for chromium and tungsten. The Figure shows how the co-ordination chemical shift varies with the atomic number *Z* of the metal atom and it is clear that the anomalies arise because there are at least two contributions. One is upfield and is due to the appearance of a bulky atom in a position adjacent to the ^{31}P nucleus, although whether it is to be identified with the diamagnetic term of Mason[19] is not clear. The other is a shift to low field arising from the change in phosphorus hybridisation and may be regarded as the true co-ordination shift; it can be estimated from the intercept with the ordinate in the Figure and varies from 95 ± 10 p.p.m. for triorganophosphines to 65 ± 10 p.p.m. for $(Me_3Sn)_3P$. These values support the view that the trimethylstannyl groups bound to phosphorus reduce the change in hybridisation which occurs on complex formation. The co-ordination chemical shift associated with the formation of triorganophosphonium ion R_3PH^+ (*i.e.* $Z = 1$) is less (only *ca.* 30 p.p.m.) than would be expected on this basis,[20] but as the phosphorus atom has a positive charge in these species the two systems are not strictly comparable.



Plots of the co-ordination chemical shift Δδ(^{31}P) against the atomic number *Z* of the metal atom in pentacarbonyl transition metal complexes. Some data are from ref. 10

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[13] K. D. Crosbie and G. M. Sheldrick, *Mol. Phys.*, 1971, **20**, 317.

[14] H. C. Marsmann, *Chem. Z.*, 1972, **96**, 288.

[15] J. D. Kennedy and W. McFarlane, *Rev. Silicon, Germanium, Tin, Lead Chem.*, in the press.

[16] S. O. Grim, W. McFarlane, and E. F. Davidoff, *J. Org. Chem.*, 1967, **32**, 781.

[17] S. O. Grim, D. A. Wheatland, and W. McFarlane, *J. Amer. Chem. Soc.*, 1967, **79**, 5573.

[18] P. R. Wells, *Det. Org. Struct. Phys. Meth.*, 1971, **4**, 233.

[19] J. Mason, *J. Chem. Soc.* (*A*), 1971, 1038.

[20] S. O. Grim and W. McFarlane, *Canad. J. Chem.*, 1968, **46**, 2071.