

Patterns of Nuclear Spin Coupling in Species with Platinum–Tin Bonds: A Comparison of Phosphorus and Tin

William McFarlane*† and Nicholas H. Rees

Department of Chemistry, City of London Polytechnic, Jewry Street, London EC3N 2EY

A range of heteronuclear magnetic multiple-resonance experiments involving ^1H , ^{31}P , ^{119}Sn , ^{195}Pt , and ^{207}Pb was used to determine the absolute signs of nuclear spin-coupling constants for platinum(II) complexes with PR_3 [$\text{R} = \text{alkyl, aryl, or alkoxy}$] and SnCl_3^- , SnPh_3^- , or PbPh_3^- as ligands. The signs of and trends in the reduced coupling constants $^1K(\text{EX})$ and $^2K(\text{EX})$ for $\text{E} = \text{Sn}(\text{Pb})$ closely parallel those for $\text{E} = \text{P}$, but the actual magnitudes for $\text{E} = \text{Sn}(\text{Pb})$ are much larger than expected when the mean excitation-energy approximation is used as a basis for the Fermi-contact contribution. This is attributed to greater s character for the hybrid orbital used by E to form the E-Pt bond when $\text{E} = \text{Sn}(\text{Pb})$ which affects the mutual polarizability and hence $K(\text{EX})$.

It has been known for many years^{1–3} that the signs and magnitudes of the nuclear spin couplings $^1J(^{195}\text{Pt}-^{31}\text{P})$ and $^2J(^{31}\text{P}-^{31}\text{P})$ in triorganophosphine complexes of platinum are sensitive to stereochemistry and other factors. They thus provide valuable electronic and structural information, and are also of diagnostic use, for example to distinguish between *cis* and *trans* pairs of isomers. It is further known^{4,5} that couplings involving $^{117/119}\text{Sn}$ in complexes of SnCl_3^- and related species show large variations in magnitude which apparently⁵ parallel those in the corresponding isoelectronic and isostructural complexes of PR_3 . However, the signs of $^1J(^{195}\text{Pt}-^{119}\text{Sn})$, $^2J(^{119}\text{Sn}-^{31}\text{P})$, and $^2J(^{119}\text{Sn}-^{119}\text{Sn})$ in these species are unknown. Without this information it is impossible to be sure that these parallels are real, or to draw valid conclusions about the mechanism of the spin-coupling interaction.

This paper therefore reports series of heteronuclear selective magnetic multiple-resonance experiments which establish the signs of these coupling constants in a range of typical platinum(II) complexes containing one or more SnCl_3^- or similar moieties. Such experiments (e.g. $^{31}\text{P}\{-^{119}\text{Sn}, ^1\text{H}\}$ and $^{195}\text{Pt}\{-^{31}\text{P}, ^1\text{H}\}$) are relatively unusual, and necessitated appropriate spectrometer modification and the use of time-sharing radio frequency (r.f.) irradiation sequences. The compounds themselves were selected on the twin criteria of (a) being sufficiently soluble (in many cases it was necessary to detect species of low abundance) and (b) presenting a suitable spin system for the purpose in hand.

The magnetogyric ratios $\gamma(^{117}\text{Sn})$ and $\gamma(^{119}\text{Sn})$ are negative, and it is therefore often convenient to use the reduced coupling constant $K(\text{XY})$ [defined⁶ as $K(\text{XY}) = J(\text{XY})4\pi^2/h\gamma(\text{X})\gamma(\text{Y})$]. $K(\text{SnX})$ is then of opposite sign to $J(^{117/119}\text{SnX})$ for $\text{X} = ^1\text{H}$, ^{31}P , or ^{195}Pt , but of the same sign for $\text{X} = ^{117/119}\text{Sn}$.

Results

Chemical shifts are in Table 1 and coupling constants in Table 2. As each compound presented different problems they are considered individually. It is well established⁷ that $^1J(^{195}\text{Pt}-^{31}\text{P})$ and hence $^1K(\text{PtP})$ is positive in this type of complex, and the absolute signs of the other coupling constants were deduced from appropriate heteronuclear multiple-resonance experiments on this basis. The samples contained the isotopes ^{117}Sn , ^{119}Sn , ^{195}Pt , and ^{207}Pb in natural abundance (7.5, 8.6, 33.6, and 20.5% respectively).

In all cases irradiation power levels were such that the

predominant observed effects arose from spin decoupling or spin tickling rather than spin-population transfer.⁸ Unless otherwise stated the experiments were conducted under conditions of broadband proton decoupling.

trans-[Pt(SnCl₃)₂(PEt₃)₂] (1).—The species containing ^{195}Pt and *one* ^{119}Sn gives (a) ^{195}Pt satellites in the ^{119}Sn n.m.r. spectrum, (b) ^{119}Sn satellites in the ^{195}Pt n.m.r. spectrum, and (c) ^{195}Pt , ^{119}Sn satellites of satellites in the ^{31}P n.m.r. spectrum. Observation of (c) with selective irradiation of components of (a) showed $^1K(\text{PtSn})$ to have the same sign as $^1K(\text{PtP})$, i.e. positive; and observation of (c) with selective irradiation of (b) showed $^2K(\text{SnP})$ to be of opposite sign to $^1K(\text{PtSn})$, i.e. the former is negative.

Species containing *one* ^{119}Sn together with *one* ^{117}Sn give satellite signals in the ^{31}P n.m.r. spectrum which are associated with ^{117}Sn satellites in the ^{119}Sn n.m.r. spectrum. Selective irradiation of the latter and observation of the former showed $^2K(\text{SnSn})$ and $^2K(\text{SnP})$ to be of opposite sign, i.e. $^2K(\text{SnSn})$ is positive. The value of $^2J(^{119}\text{Sn}-^{119}\text{Sn})$ in Table 2 was obtained by multiplying $^2J(^{119}\text{Sn}-^{117}\text{Sn})$ by $\gamma(^{119}\text{Sn})/\gamma(^{117}\text{Sn}) = 1.046$.

cis-[Pt(SnPh₃)₂(Ph₂PCH₂CH₂PPh₂)].—Although the two phosphorus atoms in this compound are chemically equivalent, species containing a single magnetic tin give an AA'X (A, A' = ^{31}P , X = ^{119}Sn) spin system so that $^2J(^{31}\text{P}-^{31}\text{P})$ can be read off directly from the ^{119}Sn or ^{117}Sn satellites in the phosphorus spectrum. Because $^2J(^{31}\text{P}-^{31}\text{P})$ is small compared with the two $^{119}\text{Sn}-^{31}\text{P}$ couplings the system is effectively AMX and $^{31}\text{P}\{-^{119}\text{Sn}\}$ experiments showed in a straightforward manner that $^2K(\text{PP})$ and $^2K(\text{SnP})_{\text{trans}}$ are of opposite sign, and that $^2K(\text{PP})$ and $^2K(\text{SnP})_{\text{cis}}$ are of like sign. The presence of ^{195}Pt has no effect upon the symmetry of this system and so $^{31}\text{P}\{-^{195}\text{Pt}\}$ experiments were used to show that $^1K(\text{PtSn})$ and $^2K(\text{SnP})_{\text{trans}}$ are of like sign and that $^1K(\text{PtSn})$ and $^2K(\text{SnP})_{\text{cis}}$ are of opposite sign.

Finally, $^{31}\text{P}\{-^{119}\text{Sn}\}$ experiments on this species demonstrated $^1K(\text{PtSn})$ and $^1K(\text{PtP})$ to be of like sign, i.e. positive.

trans-[PtH(SnCl₃)(PPh₃)₂] (3).—Selective $^1\text{H}\{-^{31}\text{P}\}$, $^{119}\text{Sn}\{-^1\text{H}\}$, and $^{31}\text{P}\{-^{119}\text{Sn}\}$ n.m.r. experiments gave the relative signs listed in Table 2.

† Present address: Department of Chemistry, The University, Newcastle upon Tyne, NE1 7RU.

Table 1. Chemical shifts for species with platinum-tin bonds^a

	Species	$\delta(^{31}\text{P})^b$	$\delta(^{119}\text{Sn})^c$	$\delta(^{195}\text{Pt})^d$	Notes
(1)	<i>trans</i> -[Pt(SnCl ₃) ₂ (PEt ₃) ₂]	+8.4	-41	-5 082	At 193 K
(2)	<i>cis</i> -[Pt(SnPh ₃) ₂ (Ph ₂ PCH ₂ CH ₂ PPh ₂)]	-8.7	-58.5	-917	At 298 K
(3)	<i>trans</i> -[PtH(SnCl ₃)(PPh ₃) ₂]	+28.2	+129	-5 195	At 183 K ^e
(4)	<i>cis</i> -[PtCl(SnCl ₃){P(C ₆ H ₄ Me- <i>p</i>) ₃ } ₂]	+7.5 ^f , +26.2 ^g	-59	-4 718	At 223 K
(5)	<i>cis</i> -[PtCl(SnCl ₃){P(C ₆ H ₄ OMe- <i>p</i>) ₃ } ₂]	+11.1 ^f , +28.1 ^g	-58	-4 742	At 213 K
(6)	<i>cis</i> -[PtPh(SnPh ₂ Cl)(PPh ₃) ₂]	+24.5 ^f , +28.3 ^g	+32	-4 780	At 298 K
(7)	<i>cis</i> -[PtPh(PbPh ₃)(PPh ₃) ₂]	+20.3 ^f , +28.0 ^g	-95.5 ^h	-102	At 298 K
(8)	<i>cis</i> -[PtPh(SnPh ₂ SnPh ₃)(PPh ₃) ₂]	+20.8 ^f , +26.6 ^g	-90.5 ⁱ	-266	At 298 K ^j
(9)	<i>trans</i> -[Pt(SnCl ₃) ₃ {P(OEt) ₃ } ₂] ⁻	+77.0	-117	-5 234	At 223 K
(10)	[Pt(SnCl ₃) ₄ (PEt ₃) ₂] ²⁻ ^k	+6.0	-83 ^k	-5 633	At 183 K
(11)	[Cl ₃ Sn]Pt{μ-(Ph ₂ P) ₂ CH ₂ } ₂ Pt(SnCl ₃)]	-3.6	+43	-633	At 193 K

^a In CH₂Cl₂ solution. ^b In p.p.m. to high frequency of 85% H₃PO₄, ± 0.1 p.p.m. ^c In p.p.m. to high frequency of SnMe₄, ± 1 p.p.m. ^d In p.p.m. to high frequency of Ξ (¹⁹⁵Pt) = 21.414 376 MHz, ± 2 p.p.m. ^e $\delta(^1\text{H}) = -8.74 \pm 0.02$. ^f *cis* to Sn. ^g *trans* to Sn. ^h Refers to $\delta(^{207}\text{Pb})$ in p.p.m. to high frequency of PbMe₄, ± 1 p.p.m. ⁱ Tin attached to Pt. ^j $\delta(^{119}\text{Sn})(\text{SnPh}_3) = -157 \pm 1$ p.p.m. ^k Axial PEt₃. ^l Equatorial Sn; $\delta(^{119}\text{Sn})_{\text{axial}} = -162 \pm 1$ p.p.m.

Table 2. Coupling constants for species with platinum-tin bonds^a

	$^1J(^{195}\text{Pt}-^{31}\text{P})^b$	$^1J(^{195}\text{Pt}-^{119}\text{Sn})^c$	$^2J(^{119}\text{Sn}-^{31}\text{P})^d$	$^2J(^{119}\text{Sn}-^{31}\text{P})^e$	$^2J(^{31}\text{P}-^{31}\text{P})^f$	Notes
(1)	+1 871	-23 529	+236		?	At 193 K ^g
(2)	+2 293	-9 649	+142	-1 611	-11 ^h	At 298 K
(3)	+2 648	-11 348	+215		?	At 183 K ⁱ
(4)	+3 623 ^j , +3 140 ^k	-16 321	+219	-4 271	-14.6	At 223 K
(5)	+3 665 ^j , +3 096 ^k	-16 650	+215	-4 302	-14.6	At 213 K
(6)	+2 139 ^j , +2 681 ^k	-14 070	+149	-2 392	-14.6	At 298 K
(7)	+1 968 ^j , +2 935 ^k	+18 374 ^l	-259 ^l	+3 462 ^l	-12.2	At 298 K
(8)	+2 009 ^j , +2 468 ^k	-11 934	+147	-1 965	-14.6	At 298 K ^m
(9)	+2 850	-18 982	+314		?	At 223 K ⁿ
(10)	+2 322	-19 262 ^o	+207	-2 392		At 183 K ^p
(11)	+2 644	-11 892	+269		400 ^q	At 193 K ^r

^a In CH₂Cl₂ solution. ^b In Hz, ± 1 Hz. ^c In Hz, ± 10 Hz. ^d In Hz, ± 1 Hz, *cis* relationship. ^e In Hz, ± 4 Hz, *trans* relationship. ^f In Hz, ± 0.1 Hz. ^g $^2J(^{119}\text{Sn}-^{117}\text{Sn}) = +34 764 \pm 10$ Hz. ^h ± 1 Hz. ⁱ $^1J(^{195}\text{Pt}-\text{H}) = +1 300 \pm 1$, $^2J(^{31}\text{P}-\text{H}) = -8.8 \pm 0.1$, $^2J(^{119}\text{Sn}-\text{H}) = -1 748 \pm 1$ Hz. ^j *cis* to Sn. ^k *trans* to Sn. ^l For ¹¹⁹Sn read ²⁰⁷Pb. ^m $^2J(^{195}\text{Pt}-^{119}\text{Sn}) = -1 724 \pm 10$, $^3J(^{119}\text{Sn}-^{31}\text{P})_{\text{cis}} = 0 \pm 1.5$, $^3J(^{119}\text{Sn}-^{31}\text{P})_{\text{trans}} = -161 \pm 1$ Hz. ⁿ $^2J(^{119}\text{Sn}-^{117}\text{Sn}) = +16 394 \pm 10$ Hz. ^o ± 20 Hz, equatorial Sn; $^1J(^{195}\text{Pt}-^{119}\text{Sn}_{\text{ax}}) = -6 470 \pm 20$ Hz. ^p $^2J(^{119}\text{Sn}_{\text{eq}}-^{117}\text{Sn}_{\text{eq}}) = +15 955 \pm 20$, $^2J(^{119}\text{Sn}_{\text{eq}}-^{117}\text{Sn}_{\text{ax}}) = -2 295 \pm 50$ Hz (estimated value). ^q ± 100 Hz, refers to $^2J(^{31}\text{P}-\text{Pt}-^{31}\text{P})$. ^r $^3J(^{119}\text{Sn}-^{31}\text{P}) = 26.3 \pm 0.5$, $^2J(^{195}\text{Pt}-^{119}\text{Sn}) = -9 370 \pm 5$, $^2J(^{31}\text{P}-\text{C}-^{31}\text{P}) = 48.9 \pm 0.1$, $^3J(^{31}\text{P}-^{31}\text{P}) = 26.3 \pm 0.2$, $^1J(^{195}\text{Pt}-^{195}\text{Pt}) = +7 805 \pm 20$ (see text for size of error), $^2J(^{195}\text{Pt}-^{31}\text{P}) = -105 \pm 2$ Hz.

cis-[PtCl(SnCl₃){P(C₆H₄Me-*p*)₃}₂] (4) and *cis*-[PtCl(SnCl₃){P(C₆H₄OMe-*p*)₃}₂] (5).—These two compounds have very similar n.m.r. parameters, but adventitious overlapping of lines in the various spectra made it necessary to perform some multiple-resonance experiments on one compound and some on the other. The spin systems are all essentially first order and sets of $^{31}\text{P}-\{^{195}\text{Pt}\}$ and $^{31}\text{P}-\{^{119}\text{Sn}\}$ n.m.r. experiments gave the required signs of the coupling constants.

cis-[PtPh(SnPh₂Cl)(PPh₃)₂] (6).—The experiments were as for compounds (4) and (5).

cis-[PtPh(PbPh₃)(PPh₃)₂] (7).—The $^{31}\text{P}-\{^{195}\text{Pt}\}$ and $^{31}\text{P}-\{^{207}\text{Pb}\}$ n.m.r. experiments gave the signs of the coupling constants. A minor complication was that, owing to the proximity of the ¹⁹⁵Pt and ²⁰⁷Pb resonance frequencies (12.783 972 and 12.497 401 MHz respectively at 1.4 T) and the large value of $^1J(^{207}\text{Pb}-^{195}\text{Pt})$, species containing both nuclei gave spectra with significant heteronuclear second-order character. By the use of a different magnetic field strength (2.1 T) it was confirmed that the deviations in the line positions in the ¹⁹⁵Pt and ²⁰⁷Pb n.m.r. spectra from their first-order values were due solely to this cause (to within 1 Hz) and not to isotope effects as has previously been considered.⁹

cis-[PtPh(SnPh₂SnPh₃)(PPh₃)₂] (8).—Sets of $^{31}\text{P}-\{^{195}\text{Pt}\}$

and $^{31}\text{P}-\{^{119}\text{Sn}\}$ multiple-resonance experiments using species with magnetic tin at either of the two sites gave the required signs of the coupling constants. It was not possible to prepare a sufficiently strong solution to determine $^1J(^{119}\text{Sn}-^{119}\text{Sn})$.

trans-[Pt(SnCl₃)₃{P(OEt)₃}₂]⁻ (9).—The coupling constant $^2J(^{119}\text{Sn}-^{117}\text{Sn})$ was shown to have the same sign as $^1J(^{117}\text{Sn}-^{31}\text{P})$ (i.e. reduced couplings of opposite sign) by a $^{31}\text{P}-\{^{119}\text{Sn}\}$ double-resonance n.m.r. experiment.

[Pt(SnCl₃)₄(PEt₃)₂]²⁻ (10).—The room-temperature fluxionality of this species renders all tin atoms equivalent, and a set of multiple-resonance experiments gave the signs of the averaged coupling constants involving at least one tin. At 183 K a fixed trigonal-bipyramidal geometry is adopted¹⁰ with an axial phosphine group, one axial tin, and three equatorial tins. The coupling constant $^1J(^{195}\text{Pt}-^{31}\text{P})$ is substantially temperature-independent implying that the phosphine remains axial during the intramolecular fluxional scrambling of the tin atoms. The observed high-temperature couplings involving tin can be calculated as the weighted averages of the values in the low-temperature spectrum, different results being obtained according to the relative signs assumed. In each case only one calculated value corresponded with the observed one, and hence it was possible to deduce the signs given in Table 2.

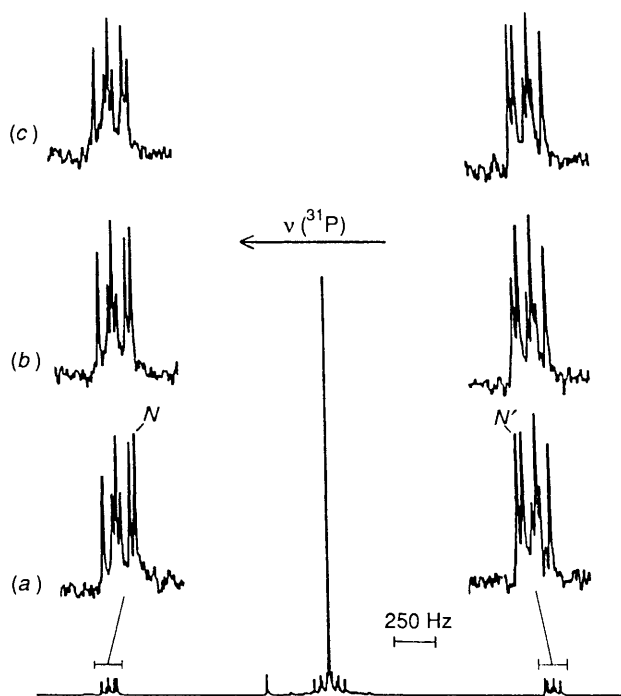


Figure. Phosphorus-31 n.m.r. spectrum at 24.2 MHz of $[(Cl_3Sn)Pt\{\mu-(Ph_2P)_2CH_2\}_2Pt(SnCl_3)]$ (II) showing satellites from species with one or two ^{195}Pt nuclei, and with expansions of the regions near $\nu(^{31}P) \pm ^1J(^{195}Pt-^{31}P)/2$. (a) Normal spectrum with peaks marked N and N' arising from species having two ^{195}Pt nuclei in either the $\alpha\alpha$ or the $\beta\beta$ spin states. (b) With simultaneous irradiation at $\gamma(^{195}Pt) - 8751$ Hz. (c) With simultaneous irradiation at $\gamma(^{195}Pt) + 8751$ Hz. In (b) part of N' is perturbed and in (c) part of N is perturbed. Hence $^1J(^{195}Pt-^{195}Pt)$ and $[^1J(^{195}Pt-^{31}P) + ^2J(^{195}Pt-^{31}P)]$ are of like sign.

$[(Cl_3Sn)Pt\{\mu-(Ph_2P)_2CH_2\}_2Pt(SnCl_3)]$ (II).—Species with one or two ^{195}Pt nuclei give AA'A''A'''X and AA'A''A'''XX' (A = ^{31}P , X = ^{195}Pt) spin systems respectively, and their ^{31}P n.m.r. spectra were analysed to yield the magnitudes of the coupling constants given in Table 2. Note that $^1J(^{195}Pt-^{195}Pt)$ differs significantly from the value (7 628 Hz) previously reported,¹¹ but this may be due to a solvent effect. Inspection of the computer-generated energy-level diagram showed that certain weak outlying lines in the ^{195}Pt n.m.r. spectrum of the second species are connected with strong (so-called 'N') lines in the ^{31}P spectrum of this species in a way which depends upon the relative signs of $^1J(^{195}Pt-^{195}Pt)$ and $N[^1J(^{195}Pt-^{31}P) + ^2J(^{195}Pt-^{31}P)]$. These ^{195}Pt lines were selectively irradiated in the $^{31}P\{-^{195}Pt\}$ experiments illustrated in the Figure which hence show that $^1J(^{195}Pt-^{195}Pt)$ has the same sign as N, and effectively as $^1J(^{195}Pt-^{31}P)$, i.e. positive.

The couplings $^1J(^{195}Pt-^{119}Sn)$ and $^2J(^{195}Pt-^{119}Sn)$ are both large, and therefore it is difficult to assign them with certainty. However, $^2J(^{119}Sn-^{31}P)$ and $^3J(^{119}Sn-^{31}P)$ are of very different sizes, the former being similar to that found in species (1)–(6) and (8)–(10) and thus the assignments in Table 1 are soundly based. It was also possible to assign $^1J(^{195}Pt-^{31}P)$ unequivocally owing to its large magnitude, and $^{119}Sn\{-^{31}P\}$ experiments on species containing both ^{195}Pt and ^{119}Sn then identified $^1J(^{195}Pt-^{119}Sn)$ as being the larger of the two $^{195}Pt-^{119}Sn$ couplings. Allied to $^{31}P\{-^{195}Pt\}$ experiments and spectral analysis these gave the remaining signs of the coupling constants listed in Table 2.

Discussion

Table 3 shows the pattern of signs and ranges of magnitudes of

nuclear spin-reduced couplings in typical complexes of platinum(II) with phosphorus and/or tin donor ligands. In all cases the sign of any reduced coupling to tin is the same as that of the corresponding coupling to phosphorus, but the magnitude is some twelve (actually between eight and sixteen) times greater. It is to be expected^{6,12} that these couplings will depend upon the valence *s*-electron density at the nucleus [$\psi^2(0)$] for each of the coupled nuclei, and for tin and phosphorus these parameters are in the ratio¹³ of ca. 3:1. The greater value for tin cannot therefore be the sole factor determining the much larger magnitudes of $K(SnX)$. This is in contrast to the situation revealed by comparisons of $K(CX)$, $K(SiX)$, and $K(SnX)$ which generally have magnitudes that follow the corresponding $\psi^2(0)$ values for carbon, silicon, and tin respectively.⁴ Furthermore, the couplings $^2K(SnSn)$ are larger by an extra factor of ten than the corresponding $^2K(SnP)$. It follows then that it is inappropriate to use the mean excitation-energy approximation¹⁴ to calculate the Fermi-contact contribution to the coupling constants $K(SnX)$ and $K(PX)$ in these transition-metal complexes; following Pople and Santry's approach⁶ the mutual polarizabilities¹⁵ of the coupled nuclei must be considered. These depend upon the relative energies of the valence *s* electrons, and even though tin and phosphorus are isoco-ordinate and isoelectronic in these complexes it is likely that the relevant energies will differ significantly and thus be able to account for the observed large ratio for $K(SnX)/K(PX)$. Notwithstanding this however, it is clear from the pattern of signs and relative constancy of this ratio for different coupling interactions that the bonding must be very similar in the tin and corresponding phosphorus species. Furthermore, in the series *cis*-[PtPh(SnPh_{3-n}X_n)(PPh₃)₂] (X = Cl, Br, or I) the magnitude of $^1J(^{195}Pt-^{119}Sn)$ is known¹⁶ to increase with the electronegativity of X. Our present study shows that this corresponds to a positive increment in $^1K(PtSn)$ with increasing electron withdrawal from tin, and this behaviour is paralleled by $^1K(MP)$ in many complexes.¹⁻³ In the case of *cis*-[PtPh(PbPh₃)(PPh₃)₂] (7) the value of 3 399 nm⁻³ for $^1K(PtPb)$ is a factor of 2.6 greater than $^1K(PtSn)$ in *cis*-[PtPh(SnPh₃)(PPh₃)₂] whereas $\psi^2(0)(Pb)/\psi^2(0)(Sn)$ is only 1.6 without any relativistic correction and is 3.4 when this correction is made.¹³

A treatment of two-bond coupling due to Jameson¹⁷ proposes the relation $^2K(XMY) \propto S_X S_Y F_{XMY}$ where S_X and S_Y refer to the X–M and Y–M bonds respectively such that when M is magnetic $^1K(XM)$ and $^1K(YM)$ are proportional to S_X and S_Y . Since the ratios $^1K(SnPt)/^1K(PPt)$ and $^2K(SnP)/^2K(PP)$ are about the same for all the species studied here it follows that F_{SnPtP} and F_{PPtP} must be very similar in these complexes. That is the bonding at platinum is essentially unaffected when a phosphorus ligand is replaced by a tin one, and the abnormally large values of the couplings involving tin must arise primarily from electronic differences at the tin atom.

In the tin complexes the interbond angles at tin that do not involve platinum are significantly less tetrahedral (typically 90–100°)^{10,18} implying high *s*-character for the tin orbital used for the Sn–Pt bond. By contrast, in the corresponding phosphorus complexes the angles at phosphorus not involving platinum are closer to tetrahedral (typically 100–106°)¹⁹ implying smaller *s* character for the phosphorus orbital forming the P–Pt bond. This may then account for the larger *s*-overlap integral for the Sn(Pb)–Pt bond that is implied by the abnormally large coupling when tin (lead) is a participant.

Experimental

All n.m.r. measurements were performed in spinning tubes (outsider diameter 10 mm) upon concentrated solutions in deaerated methylene chloride containing ca. 10% C₆D₆ to

Table 3. Reduced nuclear spin-spin coupling constants in nm⁻³ for complexes of platinum(II)

Coupling	E = P	E = Sn	Notes
¹ K(PtE)	+180 ^a , +347 ^b , +301 ^c	+1 704 ^d , (+)3 188 ^e , +2 456 ^a	f
² K(PE) _{cis}	-0.56 ^g , -0.74 ^d	-7.8 ^g , -12 ^d	h
² K(PE) _{trans}	+26 ⁱ	+89.0 ^g , +236 ^d	j
² K(EH) _{trans}	(+)4.1 ^k	+39.0 ^l	
² K(PtE) _{trans}	+62.4 ^m	+978 ⁿ	

^a In compound (1). ^b In compound (4), refers to P *trans* to Cl. ^c In compound (4), refers to P *trans* to SnCl₃. ^d In compound (4). ^e In *trans*-[PtCl(SnCl₃)(PEt₃)₂]. ^f In compound (7), ¹K(PtPb) = +3 399 nm⁻³. ^g In compound (2). ^h In compound (7), ²K(PPb)_{cis} = -25.4 nm⁻³; in *cis*-[PtCl₂(SnCl₃)₂], ²K(SnSn)_{cis} = (-)143 nm⁻³. ⁱ In *trans*-[PtCl₂(PMe₃)₂]. ^j In compound (7), ²K(PPb)_{trans} = +340 nm⁻³; in compound (1), ²K(SnSn)_{trans} = +1 985 nm⁻³. ^k In *cis*-[PtH(Me)(PPh₃)₂] (L. Abis, A. Sen, and J. Malpern, *J. Am. Chem. Soc.*, 1978, **100**, 2915). ^l In compound (3). ^m In [(Me₂PhP)Pt{μ-(Ph₂P)₂CH₂}₂Pt(PPhMe₂)]. ⁿ In compound (11).

provide a signal for the field/frequency locking circuits of the spectrometer. Compounds (2),²⁰ (4),⁵ (5),⁵ (6),¹⁶ (7),²¹ (10),¹⁰ and (11)¹¹ were prepared as described in the literature and had n.m.r. parameters in general agreement with those previously reported. Compounds (1),⁵ (3),²² and (9)⁵ were prepared *in situ* by SnCl₂ insertion into the Pt-Cl bond(s) of the corresponding chloride. Compound (8)²³ was made *in situ* by adding *cis*-[Pt(C₂H₄)(PPh₃)₂] to Ph₃SnSnPh₃.

Proton, ³¹P, ¹¹⁷Sn, ¹¹⁹Sn, ¹⁹⁵Pt, and ²⁰⁷Pb n.m.r. spectra were obtained on a JEOL FX90Q multinuclear pulsed Fourier-transform spectrometer at 89.6, 36.2, 31.9, 33.3, 19.1, and 18.7 MHz respectively, with broadband or selective proton decoupling as appropriate. R.f. power for ¹H-³¹P, ¹H-¹¹⁹Sn, ³¹P-¹¹⁷Sn, ¹¹⁷Sn-³¹P, ¹¹⁹Sn-³¹P, ¹⁹⁵Pt-³¹P, ¹⁹⁵Pt-¹¹⁹Sn, ¹¹⁹Sn-¹¹⁹Sn, and ¹⁹⁵Pt-¹¹⁹Sn, ²⁰⁷Pb-¹⁹⁵Pt, ²⁰⁷Pb-¹¹⁹Sn, ¹¹⁹Sn-²⁰⁷Pb, ¹⁹⁵Pt-²⁰⁷Pb, and ²⁰⁷Pb-¹¹⁹Sn heteronuclear multiple-resonance experiments was supplied to the double-tuned proton-decoupler coils via a tuned amplifier from a GenRad model 1061 frequency synthesizer whose oscillator was controlled by the spectrometer clock. Problems of frequency interference were minimized by reciprocal gating of the spectrometer receiver and the synthesizer output. The ³¹P-¹⁹⁵Pt, ¹⁹⁵Pt-²⁰⁷Pb, and ³¹P-²⁰⁷Pb experiments were performed upon a modified JEOL FX60 spectrometer operating at 24.2 MHz. Spectral simulations were obtained using a modified version of the LAOCOON program.²⁴

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