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INDIRECT NUCLEAR SPIN SPIN COUPLING CONSTANTS OF TIN-119 AND LEAD-207 TO NITROGEN AND PHOSPHORUS IN ORGANOMETALLIC COMPOUNDS

JOHN D. KENNEDY, WILLIAM McFARLANE, GEOFFREY S. PYNE
Department of Chemistry, City of London Polytechnic, Jewry Street, London EC3N 2EY (England)

BERND WRACKMEYER
Institut für Anorganische Chemie der Universität München, Meiserstrasse 1, 8000 München 2 (West Germany)

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Summary

Coupling constants $J(^{119}Sn^{15}N)$ and other NMR parameters are reported for $(C_6H_5NH)Sn(CH_3)_3$, $C_6H_5N[Sn(CH_3)_3]_2$, $[C_6H_5NCH_3]_{4-n}Sn(CH_3)_n$ (n = 0—3), and $[C_6H_5NP(X)(CH_3)_2]Sn(CH_3)_3$ (X = lone pair, S). $J(^{119}Sn^{15}N)$ may be of either sign in these compounds. $J(^{207}Pb^{14}N)$ for $[(CH_3)_3Pb]_2N\,Sn(CH_3)_3$ and $(CH_3)_3PbN[Sn(CH_3)_3]_2$ can be observed directly from the ^{207}Pb NMR spectrum. Factors leading to reversal of the sign of $J(^{119}Sn^{15}N)$ and differences in the behaviour of $^1K(SnP)$ and $^1K(SnN)$ in analogous molecules are noted.

Introduction

Recent improvements in multinuclear NMR instrumentation have emphasized the value of comparisons of NMR parameters involving the nuclei of elements in different parts of the periodic table. Such comparisons are of value both as a check on detailed thoretical predictions and as a source of empirical correlations with factors influencing chemical bonding. The latter approach is especially informative when data are available for related compounds in a single group or adjacent pair of groups.

A considerable number of coupling constants $^1J(EX)$ [E = ^{13}C, ^{29}Si, ^{119}Sn, ^{207}Pb; X = ^{1}H, ^{11}B, ^{13}C, etc.] have been reported [1,2], but although some isolated values of $^1J(^{119}Sn^{15}N)$, $^1J(^{119}Sn^{31}P)$, and $^1J(^{207}Pb^{15}N)$ are known there has been little attempt to discuss these in more detail, or to obtain information about the ranges, for example of $^1J(^{119}Sn^{15}N)$. It is of interest that while the reduced coupling constants * $^1K(NC)$ and $^1K(SiN)$ are generally positive [3,4],

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* $K(AB)$ is defined as $J(AB)4\pi^2/h\gamma(A)\gamma(B)$ to avoid dependence upon individual nuclear properties.

the coupling ^1K(SnN) is negative in $PhNHSnMe_3$ (I) [5], but positive in PhN(Me)$SnMe_3$ (III) [6]. By contrast ^1K(PbN) is fairly large and negative in PhN(Me)$PbMe_3$ [6].

In view of this we have now examined a series of N-substituted anilines (labelled with ^{15}N) of the type $(C_0H_5NH)Sn(CH_3)_3$ (I) [5], $C_0H_5N[Sn(CH_3)_3]_2$ (II), $[C_6H_5NCH_3]_{4-n}[Sn(CH_3)_3]_n$ $n = 3$ (III), $n = 2$ (IV), $n = 1$ (V), $n = 0$ (VI) and $[C_6H_5N(X)P(CH_3)_2]$ $Sn(CH_3)_3$ [X = lone pair (VII), X = S (VIII)] using heteronuclear double resonance experiments ^1H-{X}, where X = ^{15}N or ^{119}Sn, to obtain ^{15}N and ^{119}Sn coupling constants and chemical shifts. We also report related data on some species with tin—phosphorus and lead—nitrogen bonds.

Results

In the proton spectra of compounds II—V, VII and VIII the coupling $^3J(^{15}N—H)$ produced either a resolved splitting or a broadening of the tin satellites of the Sn-methyl groups. Irradiation at the appropriate ^{15}N resonance frequency gave selective collapse of this coupling which permitted a comparison of the signs of ^2K(SnH) [negative] and ^1K(SnN). The latter reduced coupling was thus found to be negative in II and VIII, and positive in III—V and VII. It was then possible to use similar experiments involving observation of the tin satellites of the *N*-methyl resonances [which were broadened by the unresolved coupling $^2J(^{15}N—H)$] to compare the signs of ^3K(SnH) and ^1K(SnN) and hence show ^3K(SnH) to be positive in III—V. Extrapolation of the values of this coupling then indicates that it is also positive in VI, and the sign comparison of ^1K(SnN) and ^3K(SnN) then showed that ^1K(SnN) is positive in VI. A similar procedure

TABLE 1

NMR PARAMETERS OF COMPOUNDS WITH TIN—NITROGEN, TIN—PHOSPHORUS, LEAD—NITROGEN, OR LEAD—PHOSPHORUS BONDS [a]

	Compound	$\delta(^{119}Sn)$	$\delta(^{207}Pb)$	$\delta(^{15}N)$	$\delta(^{31}P)$
I	$(CH_3)_3Sn—NHC_6H_5$	+46.4	—	+9.4	—
II	$[(CH_3)_3Sn]_2NC_6H_5$	+61.0	—	+3.4	—
III	$(CH_3)_3Sn—N(CH_3)C_6H_5$	+73.0	—	+6.2	—
IV	$(CH_3)_2Sn[N(CH_3)C_0H_5]_2$	+30.5	—	+13.4	—
V	$CH_3Sn[N(CH_3)C_6H_5]_3$	—66.0	—	+15.7	—
VI	$Sn[N(CH_3)C_6H_5]_4$	—175.6	—	+17.4	—
VII	$(CH_3)_3Sn—N[P(CH_3)_2]C_0H_5$	+63.5	—	+4.5	+25.0
VIII	$(CH_3)_3Sn—N[P(S)(CH_3)_2]C_6H_5$	+66.0	—	+29.5	+58.4
IX	$(CH_3)_3Pb—N(CH_3)C_6H_5$	—	+226.5	+15.5	—
X	$(CH_3)_3Pb—N[Sn(CH_3)_3]_2$	+94.3	+242.0	—	—
XI	$[(CH_3)_3Pb]_2N—Sn(CH_3)_3$	+103.3	+268.0	—	—
XII	$(CH_3)_3Sn—PHC_6H_5$	—18.0	—	—	—131
XIII	$[(CH_3)_3Sn]_2PC_6H_5$	+14.2	—	—	—165.2
XIV	$(CH_3)_3Sn—P(C_6H_5)_2$	—2.3	—	—	—58.3
XV	$(CH_3)_2Sn[P(C_6H_5)_2]_2$	—11.5	—	—	—49.7
XVI	$(CH_3)_3Pb—P(C_6H_5)_2$	—	+40.5	—	—35.9

[a] Chemical shifts are in ppm to high frequency of the reference: ^{119}Sn, Me_4Sn; ^{207}Pb, Me_4Ph; ^{15}N, $Me_4N^+I^-$ in $(CD_3)_2SO$; ^{31}P, 85% H_3PO_4. Coupling constants are in Hz. Reduced coupling constants are in nm^{-3}. [b] From ref. 5. [c] $^3J(^{15}NSnCH) = 0.6(5)$ Hz. [d] $^3J(^{15}NSnCH) = 0.4(7)$ Hz; $^3J(^{119}SnNCH) = —30.8$ Hz. [f] $^3J(^{15}NSnCH) <0.3$ Hz; $^3J(^{119}SnNCH) = —35.7$ Hz; $^1J(^{119}Sn^{15}N)$ was determined by selective collapse of $^3J(^{15}NSnCH)$ in a ^1H-$\{^{15}N\}$ experiment and using a signal averager to accumulate the

for IX yielded ^{1}K(PbN) negative, and ^{3}K(PbH) positive, on the basis that ^{2}K(PbH) is negative.

The tin satellites in the proton spectrum of the Sn-methyl groups of XV exhibited fine structure as a result of the coupling $^{3}J(^{31}\mathrm{PSnCH})$, and it was therefore possible to use $^{1}\mathrm{H}$-{^{31}P}experiments to show that ^{1}K(SnP) is negative [relative to ^{2}K(SnH) negative]. In addition, $^{1}\mathrm{H}$-{^{31}P}experiments gave selective asymmetric perturbations [7] of the outer components of the central Sn-methyl triplet which showed that $^{2}J(^{31}\mathrm{PSn}^{31}\mathrm{P}) = +18 \pm 5$ Hz relative to a positive sign [8] for $^{3}J(^{31}\mathrm{PSnH})$.

Direct ^{207}Pb-{$^{1}\mathrm{H}_{\mathrm{noise}}$} spectra of a mixture of X and XI gave at room temperature poorly resolved 1 : 1 : 1 triplets as a result of the coupling $^{1}J(^{207}\mathrm{Pb}^{14}\mathrm{N})$. [^{14}N has $I = 1$]; At 80°C the rate of quadrupolar relaxation was slow enough for us to show that $^{1}J(^{207}\mathrm{Pb}^{14}\mathrm{N}) = 170 \pm 10$ Hz in each compound. The magnitudes of ^{1}K(PbN) in X and XI are so close to that in IX [determined from the ^{15}N enriched sample] that it is reasonable to assume that they too are positive.

Discussion

No simple pattern emerges for the values of ^{1}K(EX) [E = Sn, Pb; X = N, P] in Table 1. As has been pointed out in other studies of one-bond tin [5] and lead [6] coupling constants this is to be expected since E is large and polarisable, and X has no (accessible) open *s*-shell configuration. It is probable that these couplings are dominated by the Fermi contact interaction and the reduced coupling constant is then given by eqn 1 [9] in which $\psi^{2}(0)$ is the valence shall electron density at the nucleus, and π_{EX} is the mutual polarizability [10] for the

$^{2}J(^{119}\mathrm{SnCH})$	$^{2}J(^{207}\mathrm{PbCH})$	$^{1}J(^{119}\mathrm{Sn}^{15}\mathrm{N})$	$^{1}K(\mathrm{SnN})$	$^{1}J(^{119}\mathrm{Sn}^{31}\mathrm{P})$	$^{1}K(\mathrm{SnP})$	Notes
+54.2	—	−26.3	−5.86	—	—	*b*
+53.0	—	−41.4	−9.22	—	—	*c*
+54.0	—	+2.2	+0.50	—	—	*d*
+55.6	—	+24.0	+5.35	—	—	*e*
+79.4	—	+87.0	+19.40	—	—	*f*
—	—	+175.0	+39.00	—	—	*g*
+54.0	—	+9.5	+2.10	—	—	*h*
+54.3	—	−21.0	−4.68	—	—	*h, i*
—	−65.3	[+261] [p]	[103.0] [p]	—	—	*j*
+52.5	−63.0	[+238] [p]	[−94.0] [p]	—	—	*k*
+52.3	−62.0	[+238] [p]	[−94.0] [p]	—	—	*k*
+52.7	—	—	—	+538	−29.5	*l*
+52.1	—	—	—	+724	−40.0	*m*
+51.9	—	—	—	+596	−33.0	*m*
+47.5	—	—	—	+808	−44.3	*n*
—	−52.0	—	—	[−1335] [p]	[−131.5] [p]	*j*

resultant increases in the height of the appropriate satellites. [g] $^{3}J(^{119}\mathrm{SnNCH}) = -61.0$ Hz. $^{1}J(^{119}\mathrm{Sn}^{15}\mathrm{N})$ was determined as in *f*. [h] Ref. 22. [i] The value of $^{1}J(^{119}\mathrm{Sn}^{15}\mathrm{N})$ in ref. 5 is a misprint. [j] From ref. 6. [k] $^{1}J(^{207}\mathrm{Pb}^{15}\mathrm{N})$ has been derived by multiplying the observed value of $^{1}J(^{207}\mathrm{Pb}^{14}\mathrm{N})$ by $\gamma(^{15}\mathrm{N})/\gamma(^{14}\mathrm{N})$. [l] Ref. 23. [m] Ref. 8. [n] $^{3}J(^{31}\mathrm{PSnCH}) = +1.9$ Hz; $^{2}J(^{31}\mathrm{PSn}^{31}\mathrm{P}) = +18 \pm 5$ Hz. [p] Refers to coupling involving Pb rather than Sn.

valence *s*-orbitals of E and X. For a small *s* overlap integral, π_{EX} and hence ${}^1K(EX)$ may pass through zero and become negative, and in general when the

$$ {}^1K(\mathrm{EX}) = \frac{4e^2h^2}{9m^2c^2} \cdot \psi_{\mathrm{E}}^2(0) \cdot \psi_{\mathrm{X}}^2(0) \cdot \pi_{\mathrm{EX}} \qquad (1) $$

s-overlap integral is small ${}^1K(EX)$ will therefore display a marked sensitivity of sign and relative magnitude to relatively small variations in the substituents of E and of X.

In the case of formally three-coordinate nitrogen it has been found [11] that ${}^1K(NC)$ is positive and has an approximate dependence upon the *s*-character associated with the N—C bond. By contrast, ${}^1K(PC)$ in organophosphines is negative [12], and this is generally ascribed to rather small values of the P—C *s*-overlap integral as a result of most of the phosphorus *s*-character residing in the lone pair. From this it is reasonable to expect that couplings ${}^1K(EP)$ will generally be more negative [or less positive] than the corresponding coupling ${}^1K(EN)$. Work [5,6] on one bond couplings involving tin or lead has also revealed a tendency for large polarisable atoms with open *s*-shell configurations to produce negative contributions to the Fermi contact term. This is especially apparent from the values of ${}^1K(SnSn)$ in hexaalkylstannanes [13], and leads to the prediction that couplings to lead should be less positive/more negative than analogous couplings to tin. The data for compounds III and IX, and XIV and XVI support this.

The electronegativity of any substituent of E or X is also important. Provided that the substituents involved are of similar bulk then an increase in the electronegativity of a substituent will tend to increase the overlap intergral β_{EX} so that π_{EX} and hence ${}^1K(EX)$ will become more positive. This can explain the trend of the values of ${}^1K(SnN)$ in the series I—VII satisfactorily, since a sign inversion from negative to positive occurs when either hydrogen (I) or trimethylstannyl (II) is replaced by the more electronegative methyl (III) or dimethylphosphinyl (VII) group. Consequently, increasing replacement of the Sn-methyl by PhMeN groups leads to larger values of β_{SnN} and to the observed increasingly positive values of ${}^1K(SnN)$. In this connection, however, it must be borne in mind that when ${}^1K(SnN)$ is small steric effects are likely to be important and so it is not possible to expect quantitative agreement. This is exemplified by VII and VIII. In the former ${}^1K(SnN)$ is small and positive, and becomes negative in VIII even though the $Me_2P(S)$ group is more electronegative than Me_2P group. Whilst it is tempting to attribute this to the greater bulk of the $Me_2P(S)$ group it must be pointed out that other factors such as interactions involving the nitrogen and phosphorus lone pairs may also be involved. Nonetheless, there is a consistent trend in ${}^1K(SnN)$ in the series of compounds I—VI which lends qualitative support to the above explanation. In compounds IX—XI the values of ${}^1K$(PbN) are of comparable size despite quite large changes in the nature of the substituents on nitrogen. This is to be expected, because this coupling is relatively large and negative, implying a fairly large negative value for π_{PbN} and correspondingly reduced relative sensitivity to changes in substituents compared with π_{SnN}.

The values for ${}^1K(SnP)$ in compounds XII—XV are all large and negative and again indicate a relatively large negative π_{SnP} so that the observed differences

TABLE 2

$^{3}J(^{119}SnNCH)$ IN Hz IN THE SPECIES $Me_nSn(NR_2)_{4-n}$

n	NEt_2	N(Me)Ph	$N(Me)SiMe_3$
3	−44.4	−26.4	−45.5
2	−45.5	−30.8	−49.5
1	−47.0	−35.7	−52.8
0	−49.8	−61.0	−66.8

are probably dominated by difference in the hybridization and effective nuclear charges of tin and or phosphorus. Thus in XII the small size of the hydrogen bound to phosphorus permits the hybridization to be closer to p^3 than in XIV where the greater bulk of phenyl leads to increased *s*-character for the phosphorus orbital used in the Sn—P bond and hence to a greater magnitude for the coupling constant. In XIII with the even bulkier Me_3Sn group replacing phenyl this is carried a stage further and the magnitude is larger, while in XV and in $(Me_3P)_3Sn$ [$^1K(SnP) = -46.7\ nm^{-3}$] it leads to even greater magnitudes of the coupling. It would clearly be of interest to know $^1K(SnN)$ in $(Me_3Sn)_3N$ in this context, but unfortunately attempts to determine $^1J(^{119}Sn—^{14}N)$ in this compound were frustrated by the rapid ^{14}N quadrupolar relaxation. However, the ^{119}Sn line-width at half height exceeded 20 Hz, implying a substantial magnitude for the coupling, in accordance with the preceding discussion.

Table 2 gives the values of $^3J(^{119}Sn—H)$ in compounds III—VI and also in the analogous species $Me_nSn(NEt_2)_{4-n}$ and $Me_nSn[N(Me)SiMe_3]_{4-n}$ [n = 0—3] which are available in the literature [14,15]. This vicinal coupling shows marked stereochemical dependence, particularly when V and VI are compared, and should have considerable diagnostic value when data have been obtained for a wider range of molecules. The sign and magnitude of $^2J(^{31}P—Sn—^{31}P)$ in XV continue the trend exhibited by other members of the series $(Ph_2P)_2E$ [E = C, +120 Hz; E = Si, +45 Hz [7].]

The ^{15}N chemical shifts of I—IX lie close to those observed for aniline or *N*-methylaniline, indicating that the nitrogen shielding is dominated by the presence of the phenyl group, and that the nitrogen hybridization remains essentially unaltered by replacement of hydrogen by the organometallic group. Inductive effects probably explain the decrease in nitrogen shielding in the sequences III→VI and VIII→IX. The ^{31}P chemical shifts show the expected behaviour, in that replacement of phenyl as a substituent by hydrogen, tin or lead increase the shielding, and the ^{119}Sn chemical shifts also vary in the ways previously established [16] for similar molecules. The known correlation [17] of tin and lead shieldings is confirmed by the results for IX—XI and XVI.

Experimental

All compounds were prepared and manipulated under an atmosphere of dry nitrogen. Aniline enriched to 96.5% in ^{15}N was obtained from Prochem Ltd., and was converted to *N*-methylaniline by treating its tosylate with dimethyl sulphate followed by acid hydrolysis [18]. The compounds II—VI and IX were prepared by transamination reactions [19] of the diethylamino derivatives with aniline [in the case of II] or *N*-methylaniline on a ca 2 mmolar scale. The preparations were repeated on a larger scale using non-enriched material to yield products which gave satisfactory elemental analyses. The mixture of X and XI was obtained as described elsewhere [20]. $Me_2Sn(PPh_2)_2$ was prepared by reacting Me_2SnI_2 with Ph_2PH in the presence of diethylamine in light petroleum [21]; similar reactions using the methyltin trihalides $MeSnX_3$ resulted in disproportionation to give $Me_2Sn(PPh_2)_2$ and $Sn(PPh_2)_4$. Benzene and/or benzene-d_6 were used as solvents for all the NMR measurements and provided field/frequency locking signals for the spectrometers. The heteronuclear double resonance experiments were performed as described elsewhere [6] using a modified JEOL C60-H spectrometer, and ^{119}Sn and ^{207}Pb spectra were recorded on a Bruker WP-200 instrument with a multinuclear probe.

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