

108. ^{119}Sn - and ^{31}P -NMR. Spectroscopy of the 5-Coordinate Complexes $[\text{Rh}(\text{SnCl}_n\text{Br}_{(3-n)})(\text{norbornadiene})(\text{tertiary phosphine})_2]$

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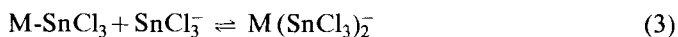
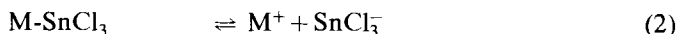
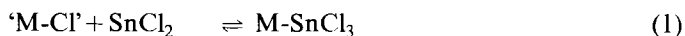
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Summary

The products of the reaction of $[\text{RhCl}(\text{NBD})]_2$ (NBD = norbornadiene), with four equivalents tertiary phosphine and two equivalents of tin(II) bromide have been studied by ^{119}Sn - and ^{31}P -NMR. spectroscopy. The solution data suggest that halogen scrambling occurs during the preparation and results in a mixture of complexes containing SnBr_3 , SnClBr_2 , SnCl_2Br and SnCl_3 ligands, and this is confirmed by independent synthesis of the SnCl_3 and SnBr_3 complexes. The metal-metal coupling constants, $^1J(^{119}\text{Sn}, ^{103}\text{Rh})$, vary from 452 to 580 Hz and are linearly related to: a) $\delta(^{119}\text{Sn})$ in the complexes $[\text{Rh}(\text{SnCl}_n\text{Br}_{(3-n)})\text{NBD}(\text{PEtPh}_2)_2]$ and b) the sum of the *Pauling* electronegativities for the halogens on tin.

Introduction. - It is well known that transition metal complexes combine with tin(II) chloride to produce effective homogeneous hydrogenation and hydroformylation catalysts [1-4]. Specifically, excellent results have been achieved using phosphine complexes of platinum [5] and palladium [6]. The chemistry of these tin complexes is not always straightforward but may be qualitatively expressed by reactions 1-3. Information concerning the identity of the various intermediates is



sometimes difficult to obtain, although for platinum complexes, several groups have shown that ^{31}P - [7] [8], ^{119}Sn - [8] [9] [10], ^{195}Pt - [10] [11] and, for hydride complexes [12], ^1H -NMR. spectroscopic methods are of value. Although many complexes contain the $\text{M}-\text{SnCl}_3$ unit these are often dynamic on the NMR. time scale [7] [8] [12]. Despite this difficulty, complexes such as *cis*- $[\text{PtCl}(\text{SnCl}_3)(\text{PPh}_3)_2]$ [14], *trans*-

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[PtCl(SnCl₃)(PEt₃)₂] [7], *trans*-[PtH(SnCl₃)(PEt₃)₂] [15], *trans*-[Pt(*p*-FC₆H₄)(SnCl₃)(PEt₃)₂] [15] and the anions Pt(SnCl₃)₃²⁻ [16] and PtCl₂(SnCl₃)₂²⁻ [17] are all well characterized. Of special interest in these complexes are the unusually large one-bond platinum-tin coupling constants, ¹J(¹⁹⁵Pt, ¹¹⁹Sn), which can exceed 30 kHz [13].

There is somewhat less known concerning complexes of rhodium with the trichlorostannate ligand. There are early reports involving the chloride bridged dimer [Rh₂Cl₂(SnCl₃)₄]⁴⁻ [17][18], the mono carbonyl complexes [Rh(CO)(SnX₃)_nX_(3-n)]²⁻ (X = Cl, Br) [19], five-coordinate complex types of similar to ours, *i.e.* [Rh(SnCl₃)(NBD)(PR₃)₂] [20], and a short report concerning catalytic dehydrogenation using RhCl₃ · 3 H₂O and SnCl₂ · 2 H₂O [21].

Recently we undertook a ³¹P-NMR. study of the complexes [Rh(SnCl₃)(NBD)(PEt_nPh_(3-n))₂] and [Rh(SnCl₃)(NBD)(Ph₂P(CH₂)_nPPh₂)] (n = 2-4), and demonstrated that several dynamic processes occur in solution on the NMR. time scale and that chelating phosphines markedly reduce ²J(¹¹⁹Sn, ³¹P) relative to the monodentate ligands [22]. During this work, we observed that the ³¹P spectra of analogous SnClBr₂ derivatives obtained from [RhCl(NBD)]₂ plus four equivalents of PR₃ and two equivalents of SnBr₂ were apparently complex. We offer here an explanation for these spectra and report new ¹¹⁹Sn-NMR. data for these rhodium-tin compounds.

Results and Discussion. - 1. ³¹P-NMR. The five-coordinate rhodium complexes [Rh(SnClBr₂)(NBD)(PR₃)₂] were prepared as previously described [22], and gave satisfactory microanalyses (see *Table 1*). For [Rh(SnCl₃)(NBD)(PEtPh₂)₂], the presence of coordinated SnCl₃ in the solid state is indicated by the usual doublet in the IR. between 300 and 350 cm⁻¹, which may be attributed to Sn-Cl stretching modes; however, similar analysis for the SnClBr₂ complexes proved difficult. The ³¹P{¹H}-spectra in CH₂Cl₂/C₆D₆ (~4:1) at -20° give sharp signals and consist of two groups of resonances (see *Fig. 1*). The large spacing corresponds to ¹J(¹⁰³Rh, ³¹P) and, at the base of each group, there are broad signals which result from coupling of

Table 1. Analytical Results for the Complexes^{a)}

Complex	% C		% H	
	Found	(Calc.)	Found	(Calc.)
[Rh(SnBr ₃)(NBD)(PEtPh ₂) ₂]	42.04	(42.81)	4.02	(3.87)
[Rh(SnClBr ₂)(NBD)(PEtPh ₂) ₂]	44.50	(44.84)	4.18	(4.05)
[Rh(SnCl ₃)(NBD)PEtPh ₂) ₂]	49.06	(49.52)	4.33	(4.48)
[Rh(SnBr ₃)(NBD)(PPh ₃) ₂]	47.78	(47.91)	3.65	(3.52)
[Rh(SnClBr ₂)(NBD)(PPh ₃) ₂]	49.62	(49.92)	3.87	(3.68)
[Rh(SnClBr ₂)(NBD)(P(<i>p</i> -FC ₆ H ₄) ₃) ₂]	45.08	(45.22)	2.58	(2.80)
[Rh(SnClBr ₂)(NBD)(P(<i>p</i> -ClC ₆ H ₄) ₃) ₂]	40.74	(41.61)	2.43	(2.58)
[Rh(SnClBr ₂)(NBD)(P(<i>m</i> -CH ₃ C ₆ H ₄) ₃) ₂]	53.38	(52.63)	4.78	(4.39)
[Rh(SnClBr ₂)(NBD)(P(<i>p</i> -CH ₃ C ₆ H ₄) ₃) ₂]	51.62	(52.66)	4.59	(4.47)

^{a)} Despite reasonable analytical data, the ³¹P{¹H}-NMR. spectra sometimes reveal an impurity which we believe may be the mono phosphine complex, *i.e.* [RhCl(NBD)(PR₃)].

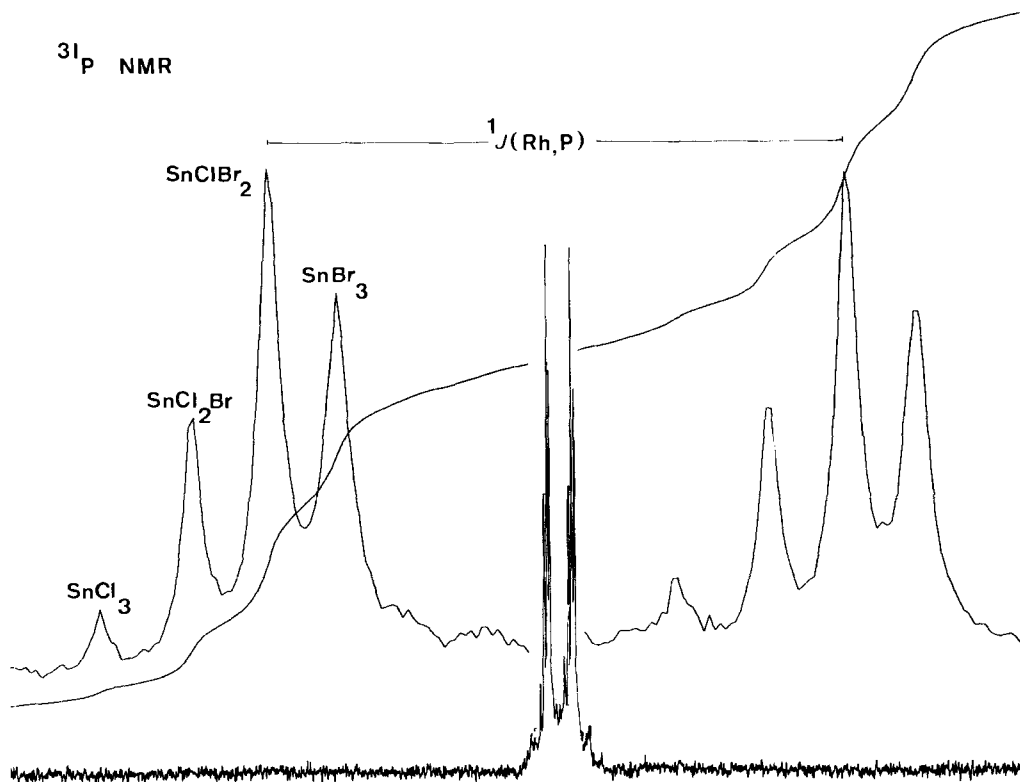


Fig. 1. $^{31}\text{P}\{^1\text{H}\}$ spectrum of the mixture $[\text{Rh}(\text{SnCl}_n\text{Br}_{(3-n)}) (\text{NBD})(\text{PPh}_3)_2]$. The broad, often overlapping, resonances due to the ^{119}Sn and ^{117}Sn satellites are just visible (243 K, $\text{CH}_2\text{Cl}_2/\text{C}_6\text{D}_6$). (404 Hz/cm for the lower trace; 17.4 Hz/cm for the expanded spectrum.)

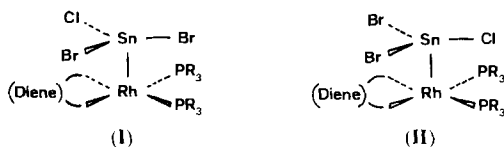
^{117}Sn and ^{119}Sn to phosphorus²⁾. These satellites confirm that, at -20° , the tin is coordinated to rhodium and the values $^2J(^{119}\text{Sn}, ^{31}\text{P})$ are in agreement with our previous work [22]³⁾.

Given the microanalytical data, it was not likely that there were significant impurities and we therefore considered the possibility of isomeric complexes. These may be of several forms: *a*) those resulting from halogen exchange, *i.e.* $\text{SnCl}_n\text{Br}_{(3-n)}$, *b*) rotational isomers due to slow rotation about the Rh,Sn-bond on the NMR. time scale and *c*) geometric isomers stemming from trigonal bipyramidal and/or square pyramidal complexes. Previous work [22] [23] suggested that the activation energy for *c* would be too low to allow us to observe static spectra at -20° . Similar considerations seemed relevant for *b* although we know of no pertinent literature. Nevertheless, the similarity of the $^1J(^{103}\text{Rh}, ^{31}\text{P})$ and

²⁾ ^{117}Sn and ^{119}Sn are 7.7 and 8.7% abundant and both have nuclear spin $I = 1/2$.

³⁾ These spectra do not readily yield this two-bond coupling constant due to considerable overlap of signals, however, the ^{119}Sn -NMR. spectrum gives these in a more straightforward manner.

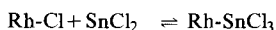
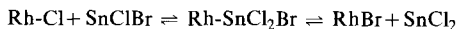
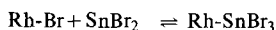
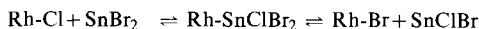
$\delta^{31}\text{P}$ values (see *Table 2*) might be compatible with conformations such as (I) or (II) and we found it necessary to consider this possibility.



For the conformers we show a tin-halogen bond bisecting the P-Rh-P angle, although equally valid would be structures in which a tin-halogen bond eclipses a Rh, P linkage. Compound I, or an eclipsed form with two different halogens should result in non-equivalent P-atoms; however, the ^{31}P -NMR. spectra are sufficiently complicated at both 36.43 and 101.27 MHz as to prevent a clear distinction. Fortunately, cases *a* and *b* should produce rather different ^{119}Sn -NMR. spectra, and consequently we turned to this method.

2. ^{119}Sn -NMR. A halogen scrambling reaction such as shown in the *Scheme*, produces four complexes containing the various 'Rh-SnCl_nBr_(3-n)' possibilities. It is

Scheme



also conceivable that the halogen exchange proceeds without Rh,Sn bond-breaking, perhaps catalyzed by traces of either phosphine or water. These complexes need not appear statistically, due to differences in stability, however, should this distribution be appropriate we may expect four groups of ^{119}Sn -resonances in the ratio 8 (SnBr₃): 12 (SnClBr₂): 6 (SnCl₂Br): 1 (SnCl₃). In any case, it seems reasonable to expect that these complexes will have markedly different chemical shifts, $\delta^{119}\text{Sn}$ [24] and coupling constants, $^1J(^{119}\text{Sn}, ^{103}\text{Rh})$. Although there are no reports of one-bond Rh,Sn-coupling constants in trihalostannate complexes⁴); the one-bond coupling constant literature consistently shows that $^1J(\text{A}, \text{X})$ for A-XCl₃ is larger than $^1J(\text{A}, \text{X})$ for A-XBr₃. Typically, $^1J(^{13}\text{C}, ^1\text{H})$ for CHCl₃ and CHBr₃ are 209 and 206 Hz, respectively [26], while $^1J(^{138}\text{W}, ^{31}\text{P})$ values for [W(CO)₅(PCl₃)] and [W(CO)₅(PBr₃)] are 426 and 398 Hz, respectively [27]. If, on the other hand, structures such as I or II were important, the Rh,Sn-bonds should be similar and therefore only minor changes in $\delta^{119}\text{Sn}$ and $^1J(^{119}\text{Sn}, ^{103}\text{Rh})$ are expected.

In *Table 2* we show ^{119}Sn -NMR. data for our complexes, and *Figure 2* shows the ^{119}Sn -NMR. spectrum for [Rh(SnCl_nBr_{3-n})(NBD)(PEtPh₂)₂]. The apparently complex spectrum consists of three groups of six lines each. Within a group we observe a doublet due to $^1J(^{119}\text{Sn}, ^{103}\text{Rh})$, each line of which is further split into a

⁴) During the preparation of this manuscript we learned that *Saito et al.* [25] have measured $^1J(^{119}\text{Sn}, ^{103}\text{Rh})$ values in some Rh(III) complexes and these range from 547-864 Hz.

Table 2. NMR. Data for the Complexes^{a)}

	$\delta^{119}\text{Sn}$	$^1J(^{119}\text{Sn}, ^{103}\text{Rh})$	$^2J(^{119}\text{Sn}, ^{31}\text{P})$	$\delta^{31}\text{P}$	$^1J(^{103}\text{Rh}, ^{31}\text{P})$
$[\text{Rh}(\text{SnBr}_3)(\text{NBD})(\text{PEtPh}_2)_2]^b)$	180.1	452	125	29.8	131
$[\text{Rh}(\text{SnClBr}_2)(\text{NBD})(\text{PEtPh}_2)_2]^b)$	158.3	482	137	28.6	132
$[\text{Rh}(\text{SnCl}_2\text{Br})(\text{NBD})(\text{PEtPh}_2)_2]^b)$	139.9	525	141	28.5	132
$[\text{Rh}(\text{SnCl}_3)(\text{NBD})(\text{PEtPh}_2)_2]^c)$	125.3	543	149	28.9	131
$[\text{Rh}(\text{SnBr}_3)(\text{NBD})(\text{PPh}_3)_2]^d)$	140.2	482	168	34.2	133
$[\text{Rh}(\text{SnClBr}_2)(\text{NBD})(\text{PPh}_3)_2]^d)$	119.6	513	177	34.3	133
$[\text{Rh}(\text{SnCl}_2\text{Br})(\text{NBD})(\text{PPh}_3)_2]^d)$	102.7	543	175	34.5	132
$[\text{Rh}(\text{SnCl}_3)(\text{NBD})(\text{PPh}_3)_2]^e)$	91.1	580	184	34.8	132
$[\text{Rh}(\text{SnCl}_n\text{Br}_{3-n})(\text{NBD})(\text{P}-\text{X})_3]^f)$					
<i>X</i>					
<i>m</i> -CH ₃				33.0	134
<i>p</i> -Cl				33.4	134
<i>p</i> -F				32.4	135

^{a)} For solutions in CH₂Cl₂/benzene-*d*₆, 4:1 see experimental part for details. NBD = norbornadiene.

^{b)} Data from the mixture of isomers at 253 K. The data for the complex synthesized independently, are in good agreement with these.

^{c)} Pure substance from independent synthesis; 253 K.

^{d)} Data from the mixture of isomers at 243 K.

^{e)} Data from the independent synthesis; 253 K.

^{f)} There is little qualitative difference between these complexes, for which we have ³¹P-NMR. data only. *m*-CH₃ and *p*-Cl at 218 K, *p*-F at 198 K. Data given are for the most abundant isomer.

triplet from the equivalent tertiary phosphines. The significantly different chemical shifts and coupling constants point to halogen-scrambling and this has been confirmed by the independent synthesis of $[\text{Rh}(\text{SnBr}_3)(\text{NBD})(\text{PEtPh}_2)_2]$ whose ¹¹⁹Sn-resonances are at lowest field. We have also prepared $[\text{Rh}(\text{SnCl}_3)(\text{NBD})(\text{PEtPh}_2)_2]$ which we have been unable to detect in the ¹¹⁹Sn-NMR. spectrum of the product mixture, but whose NMR. parameters (highest field $\delta^{119}\text{Sn}$, largest $^1J(^{119}\text{Sn}, ^{103}\text{Rh})$) conform to our expectations. This halogen-scrambling implies that, after reaction of SnBr₂ with the chloro-complexes, there are indeed a series of further steps which equilibrate the complexes. Recently *Fortune & Manning* [28] have found an intramolecular halogen migration in the complex $[\text{Co}(\eta\text{-dienyl})(\text{CO})\text{Br}(\text{SnBr}_2)]$ to give $[\text{Co}(\eta\text{-dienyl})(\text{CO})\text{I}(\text{SnBr}_2\text{I})]$ and also suggest equilibria to account for this result. It could well be that this halogen-scrambling will have some generality in trihalostannate complexes. The isomeric composition is similar to, but not identical with that, expected from statistical halogen distribution⁵⁾.

In *Figure 3* we show plots of $^1J(^{119}\text{Sn}, ^{103}\text{Rh})$ vs. *a)* $\delta^{119}\text{Sn}$ and *b)* the sum of the *Pauling* electronegativities for the three halogens on tin. Although only four points are available, it seems clear that increasing the withdrawing power of the substituent increases $^1J(^{119}\text{Sn}, ^{103}\text{Rh})$ and shifts $\delta^{119}\text{Sn}$ to higher field. It is difficult to judge the significance of the coupling constant data due to lack of relevant comparison compounds; however, several points are noteworthy: *a)* $^1J(^{119}\text{Sn}, ^{103}\text{Rh})$ is

⁵⁾ The spectrum signal-to-noise ratio is insufficient, consequently, a quantitative analysis is not possible. We estimate SnBr₃:SnClBr₂:SnCl₂Br ratios of 1.0:1.0:0.6 and 1.0:1.0:0.4 for the PPh₃ and PEtPh₂ complexes, respectively.

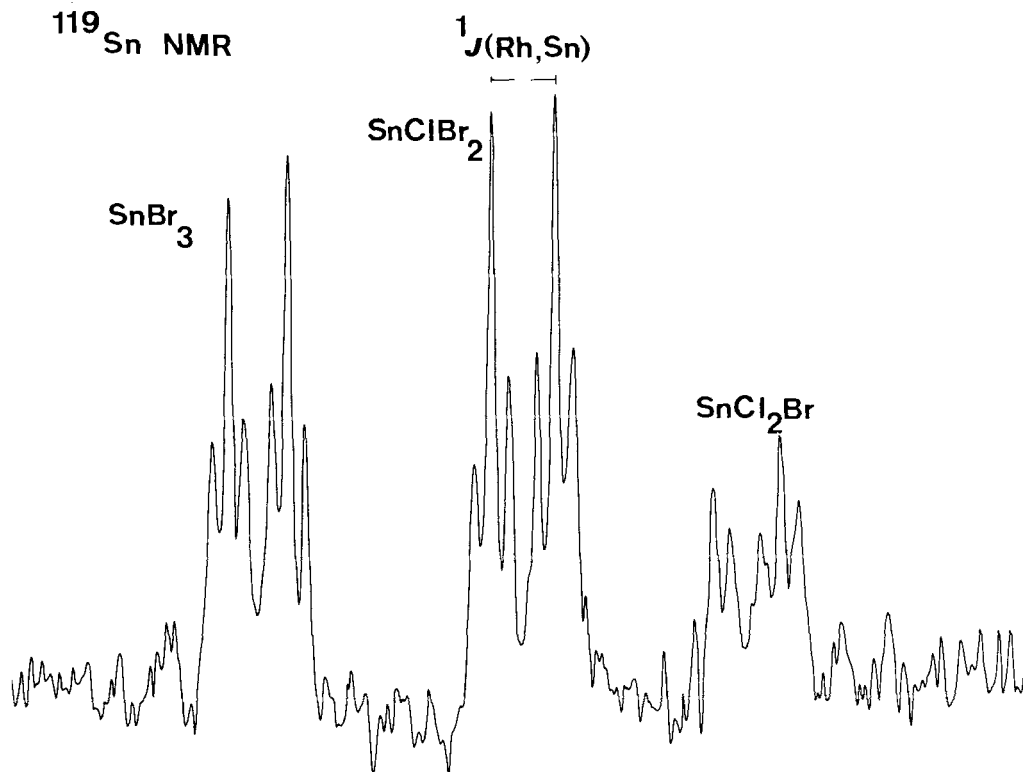


Fig. 2. ^{119}Sn -NMR. spectrum of the mixture $[\text{Rh}(\text{SnCl}_n\text{Br}_{3-n})(\text{NBD})(\text{PEtPh}_2)_2]$. The doublet splitting stems from $^1J(^{119}\text{Sn}, ^{103}\text{Rh})$ and the triplet structure from $^2J(^{119}\text{Sn}, ^{31}\text{P})$ ($7 \times 10^{-3}\text{M}$, 253 K, $\text{CH}_2\text{Cl}_2/\text{benzene-}d_6$).

considerably larger (\approx a factor of three) than $^1J(^{103}\text{Rh}, ^{31}\text{P})$, *b*) both $^1J(^{119}\text{Sn}, ^{103}\text{Rh})$ and, to a lesser extent, $^2J(^{119}\text{Sn}, ^{31}\text{P})$ depend upon the nature and number of halogens, *c*) there is a dependence on the phosphine with the one-bond metal-metal coupling somewhat larger for PPh_3 than PEtPh_2 , and *d*) the Rh, P-coupling is insensitive to changing the halogen. Given the sizeable changes in $^1J(^{119}\text{Sn}, ^{103}\text{Rh})$, *d* suggests that changes in metal-ligand bonding are restricted to the Rh, Sn- and Sn, X-bonds⁶).

The differences between $^1J(^{119}\text{Sn}, ^{103}\text{Rh})$ and $^1J(^{103}\text{Rh}, ^{31}\text{P})$ could result from changes in the $|\psi(0)|^2$ terms on going from Sn to Rh [32] and are probably not interpretable in terms of bonding phenomena; however, the ≈ 100 Hz difference in $^1J(^{119}\text{Sn}, ^{103}\text{Rh})$ on going from SnBr_3 to SnCl_3 suggests that this coupling constant may prove to have analytical value.

The ^{119}Sn chemical shifts for our complexes lie to low field of both SnCl_2 [29] and SnCl_3^- [30] which appear at $\delta = -236$ and $\delta = -388$ respectively. Since SnCl_3^- coordinated to Rh(III) can have $\delta \approx -1000$ [25] and $\text{Rh}(\text{SnCl}_3)_4^{3-}$ has $\delta \approx 8$ [25] [31], a large range of coordination chemical shifts is to be expected.

⁶) We thank the referee for suggesting we emphasize this point.

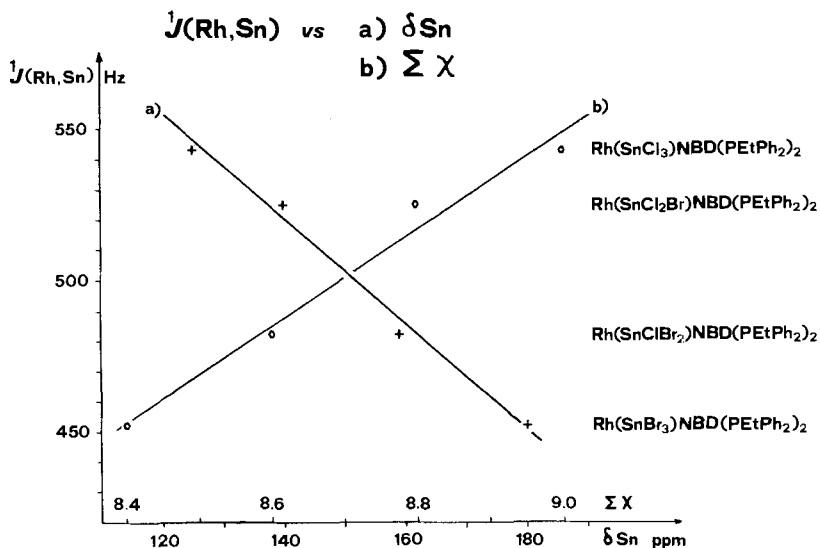


Fig. 3. Plot of $^1J(^{119}\text{Sn}, ^{103}\text{Rh})$ vs. a) $\delta^{119}\text{Sn}$ and b) the sum of the Pauling electronegativities for the halogens bound to tin

The high field shift of $\delta^{119}\text{Sn}$ on replacing Br by Cl is not readily explainable and presumably derives from the simultaneous change of several terms in the screening of the Sn-nucleus. Thus, SnBr_4 ($\delta = -638$) lies at higher field than SnCl_4 ($\delta = -150$) [29] as does CH_3SnBr_3 ($\delta = -170$) relative to CH_3SnCl_3 ($\delta = +6.3$) [24]. A more systematic and expanded study may prove useful in the future.

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Experimental Part. - The complexes $[\text{Rh}(\text{SnCl}_n\text{Br}_{3-n})\text{NBD}(\text{tertiary phosphine})_2]$ were prepared from $[\text{RhCl}(\text{NBD})]_2$, four equivalents of PR_3 and two equivalents of SnBr_2 as described previously [22] and the appropriate microanalytical results are shown in Table 1.

^{31}P -NMR. spectra were measured as $\text{CH}_2\text{Cl}_2/\text{benzene-}d_6$ solutions in 10 mm tubes using Bruker HX-90 and WM-250 NMR. spectrometers (36.43 and 101.27 MHz respectively). Chemical shifts are ± 0.1 ppm (external H_3PO_4) and coupling constants ± 3 Hz. Typically, 45° pulse angles and 0.7 s acquisition times were employed.

^{119}Sn -NMR. spectra were measured as $7 \times 10^{-3}\text{M}$ solutions in 15 mm tubes (solvent as above) using the WM-250 operating at 93.14 MHz. Chemical shifts are ± 0.2 ppm (external Me_4Sn) and coupling constants are ± 12 Hz. Routinely, 50 kHz-spectra were measured with 70° pulse angles and 0.2 s acquisition times. Between four and seven hours were required for a reasonable signal-to-noise ratio. Line widths are often of the order of 50 Hz, thus preventing the observation of small coupling constants. The ^{119}Sn -NMR. spectra were measured without ^1H -decoupling, whereas the ^{31}P -NMR. spectra were all ^1H -decoupled. IR. spectra were recorded on a Beckmann 4250 spectrophotometer over the range $4000\text{--}200\text{ cm}^{-1}$.

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