Tin-119 Fourier-transform Nuclear Magnetic Resonance Study of Rhodium–Tin Complexes formed in Aqueous Hydrochloric Acid Solutions of $RhCl_3$ and $SnCl_2$

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Rhodium–tin complexes, formed in aqueous hydrochloric acid solutions of $RhCl_3$ and $SnCl_2$, have been investigated by ^{119}Sn Fourier-transform n.m.r. spectroscopy. Satellite peaks due to the ^{117}Sn isotope revealed fast intramolecular scrambling of the ligands. The redox process between rhodium(III) and tin(II) species to form a rhodium(I) complex with five tin(II) ligands was demonstrated at a molar ratio of [Sn] : [Rh] = 6 : 1. Nuclear magnetic resonance properties of the rhodium(I) complex and of a series of $[Rh(SnCl_3)_nCl_{6-n}]^{3-}$ (n = 1—5) complexes are determined and discussed.

IN the course of our study on photo-enhanced catalytic dehydrogenation of propan-2-ol with rhodium–tin complexes,[1] we intended to determine the species present in the aqueous hydrochloric acid solution of $RhCl_3$ and $SnCl_2$. The solution, containing $SnCl_2$ in excess, has been used for the photometric analysis of $RhCl_3$.[2] Furlani *et al.*[3] reported that a rhodium(I) complex, $[AsPh_4]_3[Rh(SnCl_3)_4]\cdot SnCl_2$, was isolated from solutions with a molar ratio of [Sn] : [Rh] as high as 100—500 : 1 and supported the view that the rhodium(III) species is reduced by tin(II) under the preparative conditions for the photometric analysis. Young and co-workers [4,5] and Klinskaya *et al.*[6] suggested that the rhodium(I) species are formed even for solutions in which the concentration of tin is of the same order as that of rhodium. From solutions with a [Sn] : [Rh] ratio of 1—4 : 1, however, Kimura *et al.*[7,8] have isolated a series of rhodium(III) complexes, $[N(CH_3)_4]_3[Rh(SnCl_3)_nCl_{6-n}]$ (n = 1—4). ^{119}Sn Mössbauer spectroscopy is one of the useful tools for the characterization of tin compounds.[9] The existence of rhodium(III)–tin(II) complexes of $[N(CH_3)_4]_3[Rh(SnCl_3)_nCl_{6-n}]$ (n = 2—5) was confirmed recently by this method.[10]

Tin-119 ($I = \frac{1}{2}$, natural abundance 8.68%) n.m.r. spectroscopy has also been applied effectively for the characterization of tin compounds [11–14] since the first report of Burke and Lauterbur.[15] Spectral data for more than 600 organotin compounds have been reviewed recently by Smith and Tupčiauskas.[16] High-resolution and high-sensitivity methods in pulse Fourier-transform ^{119}Sn n.m.r. spectroscopy are particularly profitable for the elucidation of inorganic tin species,[17] especially for *in situ* solution analysis. With respect to rhodium–tin complexes, the following additional advantages apply. (*i*) Evidence for the co-ordination of tin ligands to rhodium is obtained by the appearance of a doublet due to the spin coupling with ^{103}Rh ($I = \frac{1}{2}$, natural abundance 100%). (*ii*) Rhodium complexes containing more than one tin ligand should give satellite peaks due to the ^{117}Sn isotope ($I = \frac{1}{2}$, natural abundance 7.67%), which provide information on the structure and fluxional behaviour of the complex. (*iii*) Nuclear magnetic resonance parameters, such as $\delta(^{119}Sn)$, $^1J(^{119}Sn-^{103}Rh)$, and $^2J(^{119}Sn-^{117}Sn)$, are useful in assigning the complexes. Moreover, (*iv*) the composition of the solution and the stoicheiometry of the redox reaction between rhodium(III) and tin(II) are ascertainable *in situ* by the quantitative determination of tin(II) and tin(IV) species.

In this respect, we have attempted to apply pulse Fourier-transform ^{119}Sn n.m.r. spectroscopy to rhodium-tin complexes in aqueous hydrochloric acid solutions.

EXPERIMENTAL

All chemicals were commercially available (reagent grade) and used without further purification. The samples for n.m.r. measurement were prepared as follows: $RhCl_3\cdot 3H_2O$ (0.263 g, 1.0 mmol) and a calculated amount of $SnCl_2\cdot 2H_2O$ ([Sn] : [Rh] = 0.5—10.0 : 1) were dissolved in a 3 mol dm^{-3} HCl solution (2.0 cm^3) and stirred at room temperature for several hours. For the case of [Sn] : [Rh] = 1 : 1, the following solution was also prepared according to the procedure of Kimura:[8] $RhCl_3\cdot 3H_2O$ (1.00 g, 3.8 mmol) was mixed with $SnCl_2\cdot 2H_2O$ (0.86 g, 3.8 mmol) in 12 mol dm^{-3} HCl solution (2.0 cm^3) and allowed to stand on a boiling-water bath for 60 min. All the solutions were homogeneous. With increasing amounts of $SnCl_2\cdot 2H_2O$ ([Sn] : [Rh] > 6 : 1), the colour of the solution changed from orange-red to purple-red.

Tin-119 n.m.r. spectra were recorded at 25 °C (unless otherwise noted) using a sample tube (10 mm in diameter) on a JEOL JNM-FX 100 or JNM-FX 90Q spectrometer with a tunable probe, operating in the Fourier-transform mode at 37.1 MHz (FX 100) or 33.34 MHz (FX 90Q). The pulse interval was adjusted to allow for the quantitative analysis of the co-ordinated tin (1.0 s) or the free tin(IV) species (5.0 s). All chemical shifts are given relative to the external $Sn(CH_3)_4$ reference, where a negative sign indicates a shift to higher field. The number of pulses (6 500—55 000) depended on the amount of $SnCl_2\cdot 2H_2O$ added. Since the observable spectral width was limited to 20 000 Hz, several spectra with different observation frequencies were necessary for the same sample.

RESULTS AND DISCUSSION

Change in N.M.R. Spectrum with [Sn] : [Rh] *Ratio.*—A typical ^{119}Sn n.m.r. spectrum of the rhodium–tin complexes is shown in Figure 1, where the solution contains equimolar amounts of $RhCl_3\cdot 3H_2O$ (3.8 mmol) and $SnCl_2\cdot 2H_2O$ (3.8 mmol), dissolved in 12 mol dm^{-3} HCl solution. It is obvious that the spectrum is composed of three main doublet peaks and two sets of satellites.

The doublet multiplicity of these peaks shows that the tin species is co-ordinated to rhodium with no intermolecular exchange process on the n.m.r. time scale.* It is also apparent that the solution contains neither free tin(II) nor tin(IV) species. No tin species other than those mentioned above were found in the solution in the range δ 60 to −1 050 p.p.m. When an equimolar amount of $RhCl\cdot3H_2O$ (1.0 mmol) and $SnCl_2\cdot2H_2O$ (1.0 mmol) was dissolved in 3 mol dm^{-3} HCl solution, some of the peaks were broadened.

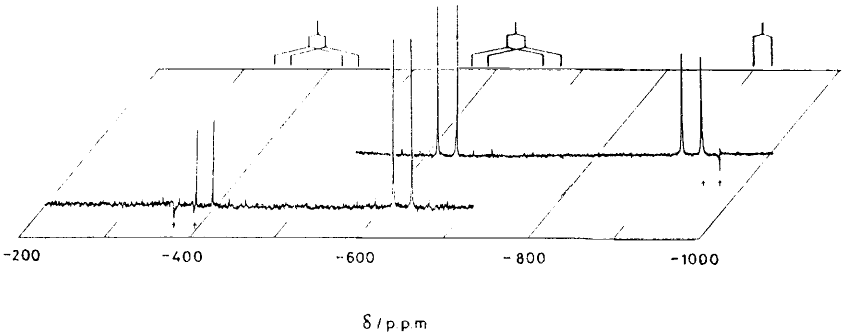

FIGURE 1 ^{119}Sn n.m.r. spectrum of rhodium–tin complexes formed in the solution composed of $RhCl_3\cdot3H_2O$ (3.8 mmol), $SnCl_2\cdot2H_2O$ (3.8 mmol), and 12 mol dm^{-3} HCl (2.0 cm^3). The spectra were measured at 25 °C and 37.1 MHz (FX 100). Arrows indicate folding-back signals

The spectral pattern was very sensitive to the ratio of [Sn] : [Rh], as depicted in Figure 2, for solutions with a ratio from 1 : 1 to 7 : 1 (3 mol dm^{-3} HCl). Since the relative intensities for the main peaks were quite different, each main peak should be assigned to a different complex. A broad doublet peak at δ −991.6 p.p.m. and another doublet peak at δ −654.4 p.p.m. were drastically decreased, as the ratio of [Sn] : [Rh] was increased over the range 1 : 1 to 3 : 1. Very close to this latter peak, a set of peaks due to a different type of tin species appeared for solutions with [Sn] : [Rh] ⩾ 3 : 1. This set of peaks at *ca.* −643 p.p.m. was assignable to free tin(IV) species, determined by measuring the 3 mol dm^{-3} HCl solution of $SnCl_4$. The relative intensity of the doublet peak at δ −411.1 p.p.m. was large in the range of [Sn] : [Rh] = 2—3 : 1 but disappeared completely for [Sn] : [Rh] ⩾ 6 : 1. On the other hand, the doublet peak at δ 8.5 p.p.m. became dominant for [Sn] : [Rh] = 6 : 1. No peak was detected in the lower-field range other than the peak at δ 8.5 p.p.m.

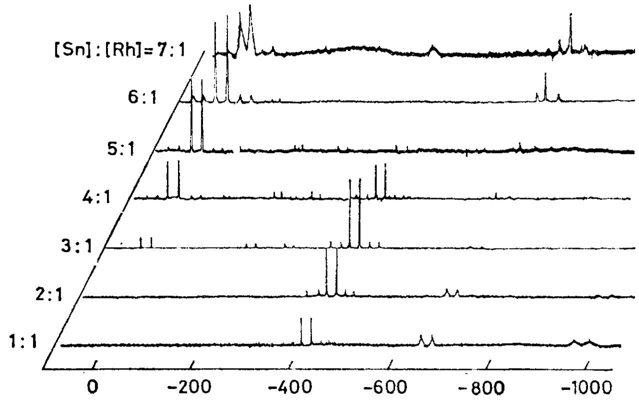

FIGURE 2 Variation of the ^{119}Sn n.m.r. spectrum of the aqueous hydrochloric acid solution of $RhCl_3\cdot3H_2O$ and $SnCl_2\cdot2H_2O$ with [Sn] : [Rh] ratio ($RhCl_3\cdot3H_2O$, 1.0 mmol; 3 mol dm^{-3} HCl, 2.0 cm^3). The spectra were measured at 25 °C and 33.34 MHz (FX 90Q)

A broad peak at δ −371.1 p.p.m. was assignable to free tin(II) species, as confirmed with a 3 mol dm^{-3} HCl solution of $SnCl_2\cdot2H_2O$. It is worth noting that free tin(II) species were not observed in the range [Sn] : [Rh] ⩽ 6 : 1. When the ratio of [Sn] : [Rh] was increased from 7 : 1 to 10 : 1, the peak became large and gradually shifted from δ −371.1 to δ −403.6 p.p.m., while the lowest double peak at δ 8.5 p.p.m. shifted to δ 5.1 p.p.m. and broadened.

Role of Satellite in Peak Assignment.—From the solution with the [Sn] : [Rh] ratio of 1 : 1, Kimura[8] isolated four kinds of six-co-ordinate rhodium(III) complexes as the salts of $[N(CH_3)_4]^+$: $[Rh(SnCl_3)Cl_5]^{3-}$, *cis*- and *trans*-$[Rh(SnCl_3)_2Cl_4]^{3-}$, and *fac*-$[Rh(SnCl_3)_3Cl_3]^{3-}$. The yields of *cis*- and *trans*-$[N(CH_3)_4]_3[Rh(SnCl_3)_2Cl_4]$ were as high as 66% and 20% respectively, based on tin.

The doublet peak at δ −914.1 p.p.m. lacked its own satellite (Figure 1). Since the satellites in the ^{119}Sn n.m.r. spectrum originate from the ^{117}Sn isotope, the doublet peak without accompanying satellites should appear only when one tin ligand is co-ordinating to rhodium. For this reason, the highest-field peak (δ −914.1 p.p.m.) is assigned to $[Rh(SnCl_3)Cl_5]^{3-}$.

With regard to $[Rh(SnCl_3)_2Cl_4]^{3-}$, satellite peaks should be observed, assuming that the two $SnCl_3^-$ ligands contain both ^{119}Sn and ^{117}Sn nuclei. On a statistical basis, the value of the peak intensity ratio, I(satellite)/I(main), should be 4.2%; the observed value for the doublet peak at δ −628.6 p.p.m. was 4.2%, coinciding well with the calculated one.

The satellites of the doublet peak at δ −411.1 p.p.m.

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* The ^{119}Sn Mössbauer spectrum measured for the aqueous hydrochloric acid solution with [Sn]:[Rh] = 3:1 at liquid-nitrogen temperature using $Ba[SnO_3]$ as a source indicated the existence of covalent tin(II) species (isomer shift = 1.83 mm s^{-1}, quadrupole split = 1.92 mm s^{-1}) in conformity with the co-ordination to rhodium.[9]

account for 8.2% of the peak intensity, which is very close to the calculated value of 8.3% for $[Rh(SnCl_3)_3Cl_3]^{3-}$. Furthermore, it was confirmed that the dominant peak at δ −411.1 p.p.m. for the solution with the [Sn] : [Rh] ratio of 2 : 1 disappeared completely after the precipitation procedure, by which *fac*-$[N(CH_3)_4]_3[Rh(SnCl_3)_3Cl_3]$ was isolated. Consequently, three main peaks at δ −914.1, −628.6, and −411.1 p.p.m. are assigned to $[Rh(SnCl_3)Cl_5]^{3-}$, $[Rh(SnCl_3)_2Cl_4]^{3-}$, and $[Rh(SnCl_3)_3Cl_3]^{3-}$ respectively.

Intramolecular Scrambling of Tin Ligands.—Although the *cis* and *trans* isomers of $[Rh(SnCl_3)_2Cl_4]^{3-}$ were isolated from the solution, the main peaks due to these isomers were not detected separately in the n.m.r. spectrum. The peak assignment for $[Rh(SnCl_3)_2Cl_4]^{3-}$ can only be explained by fast intramolecular scrambling of the tin ligands. A similar situation may exist between the *fac* and *mer* isomers of $[Rh(SnCl_3)_3Cl_3]^{3-}$, even though only the former was isolated from the solution.

According to the results of Kimura,[8] $[N(CH_3)_4]_3[Rh(SnCl_3)_4Cl_2]$ was isolated from a hot 3 mol dm^{-3} HCl solution with a [Sn] : [Rh] ratio of 4 : 1. Correspondingly, the intensity of the doublet peak at δ −204.3 p.p.m. became large at high probe temperature (75 °C) with no appreciable shift of the resonance position. The change in the peak intensity with temperature was reversible, as shown by measuring again after the sample was cooled to room temperature. Hence, the assignment of this peak to $[Rh(SnCl_3)_4Cl_2]^{3-}$ seems plausible.

Provided that the tin ligands are fixed in the *cis*-$[Rh(SnCl_3)_4Cl_2]^{3-}$ configuration, two resonance positions should be found, since the tin ligands are not chemically equivalent; even in the case of the *trans*-$[Rh(SnCl_3)_4Cl_2]^{3-}$ configuration with four equivalent tin ligands, two kinds of satellite peaks should be observed, due to the ^{119}Sn and ^{117}Sn nuclei (*cis* and *trans*) in this configuration being magnetically distinct. Therefore, the observed spectral pattern of just one set of main and satellite peaks is ascribed to the magnetically equivalent behaviour of the four $SnCl_3^-$ ligands of the $[Rh(SnCl_3)_4Cl_2]^{3-}$ complex. The value of *I*(satellite)/*I*(main) was found to be 11.6%.

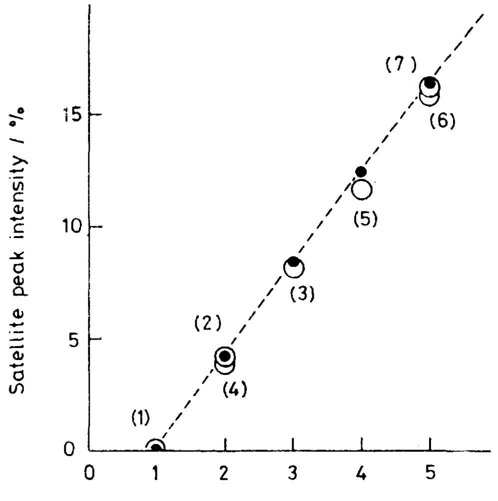

FIGURE 3 Assignment of the number of tin ligands in rhodium–tin complexes based on the ^{117}Sn satellite peak intensity in the ^{119}Sn n.m.r. spectrum; relative intensity calculated statistically as a function of the number of magnetically equivalent tin ligands (●), relative intensity determined experimentally (○). Numerical labels correspond to the complexes in the Table

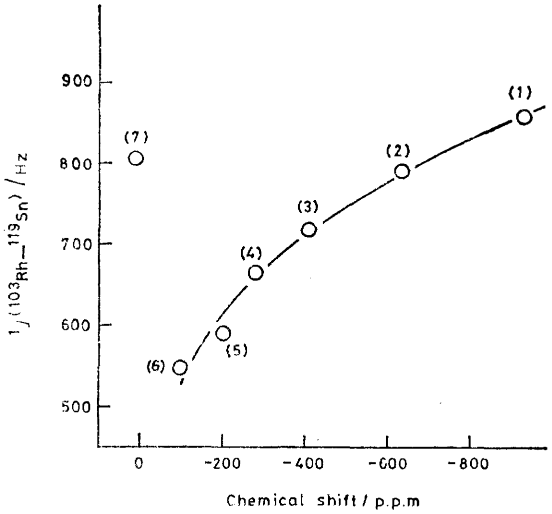

FIGURE 4 Plot of $^1J(^{103}Rh—^{119}Sn)$ as a function of ^{119}Sn chemical shift. Numerical labels correspond to the complexes in the Table

The feature of showing only one kind of satellite peak was also observed for the doublet peak at δ 8.5 p.p.m., the value of *I*(satellite)/*I*(main) being 16.2% (Figure 2). This fact strongly suggests that fast intramolecular scrambling of five $SnCl_3^-$ ligands occurs in this case too. As for the peak at δ −100.5 p.p.m., which was observed most clearly in the solution composed of $RhCl_3·3H_2O$ (0.263 g, 1.0 mmol), $SnCl_2·2H_2O$ (0.338 g, 1.5 mmol), 6 mol dm^{-3} HCl (0.5 cm^3), and hexamethylphosphoramide (1.5 cm^3), we again observed only one kind of satellite peak, corresponding to five tin ligands (see below).

Satellite Peak Intensities due to Magnetically Equivalent Ligands.—For the rhodium–tin complexes, exhibiting fast intramolecular scrambling, the satellite peak intensities should reflect the number of magnetically equivalent $SnCl_3^-$ ligands. In Figure 3, the calculated value of *I*(satellite)/*I*(main) is plotted as a function of the number of magnetically equivalent $SnCl_3^-$ ligands. The close agreement of the observed value with the theoretical one for each complex is obvious. The number of tin ligands for each rhodium complex can be determined in this manner.

Correlation of Tin Chemical Shifts with Rhodium–Tin Coupling Constants.—In Figure 4, the value of the ^{103}Rh–^{119}Sn one-bond coupling constant is plotted against the chemical shift for all the main peaks observed.

It was noticed that the one-bond coupling constant decreases as the ^{119}Sn chemical shift moves to lower field, except for the point relevant to the peak at the lowest field (δ 8.5 p.p.m.). The peak at δ −100.5 p.p.m.

may be assigned to $[\mathrm{Rh(SnCl_3)_5Cl}]^{3-}$,[10] because the point for this peak was placed along the extrapolation of the line joining the points for $[\mathrm{Rh(SnCl_3)}_n\mathrm{Cl}_{6-n}]^{3-}$ (n = 1—4).

As for the relation between $^2J(^{117}\mathrm{Sn}-^{119}\mathrm{Sn})$ * and the chemical shift, a trend similar to that for $^1J(^{103}\mathrm{Rh}-^{119}\mathrm{Sn})$ was observed (*cf.* the Table); an anomaly was also seen for the peak at δ 8.5 p.p.m.

The Redox Process between Rhodium(III) *and Tin*(II) *Species*.—As stated previously, the doublet peak at δ 8.5 p.p.m. is due to a rhodium complex co-ordinated to five magnetically equivalent $\mathrm{SnCl_3}^-$ ligands. A certain correlation between the peak intensities of this complex and tin(IV) species was noticed in the spectra of Figure 2. In order to clarify this point, the peak intensities were determined accurately for the solution with [Sn] : [Rh] = 6 : 1 (Figure 5), in which only this complex and tin(IV) species are present, as is seen in Figure 2.

From analysis of Figure 5, it was confirmed that one mole of $\mathrm{SnCl_2}$ was converted to tin(IV) per mole of $\mathrm{RhCl_3}$. This we considered as being strong evidence for the redox process; the reduction of rhodium(III) to rhodium(I), coupled with the oxidation of tin(II) to tin(IV). The stoicheiometry of this reaction may be represented by the following: $\mathrm{Rh^{III}} + 6\mathrm{Sn^{II}} \longrightarrow \mathrm{Rh^{I}(Sn^{II})_5} + \mathrm{Sn^{IV}}$. The structure of this complex in solution remains uncertain; † $[\mathrm{Rh(SnCl_3)_5}]^{4-}$ [21] might be a possibility, since the isoelectronic platinum(II) complex of $[\mathrm{Pt(SnCl_3)_5}]^{3-}$ [22,23] is well known. The rhodium(I) complex was relatively unstable in solution. The peak gradually weakened and finally disappeared upon heating or after a long period of standing, with an increase in the rhodium(III) complexes.

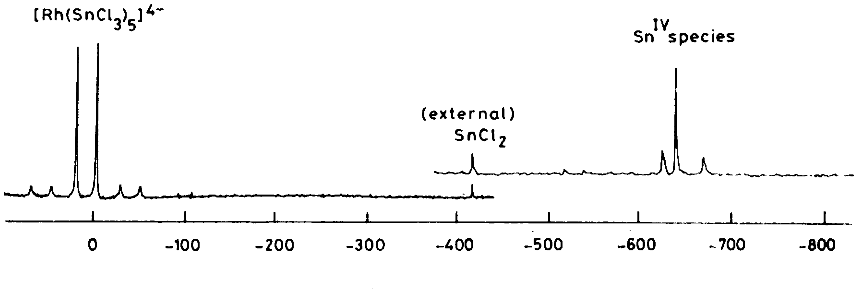

FIGURE 5 ^{119}Sn n.m.r. spectrum of $[\mathrm{Rh(SnCl_3)_5}]^{4-}$ and tin(IV) species formed in the aqueous hydrochloric acid solution (3 mol dm^{-3} HCl, 2.0 cm^3) of $\mathrm{RhCl_3{\cdot}3H_2O}$ (1.0 mmol) and $\mathrm{SnCl_2{\cdot}2H_2O}$ (6.0 mmol; [Sn] : [Rh] = 6 : 1). Normalization was made by use of the resonance peak intensity of $\mathrm{SnCl_2{\cdot}2H_2O}$ (in $\mathrm{D_2O}$), contained in a concentric capillary tube

Although the proposal for the chloro-bridged rhodium(I) dimer, $[\mathrm{Rh_2Cl_2(SnCl_3)_4}]^{4-}$,[4,5] was once supported by a far-i.r. study,[24] we failed to detect this dimeric complex in our ^{119}Sn n.m.r. measurements; if the two-bond $^{103}\mathrm{Rh}-^{119}\mathrm{Sn}$ coupling constant is large enough to give second-order splitting, an analyzable but complicated spectrum should be observed. However, no second-order peaks were found in the spectra. Moreover, the abundance of the observed tin(IV) species was not sufficient to explain the stoicheiometry suggested by Young and co-workers,[4] $2\mathrm{RhCl_3} + 6\mathrm{SnCl_3}^- \longrightarrow [\mathrm{Rh_2Sn_4Cl_{14}}]^{4-} + 2\mathrm{SnCl_5}^-$. We now believe non-existence of this dimeric complex, at least in the solution examined by him.

On the contrary, preservation of the rhodium(III) valency was confirmed for the doublet peak at δ −281.4 p.p.m. by mass balance of tin(IV) species. Although the identification of the complex is not yet conclusive, the co-ordination of two tin ligands was inferred on the basis of the satellite peak intensity.

Variation of Rhodium Complex Composition.—The relative amount of each rhodium–tin complex is reflected in the area of the corresponding peak, if corrected by dividing by the number of co-ordinated tin atoms. Taking into account the total amount of added tin and the mole fractions of co-ordinated and unco-ordinated tin, the amount of rhodium co-ordinated with tin was calculated by summing up the above peak area. In the region of [Sn] : [Rh] $\geqslant$ 3 : 1, the total calculated amount of rhodium co-ordinated with tin coincided with the total amount of added rhodium within 1%. Moreover, the amounts of rhodium(I) complex, $[\mathrm{Rh(SnCl_3)_5}]^{4-}$, were in excellent agreement with the amounts of tin(IV) species. On the other hand, in the region of [Sn] : [Rh] < 3 : 1, it was necessary to assume the existence of a rhodium species unco-ordinated to tin species, $[\mathrm{RhCl_6}]^{3-}$, in order to compromise the mass balance of rhodium and tin.

Thus, the compositions of the various rhodium–tin complexes were determined in the 3 mol dm^{-3} HCl solution at 25 °C, as shown in Figure 6. It is important that the experimental conditions to isolate the complexes, $[\mathrm{N(CH_3)_4}]_3[\mathrm{Rh(SnCl_3)}_n\mathrm{Cl}_{6-n}]$ (n = 1—4),[7,8] were quite adequate in view of the curves for the composition of the rhodium complex.

Consideration of ^{119}Sn *N.M.R. Characteristics*.—The ^{119}Sn n.m.r. parameters for the rhodium–tin complexes are given in the Table.

In the series of complexes, $[\mathrm{Rh(SnCl_3)}_n\mathrm{Cl}_{6-n}]^{3-}$ (n = 1—5), the ^{119}Sn n.m.r. resonance is deshielded as the

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* The values of $^2J(^{117}\mathrm{Sn}-^{119}\mathrm{Sn})$ for these complexes are very large in comparison with those for organotin compounds, *e.g.* $\mathrm{SnBu^i_2(SnEt_3)_2}$ (430 Hz), $\mathrm{O(SnClBu_2)_2}$ (72 Hz),[18] $[\{\mathrm{SnMe(OC_2H_4)_3N}\}_3]$ (156 Hz), $[\{\mathrm{SnEt(OC_2H_4)_3N}\}_3]$ (220 Hz).[19]

† Recently, Kimura and Sakurai [20] isolated a purple complex $[\mathrm{Rh^{III}(NH_3)_6}]_3[\mathrm{Rh^{I}(Sn^{II}Cl_3)_4(Sn^{II}Cl_4)}][\mathrm{Sn^{II}Cl_6}]{\cdot}4\mathrm{H_2O}$, from a solution with [Sn] : [Rh] = 7—9 : 1, and determined its crystal and molecular structure by single-crystal *X*-ray diffraction.

Tin-119 n.m.r. characteristics of various rhodium–tin complexes. The data were determined in 3 mol dm^{-3} HCl solution unless stated otherwise

Structure assignment	Oxidation number of rhodium	Number of co-ordinated tin ligands	δ/p.p.m.			$^1J(^{103}Rh–^{119}Sn)$/Hz			$^2J(^{117}Sn–^{119}Sn)$/Hz		
(1) $[Rh(SnCl_3)Cl_5]^{3-}$	III	1	−991.6,	−932.4,[a]	−914.1[b]	864,	860,[a]	850[b]		none[a,b]	
(2) $[Rh(SnCl_3)_2Cl_4]^{3-}$	III	2	−654.4,	−637.0,[a]	−626.0[b]	796,	791,[a]	780[b]		3 056,[a] 3 091[b]	
(3) $[Rh(SnCl_3)_3Cl_3]^{3-}$	III	3	−411.1		−395.4[b]	718		708[b]	2 804	2 840,[b]	2 754[c]
(4) *d*	III	2	−281.4			664					2 222[c]
(5) $[Rh(SnCl_3)_4Cl_2]^{3-}$	III	4	−204.3			590			2 158		
(6) $[Rh(SnCl_3)_5Cl]^{3-}$	III	5	−100.5			547					1 952[c]
(7) $[Rh(SnCl_3)_5]^{4-}$	I	5	8.5			806			3 634		

[a] Concentrated residue after the separation of $[N(CH_3)_4]_3[Rh(SnCl_3)_3Cl_3]$. [b] 12 mol dm^{-3} HCl solution (Figure 1). [c] Hexamethylphosphoramide solution. [d] Structure unassigned, see text.

number of tin ligands is increased. The observed values of δ(^{119}Sn) (−991.6 to −100.5 p.p.m.) vary widely; the scattered range is larger than the chemical-shift difference between $Sn(CH_3)_4$ and $SnCl_4$ (147.8 p.p.m.) [17] or the whole range of δ(^{31}P) known for the phosphorus(III) compounds (−461 to 245 p.p.m.).[25] Thus, the electronic properties of the rhodium–tin complexes are highly sensitive to substitution of the tin ligand. The chemical shifts of $SnCl_2$ dissolved in aqueous hydrochloric acid solutions range over δ −341 p.p.m. (12 mol dm^{-3} HCl) to −521 p.p.m. (0 mol dm^{-3} HCl).[15] As the chemical-shift range due to the free tin(II) species is smaller than that of the co-ordinated one, it is decided that the ^{119}Sn resonance is shifted to both higher and lower fields upon co-ordination to rhodium. This is in contrast to amino- [26-28] and alkyl (and/or aryl) tertiary phosphine [29] ligands, which usually show a high-field and low-field co-ordination shift respectively, in Group 8 transition-metal complexes.

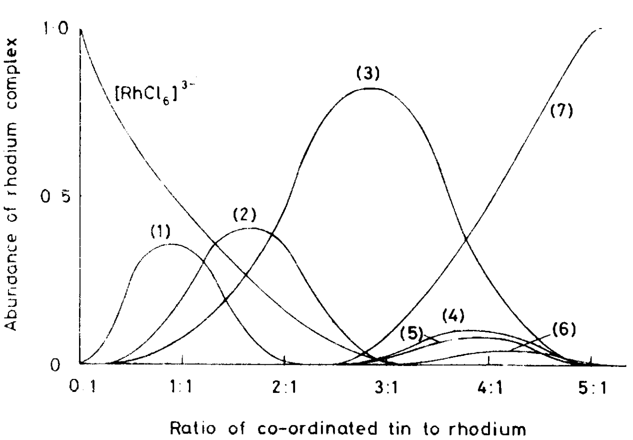

FIGURE 6 Distribution of rhodium complexes in 3 mol dm^{-3} HCl solution as a function of mole ratio of total co-ordinated tin to total rhodium (1.0 mmol). Numerical labels correspond to the complexes in the Table

Taking into account the fact that $SnCl_3^-$ is a strong π-acceptor ligand,[30] the trend in δ(^{119}Sn) values within the complexes $[Rh(SnCl_3)_nCl_{6-n}]^{3-}$ (n = 1—5) may be interpreted simply in terms of the charge on the tin atom, although the theory of ^{119}Sn magnetic shielding is still in its infancy.[31a]

The reduced nuclear spin–spin coupling constant, $K_{XY} = (2\pi/\hbar\gamma_X\gamma_Y) \cdot J_{XY}$,[32] is convenient to compare the values involving different nuclei. As the number of tin ligands increased, the value of $^1J(^{119}Sn–^{103}Rh)$ changed from 547 to 864 Hz, corresponding to a change in the ^1K value from 3.88 × 10^{23} to 6.13 × 10^{23} cm^{-3}. The reported magnitudes of $^1K(^{103}Rh–X)$ (X = ^{31}P, ^{15}N, and ^{1}H) are as follows: ^{31}P (0.48 × 10^{23}—1.27 × 10^{23} cm^{-3}),[29] ^{15}N (0.37 × 10^{23}—0.47 × 10^{23} cm^{-3}),[28] and ^{1}H (0.04 × 10^{23}—0.08 × 10^{23} cm^{-3}).[31b] It should be noted that the *s* electron-density term, $\psi(0)^2$, of these atoms decreases in the same order (Sn: 12.680, P: 5.628, N: 4.775, and H: 0.55 a.u.) [29] as the reduced coupling constant. This is reasonable since $\psi(0)^2$ is included as a constituent of the Fermi contact term which is frequently considered as the most important one for determining the absolute magnitude of K.[31c]

As far as the one-bond coupling constant between tin and transition metals is concerned, only the following two tungsten complexes were examined: $[W(CO)_5(SnCl_2)(thf)]$ (thf = tetrahydrofuran) (1 594 Hz) and $[W(CO)_5(SnCl_2)(PBu^t_3)]$ (1 470 Hz).[33] Their $^1K(^{183}W–^{119}Sn)$ values are calculated to be 6.85 × 10^{23} and 7.97 × 10^{23} cm^{-3} respectively. With the *s* electron densities of Rh (4.650 a.u.) and W (8.137 a.u.) taken into consideration,[29] the *s*-orbital participation would be similar between the two kinds of transition metal–tin co-ordination bonds.

It has been observed that the value of the metal–ligand one-bond coupling constant is a good measure of the strength of the metal–ligand σ bonding from the viewpoint of *trans* (and/or *cis*) influence of ligands.[34] Hence the trend of $^1J(^{103}Rh–^{119}Sn)$ within the complexes, $[Rh(SnCl_3)_nCl_{6-n}]^3$ (n = 1—5), indicates that the rhodium–tin σ-bond strength decreases as the number of $SnCl_3^-$ ligands increases. The correlation between $^1J(^{103}Rh–^{119}Sn)$ and $^2J(^{117}Sn–^{119}Sn)$, observed for these complexes (Table), supports this view. The relatively large value of $^1J(^{103}Rh–^{119}Sn)$ for the doublet peak at δ 8.5 p.p.m. may be associated with the low valency [35] of rhodium for the complex $[Rh(SnCl_3)_5]^{4-}$.

We are grateful to Miss K. Takada of the Kawamura Institute of Chemical Research and Dr. M. Suzuki of the National Research Laboratory for Pollution and Resources for the use of ^{119}Sn n.m.r. facilities. We also thank Dr. H. Sato for the ^{119}Sn Mössbauer experiment.

[0/1150 *Received, 21st July*, 1980]

REFERENCES

[1] S. Shinoda, H. Moriyama, Y. Kise, and Y. Saito, *J. Chem. Soc., Chem. Commun.*, 1978, 348.

[2] E. B. Sandell, ‘ Colorimetric Determination of Traces of Metals,’ 3rd edn., Interscience, New York, 1959.

[3] C. Furlani, E. Zinato, and F. Furlan, *Atti Acc. Naz. Lincei, Cl. Sci. Fis., Mat. Nat., Rend.*, 1965, **38**, 517.

[4] A. G. Davies, G. Wilkinson, and J. F. Young, *J. Am. Chem. Soc.*, 1963, **85**, 1692.

[5] J. F. Young, R. D. Gillard, and G. Wilkinson, *J. Chem. Soc.*, 1964, 5176.

[6] I. Yu. Klinskaya, M. B. Rosenkevich, and Yu. A. Sakharovski, *Kinet. Katal.*, 1978, **19**, 329.

[7] T. Kimura, E. Miki, K. Mizumachi, and T. Ishimori, *Chem. Lett.*, 1976, 1325.

[8] T. Kimura, *Sci. Pap. Inst. Phys. Chem. Res.* (*Jpn.*), 1979, **73**, 31.

[9] R. V. Parish, *Prog. Inorg. Chem.*, 1972, **15**, 101.

[10] P. G. Antonov, Yu. N. Kukushikin, V. I. Anufriev, L. N. Vasil'ev, and L. V. Konovalov, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1979, **24**, 231.

[11] B. K. Hunter and L. W. Reeves, *Can. J. Chem.*, 1968, **46**, 1399.

[12] A. G. Davies, P. G. Harrison, J. D. Kennedy, T. N. Michell, R. J. Puddephatt, and W. McFarlane, *J. Chem. Soc. C*, 1969, 1136.

[13] W. McFarlane, J. C. Marie, and M. Delmas, *J. Chem. Soc., Dalton Trans.*, 1972, 1862.

[14] D. H. Harris, M. F. Lappert, J. S. Poland, and W. McFarlane, *J. Chem. Soc., Dalton Trans.*, 1975, 311.

[15] J. J. Burke and M. F. Lauterbur, *J. Am. Chem. Soc.*, 1961, **83**, 326.

[16] P. J. Smith and A. P. Tupčiauskas, *Ann. Rep. NMR Spectros.*, 1978, **8**, 291.

[17] C. R. Lassigne and E. J. Wells, *Can. J. Chem.*, 1977, **55**, 927.

[18] T. N. Michell, *J. Organomet. Chem.*, 1974, **70**, C1.

[19] K. Jurkhsat, C. Mügge, A. Tzschach, A. Zschunke, G. Engelhardt, E. Lippmaa, M. Mägi, M. F. Larin, V. A. Pestunovich, and M. G. Voronkov, *J. Organomet. Chem.*, 1979, **171**, 301.

[20] T. Kimura and T. Sakurai, *J. Solid State Chem.*, in the press.

[21] E. N. Yurchenko, V. A. Varnek, G. L. Elizarova, L. G. Matvienko, and M. S. Ioffe, *Koord. Khim.*, 1975, **1**, 1406.

[22] R. D. Cramer, E. L. Jenner, R. V. Lindsey, and U. G. Stolberg, *J. Am. Chem. Soc.*, 1963, **85**, 1691.

[23] R. D. Cramer, R. V. Lindsey, C. T. Prewitt, and U. G. Stolberg, *J. Am. Chem. Soc.*, 1965, **87**, 658.

[24] D. M. Adams and P. J. Chandler, *Chem. Ind.* (*London*), 1965, 269.

[25] B. E. Mann, in ‘ NMR and the Periodic Table,’ eds. R. K. Harris and B. E. Mann, Academic Press, London, 1978, ch. 4.

[26] H. Motschi, P. S. Pregosin, and L. M. Venanzi, *Helv. Chim. Acta*, 1979, **62**, 667.

[27] M. Alei, jun., P. J. Vergamini, and W. E. Wageman, *J. Am. Chem. Soc.*, 1979, **101**, 5415.

[28] K. S. Bose and E. H. Abbott, *Inorg. Chem.*, 1977, **16**, 3190.

[29] P. S. Pregosin and R. W. Kunz, ‘ ^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes,’ Springer–Verlag, Berlin, 1979.

[30] J. F. Young, *Adv. Inorg. Chem. Radiochem.*, 1968, **11**, 91.

[31] (*a*) R. K. Harris, J. D. Kennedy, and W. McFarlane, in ‘ NMR and the Periodic Table,’ eds. R. K. Harris and B. E. Mann, Academic Press, London, 1978, ch. 10; (*b*) R. G. Kidd and R. J. Goodfellow, *ibid.*, ch. 8; (*c*) G. A. Webb, *ibid.*, ch. 3.

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

[33] W-W. du Mont, *J. Organomet. Chem.*, 1978, **153**, C11.

[34] T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, 1973, **10**, 335.

[35] P. S. Pregosin and L. M. Venanzi, *Chem. Br.*, 1978, **14**, 276.