^{119}Sn and ^{1}H NMR Evidence for the Formation of a Chloro(trichlorostannato)rhodium Hydrido Anion on Extraction of Rhodium(III) Chlorides into 4-Methylpentan-2-one from Dilute Hydrochloric Acid Containing Tin(II) Chloride

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The reaction between tin(II) chloride and rhodium(III) chlorides in dilute hydrochloric acid continues to draw much attention. The first complex anions involving the $SnCl_3^-$ moiety directly co-ordinated, via the tin atom, to *inter alia* rhodium were isolated more than two decades ago [1]. Kimura [2] and others [3] have isolated a series of rhodium(III) complex anions, $[(CH_3)_4N]_3[RhCl_n(SnCl_3)_{6-n}]$ (n = 2, 3 and 4). On the other hand, Saito *et al.* [4] have shown by means of ^{119}Sn NMR, that in aqueous hydrochloric acid, the presence of sufficient tin(II) chloride also leads to the reduction of rhodium(III), forming at least one Rh(I) complex anion, assigned to be $[Rh(SnCl_3)_5]^{4-}$. Recently a kinetic investigation [5] revealed that excess $SnCl_2$ slowly reacts with chloro(trichlorostannato)rhodium(III) species in hydrochloric acid, to yield a 'purple species' assumed to be $[Rh(SnCl_3)_5]^{4-}$.

As part of our study of the liquid–liquid extraction of the platinum group metals in the presence of tin(II) chloride [6], we examined the ^{119}Sn NMR spectra of 4-methylpentan-2-one (MIBK) extracts obtained from dilute hydrochloric acid solutions containing rhodium(III) chloride and various amounts of tin(II) chloride.

Experimental

All solutions were prepared using degassed, distilled H_2O, analytical grade HCl and MIBK, which were kept under Ar. Commercially-available reagent grade $RhCl_3 \cdot 3H_2O$ and $SnCl_2 \cdot 2H_2O$ were used without further purification. Aqueous solutions of desired composition were prepared and allowed to stand for 16–20 h at room temperature under Ar before being extracted with MIBK.

Once the aqueous and organic phases had separated, MIBK extracts were transferred to Ar-flushed 10 mm NMR tubes, followed by addition of a few drops of acetone-d_6 for lock purposes. Pulsed F.T. NMR spectra were recorded at 186.4 MHz for ^{119}Sn and 90.0 MHz for ^{1}H nuclei, using Brucker WM-500 and WH-90 spectrometers. All spectra were recorded at 303 K using external neat $Sn(CH_3)_4$ and internal $Si(CH_3)_4$ as references, respectively. Spectra of adequate S/N ratio were usually obtained within 40–60 min in the case of ^{119}Sn nuclei.

Results and Discussion

A typical ^{119}Sn NMR spectrum of the yellow-orange MIBK extract, obtained from 2 mol dm^{-3} HCl solutions containing rhodium(III) and tin(II) chlorides (in Sn(II):Rh(III) mole ratio 5–6:1), is shown in Fig. 1 (pertinent NMR parameters are shown in Table I). All extractions were performed under strictly anaerobic conditions. The aqueous

TABLE I. ^{119}Sn and ^{1}H NMR Parameters and Assignments.[a]

	$\delta(^{119}Sn)$/ppm	$^{1}J(^{103}Rh-^{119}Sn)$/Hz	$^{2}J(^{117}Sn-^{119}Sn)$/Hz	$^{2}J(^{1}H-^{119}Sn)$/z	I(sat)/I(main) %
$RhH(SnCl_3)_4Cl^{3-}$	−14.6	600 ± 3	1927 ± 10	57 ± 1	12.9(12.3)
[b]	−54.7	522 ± 3	1691 ± 10	–	17.3(16.3)
$Rh(SnCl_3)_5Cl^{3-}$	−117.5	558 ± 3	1943 ± 10	–	[e]
$Rh(SnCl_3)_3Cl_3{}^{3-}$	−370.0	732 ± 3	3023 ± 10	–	8.4(8.2)
Sn(IV) species[c]	−640.2	–	–	–	–
	$\delta(^{1}H)$/ppm	$^{1}J(^{103}Rh-^{1}H)$/Hz	$^{2}J(^{119}Sn-^{1}H)$/Hz		
$RhH(SnCl_3)_4Cl^{3-}$	−13.2	9.6 ± 0.1	58.2 ± 0.1[d]		

[a] Statistical value in parentheses. [b] Assignment uncertain, see text. [c] Possibly $SnCl_5^-$ or $SnCl_6{}^{2-}$; ref. [4]. [d] Average value of $^{2}J(^{117}Sn-^{1}H)$ and $^{2}J(^{119}Sn-^{1}H)$. [e] Not accurately measurable due to low intensity.

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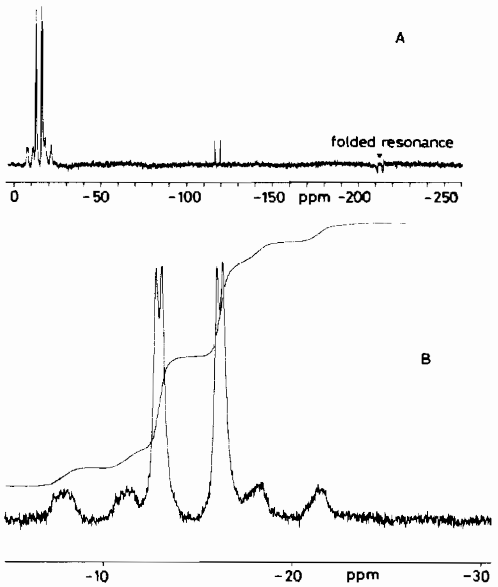
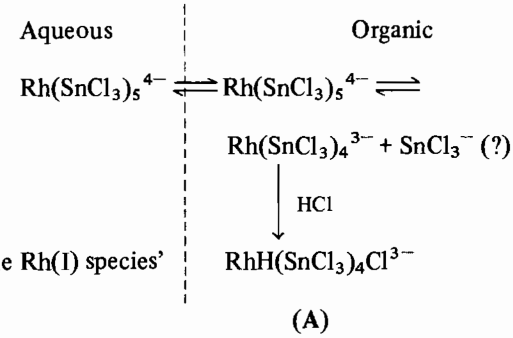


Fig. 1. The 186.4 M ^{119}Sn NMR spectrum of a fresh MIBK extract of a 2.0 mol dm^{3} HCl solution containing Rh(III): Sn(II) in mole ratio 1:5: (A) spectrum as recorded, (B) expanded multiplet at δ(^{119}Sn) = –14.6 ppm.

phase of desired composition was allowed to stand at room temperature under Ar for 16–20 h prior to extraction. On injection of an appropriate amount of MIBK and shaking, the deep purple-red aqueous phase rapidly changed colour to pale orange-yellow, as did the organic phase. Unexpectedly, we found that the predominant species initially present in the MIBK phase is to be best described as a tetrakis(trichlorostannato)rhodium(III) hydrido anion, [RhH(SnCl$_3$)$_4$Cl]$^{3-}$. Although we have not been able to isolate this species for further characterisation, we infer this structure for the complex hydride anion (A), on the basis of the relevant ^{119}Sn and ^{1}H NMR data (Table I).

Saito [4] has shown that the number of SnCl$_3^-$ groups co-ordinated to the central rhodium atom may be deduced from: (i) the intensity ratio, I(satellite)/I(main), due to the ^2J(^{119}Sn–^{117}Sn) coupling, if more than one SnCl$_3$ group is attached to the rhodium atom, and (ii) the correlation of the δ(^{119}Sn) shift values with the ^1J(^{103}Rh–^{119}Sn) coupling constants for a series of related structures. In the present case it may be seen that for (A) the observed I(satellite)/I(main) ratio of 12.9% compares well with the statistically expected value of 12.3% (Table I).

Examination of various aqueous phases prior to and following extraction with MIBK did not reveal the presence of any hydride species, as was found in the organic phase. Evidently (A) appears to be formed in the organic phase immediately after extraction (the above-mentioned rapid colour change from purple-red to yellow also suggests reaction). We suggest that (A) is formed by rapid oxidative addition of a highly associated HCl ion pair in the MIBK phase [7], to an extracted (trichlorostannato)-rhodium(I) anion according to Scheme 1:



Scheme 1.

The hydride anion resonance in the MIBK phase only is dominant for those extractions in which the initial Sn(II)/Rh(III) ratio in the aqueous phase is ⩾5. These conditions correspond to those in which Saito [4] observed a redox reaction between Rh(III) and Sn(II), while reporting a predominance of the Rh(SnCl$_3$)$_5^{4-}$ species (δ(^{119}Sn) = +8.5 ppm ^1J(^{103}Rh–^{119}Sn) = 806 Hz, ^2J(^{117}Sn–^{119}Sn) = 3634 Hz), in 3.0 mol dm^{-3} hydrochloric acid.

The stability of (A) in solution is low, since after storage of a fresh extract (in the NMR tube) for 30 h at *ca.* 277 K, extensive disproportionation is evident. Two new signals at δ(^{119}Sn) = –54.7 ppm and –370.0 ppm appear with the concomitant disappearance of the resonance due to (A). It is probable that (A) is unstable in the presence of air, since during storage no particular precautions were taken to exclude air. Further evidence for the apparent air sensitivity of (A) may be seen from Fig. 2 in

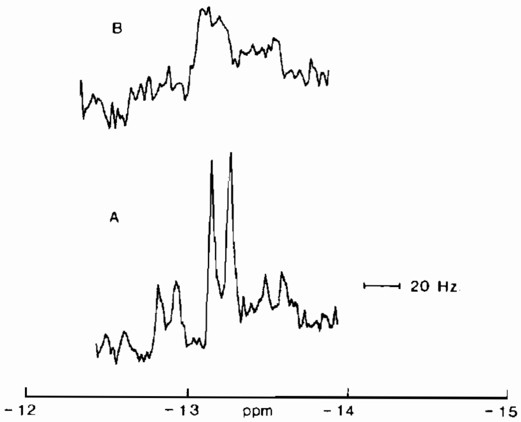


Fig. 2. A ^{1}H NMR spectrum of a similar extract as in Fig. 1: (A) fresh extract, (B) spectrum after bubbling air for 30 sec through solution at room temperature and warming to 60 °C for 30 sec.

which a ^{1}H NMR spectrum of a freshly prepared extract is shown, before and after bubbling air through the solution.

The doublet at $\delta(^{119}Sn) = -370.0$ ppm may be assigned to a $[Rh(SnCl_3)_3Cl_3]^{3-}$ species by comparison with the observations of others [4], with the $SnCl_3^-$ moieties presumably undergoing rapid intramolecular scrambling. Such scrambling renders the *fac* and *mer* isomers indistinguishable from the NMR point of view. On the other hand, assignment of the resonance at $\delta(^{119}Sn) = -54.7$ ppm is less clear. The observed value of the I(satellite)/I(main) ratio of 17.1 ± 0.5% suggests five $SnCl_3^-$ ligands co-ordinated to the rhodium atom. Furthermore, the relatively low $^1J(^{103}Rh-^{119}Sn)$ and $^2J(^{117}Sn-^{119}Sn)$ values of 522 ± 3 Hz and 1691 ± 10 Hz respectively, suggest a Rh(III) species [4].

The values of $^1J(^{103}Rh-^{119}Sn)$ and $\delta(^{119}Sn)$ also fall well on a correlation plot of ^1J as a function of the ^{119}Sn chemical shift for the series of complexes $[Rh(SnCl_3)_nCl_{6-n}]^{3-}$ (n = 1–5) in 3.0 mol dm^{-3} hydrochloric acid as found by Saito *et al.* [4]. We thus tentatively propose to formulate this species as $[Rh(SnCl_3)_5]^{2-}$ in which a solvent molecule occupies (probably loosely) a vacant co-ordination site, in accordance with the octahedral geometry normally preferred by Rh(III). In the absence of additional data, however, this assignment must be considered speculative.

Recently a study of the photoenhanced catalytic dehydrogenation of propanol utilizing rhodium–tin complexes reported evidence of the involvement of a rhodium–hydride complex [8], although no assignments were made. The formation of a rhodium–hydride complex is perhaps not unexpected in the presence of propan-2-ol and conditions of hydrogen evolution as reported in this study. Comparison between the reported NMR parameters and our measurements suggests that the same species is involved. In our case, however, the relatively facile fomation of (A) under conditions of liquid–liquid extraction came as an interesting surprise.

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