# Synthesis and Tin-119 Nuclear Magnetic Resonance Studies of Trichlorostannate(II) Complexes of Ruthenium, Osmium, and Iridium

**Hiroshi Moriyama and Paul S. Pregosin** *
*Laboratorium für Anorganische Chemie, ETH-Zürich, Universitätstrasse 6, CH-8092 Zürich, Switzerland*
**Yasukazu Saito * and Tetsu Yamakawa**
*Institute of Industrial Science, University of Tokyo, 22–1 Roppongi 7 chome, Minato-ku, Tokyo 106, Japan*

The synthesis and $^{119}$Sn n.m.r. characteristics of the complexes *trans*-$[NMe_4]_4[RuCl_2(SnCl_3)_4]$, $[PPh_4]_4[Ru(SnCl_3)_6]$, $[PPh_4]_4[Os(SnCl_3)_6]$, and *trans*-$[PPh_4]_3[IrCl_2(SnCl_3)_4]$ are reported. In solution the *trans* iridium complex slowly isomerizes to give the *cis* isomer. The $^{119}$Sn chemical shifts for the ruthenium complexes move progressively to lower field with increasing number of $SnCl_3^-$ ligands. The values $^2J(^{119}Sn-^{117}Sn)_{trans}$ vary from 11 250 to 40 759 Hz and are dependent upon the metal and the number of $SnCl_3^-$ ligands. Values of 756 and 1 123 Hz have been found for $^1J(^{99}Ru-^{119}Sn)$ and $^1J(^{187}Os-^{119}Sn)$ of $[Ru(SnCl_3)_6]^{4-}$ and $[Os(SnCl_3)_6]^{4-}$, respectively.

There is continuing interest in complexes containing the trichlorostannate ligand, $SnCl_3^-$, since they function as hydrogenation [1] and hydroformylation [2] catalysts. During our studies on these and related molecules [3-10] we have observed a number of interesting n.m.r. properties, Specifically, $^2J(^{119}Sn-^{117}Sn)$ were found to be unexpectedly large with values routinely exceeding 20 000 Hz.[5,11-13] Although there are now a relatively large number of stable $SnCl_3^-$ complexes of Pt$^{II}$,[8] Rh$^{I}$,[4,6,7,14] Rh$^{III}$,[4] Ir$^{I}$,[6,7,15] and Ir$^{III}$,[10,15] there are relatively few trichlorostannate complexes of Ru and Os.[16,17] To extend our knowledge of the chemistry and $^{119}$Sn n.m.r. of this ligand we have prepared several new octahedral complexes of Ru$^{II}$, Os$^{II}$, and Ir$^{III}$ and report here our results.

## Results and Discussion

(*a*) *Solution Chemistry.*—All of the complexes were prepared by adding hydrochloric acid to a mixture of the appropriate transition-metal chloride and aquated tin(II) chloride as solids and then heating at 90—100 °C for several hours. For Ru and Os the products obtained depend upon the metal-to-tin(II) chloride ratios. Attempts to isolate ruthenium complexes with less than four $SnCl_3^-$ ligands by using a suitably smaller Sn : Ru ratio were not successful. Tin-119 n.m.r. measurements on such solutions show significant quantities of the pentakis and tetrakis $SnCl_3^-$ complexes suggesting that $[RuCl_n(SnCl_3)_{(6-n)}]^{4-}$, for $n = 3$—5, are less stable under these conditions. Qualitatively similar results were found for reactions at room temperature. Figure 1 shows the $^{119}$Sn n.m.r. spectra of 3 mol dm$^{-3}$ HCl solutions of different Sn : Ru ratios, measured after 1 h. As may be seen, the tetrakis and the known [17] pentakis compounds are the most abundant. Prolonged heating with excess of $SnCl_2$ affords the $[Ru(SnCl_3)_6]^{4-}$ anion, suggesting that the kinetics for its formation are slow, although excess of $SnCl_2$ and $RuCl_3$ do react to give some $[Ru(SnCl_3)_6]^{4-}$ at room temperature after 1 d. For both Ru and Os, half an equivalent of tin(II) chloride is required to reduce the metal from the III to II oxidation state, and the appropriate signals for the tin(IV) species are always observed in the $^{119}$Sn spectra. Reaction of $IrCl_3$ with excess of $SnCl_2$ in HCl gives analytically pure *trans*-$[PPh_4]_3[IrCl_2(SnCl_3)_4]$ which slowly isomerizes to a mixture of *cis* and *trans* complexes.

The assignment of a given set of resonances to a particular structure has been made from symmetry considerations, microanalytical data, and the following points: (*a*) $\delta(^{119}Sn)$ shifts to successively lower fields with increasing number of $SnCl_3^-$ ligands;[4] (*b*) $^2J(^{119}Sn-^{117}Sn)_{trans}$ is always $>$ 10 000 Hz and a factor of five or more greater than $^2J(^{119}Sn-^{117}Sn)_{cis}$;[8,18] and (*c*) the statistical distribution of $^{117}$Sn and $^{119}$Sn isotopomers with respect to the relative intensities of $^{117}$Sn satellites is known [19] and assists in determining the number of co-ordinated Sn atoms. In essence, $^{119}$Sn n.m.r. spectroscopy is our major structural tool.

(*b*) $^{119}$Sn *N.M.R. Spectroscopy.*—Although we have already reported [18] preliminary results for $[Ru(SnCl_3)_6]^{4-}$, a more detailed spectrum of this and the corresponding osmium anion is presented in Figure 2. In addition to signals arising from the different tin isotopomers, there is a group of six lines arising from coupling to ruthenium-99 ($I = \frac{5}{2}$, natural abundance 12.73%). The observed value of $^1J(^{99}Ru-^{119}Sn)$, 756 Hz, is somewhat smaller than that found for the $[RuCl(SnCl_3)_5]^{4-}$ anion, 846 Hz.[17] For the $[Os(SnCl_3)_6]^{4-}$ anion [Figure 2(*b*)] we find $^1J(^{187}Os-^{119}Sn) = 1\,123$ Hz {1 290 Hz for $[OsCl(SnCl_3)_5]^{4-}$}.[17]

Moriyama *et al.*[4] have found a correlation between $^1J(^{103}Rh-^{119}Sn)$ and $^2J(^{119}Sn-^{117}Sn)$ in the complexes $[RhCl_n(SnCl_6)_{(6-n)}]^{3-}$. Our $^1J(^{187}Os-^{119}Sn)$ and $^1J(^{99}Ru-^{119}Sn)$ data are few but we note that, for $[Ru(SnCl_3)_6]^{4-}$ and $[RuCl(SnCl_3)_5]^{4-}$, $^1J(^{99}Ru-^{119}Sn)$ changes only slightly (756 *vs.* 846 Hz) whereas $^2J(^{119}Sn-^{117}Sn)_{trans}$ is markedly affected (13 034 *vs.* 21 254 Hz). The same trend is seen for $[Os(SnCl_3)_6]^{4-}$ and $[OsCl(SnCl_3)_5]^{4-}$.

The *cis* and *trans* two-bond coupling constants, $^2J(^{119}Sn-^{117}Sn)$, differ significantly in magnitude, *e.g.* for $[Ru(SnCl_3)_6]^{4-}$ (2 429 and 13 034 Hz, respectively). The Table summarizes all of the coupling constant data and we note the following: (*a*) substitution of $SnCl_3$ for Cl decreases $^2J(^{119}Sn-^{117}Sn)_{cis}$; (*b*) $^2J(^{119}Sn-^{117}Sn)_{trans}$ for $[Ru(SnCl_3)_6]^{4-}$ is 13 034 Hz, but that for $[Os(SnCl_3)_6]^{4-}$ is only 11 250 Hz; and (*c*) $^2J(^{119}Sn-^{117}Sn)_{trans}$ can vary from 11 250 to 40 759 Hz with the largest values found for *cis*-$[IrCl_2(SnCl_3)_4]^{3-}$.

Although our two-bond coupling constants may seem somewhat specialized we find parallels to other literature. For $^2J(^{31}P-^{31}P)$ in octahedral metal complexes it is known [20,21]

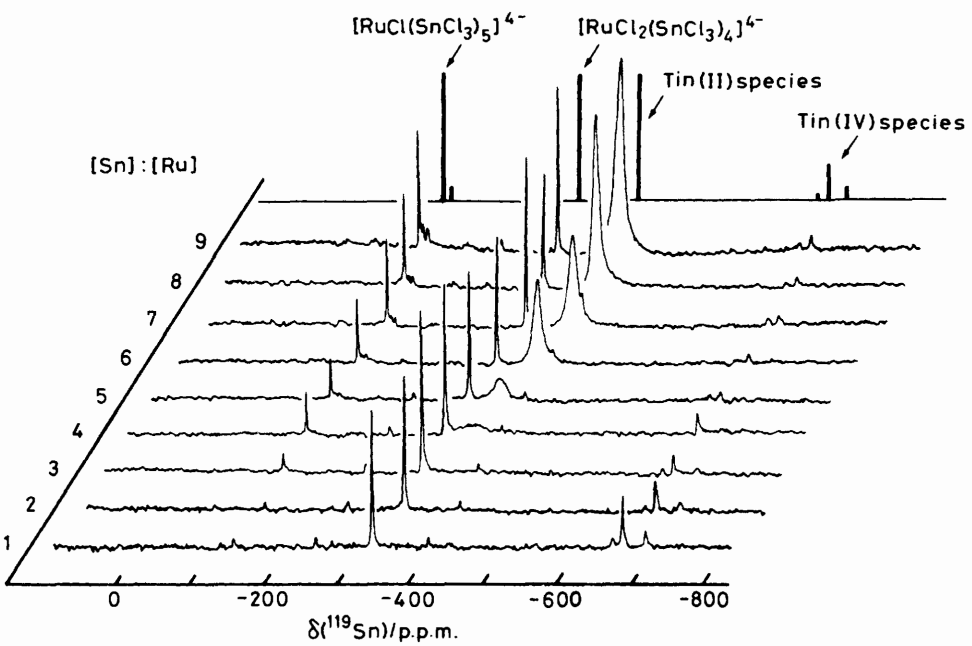

**Figure 1.** 22.30-MHz $^{119}$Sn n.m.r. spectra of a solution of $RuCl_3$ (1.0 mmol) and $SnCl_2 \cdot 2H_2O$ (1.0—9.0 mmol) dissolved in 3 mol dm$^{-3}$ HCl (3 cm$^3$) after 1 h at room temperature. Acquired at 25° C using 90° pulses with 1.0-s delays

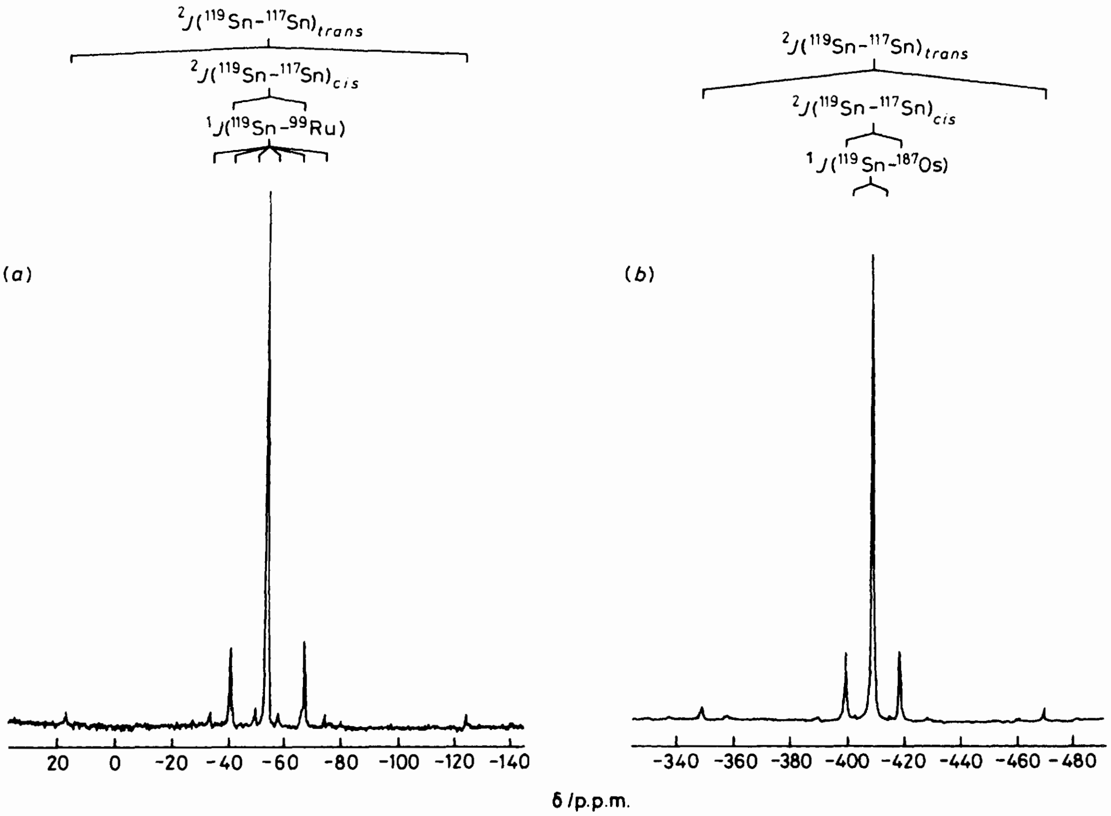

**Figure 2.** 93.27-MHz $^{119}$Sn n.m.r. spectra of $[PPh_4]_4[Ru(SnCl_3)_6]$ (*a*) and $[PPh_4]_4[Os(SnCl_3)_6]$ (*b*) in $CH_3NO_2$–$(CD_3)_2CO$. Accumulated at 20 °C using 80° pulses with 1.0-s delays

**Table.** $^{119}$Sn N.m.r. data for the complexes [a]

| Complex | $\delta(^{119}Sn)$ | $^2J(^{119}Sn-^{117}Sn)_{trans}$ | $^2J(^{119}Sn-^{117}Sn)_{cis}$ |
|---|---|---|---|
| $[Ru(SnCl_3)_6]^{4-}$ [b] | −54.2 | 13 034 | 2 429 |
| $[RuCl(SnCl_3)_5]^{4-}$ [c] | −167.9, −149.2<br>(eq) (ax) | 21 254 | 2 938 (eq–eq)<br>2 581 (eq–ax) |
| *trans*-$[RuCl_2(SnCl_3)_4]^{4-}$ [b] | −381.2 | 26 914 | 3 455 |
| $[Os(SnCl_3)_6]^{4-}$ [b] | −408.9 | 11 250 | 1 775 |
| $[OsCl(SnCl_3)_5]^{4-}$ [c] | −531.8, −581.8<br>(eq) (ax) | 18 600 | 2 169 (eq–eq)<br>1 542 (eq–ax) |
| $[RhCl_2(SnCl_3)_4]^{3-}$ [d] | −204.3 | 2 158 | |
| *trans*-$[IrCl_2(SnCl_3)_4]^{3-}$ [e] | −514.5 | 37 672 | 2 025 |
| *cis*-$[IrCl_2(SnCl_3)_4]^{3-}$ [e] | −477.9, −589.6<br>(*trans*) (*cis*) | 40 759 | 1 744 (eq–eq) |
| $[N(PPh_3)_2][Pd(SnCl_3)_3(cod)]$ [f] | 33.2 | 1 092 | |
| $[N(PPh_3)_2][Pt(SnCl_3)_3(cod)]$ [f] | −132.5 | 619 | |
| *trans*-$[Pd(SnCl_3)_2(AsEt_3)_2]$ [g] | 11 | 37 164 | |
| *trans*-$[Pt(SnCl_3)_2(AsEt_3)_2]$ [g] | −39 | 35 090 | |

[a] Coupling constants in Hz, chemical shifts in p.p.m. relative to $SnMe_4$. [b] $CH_3NO_2$–$(CD_3)_2CO$, *ca.* 4 : 1. [c] From ref. 17. [d] Suggested from ref. 4 to be dynamic on the n.m.r. time-scale. [e] $CH_2Cl_2$–$(CD_3)_2CO$, *ca.* 4 : 1; 0 °C. [f] From ref. 7, average $^2J(^{119}Sn-^{117}Sn)$; cod = cyclo-octa-1,5-diene. [g] From ref. 8.

that (1) the coupling is larger when the spins are *trans* and (2) $^2J$ can be larger for second-row transition metals than for third row. In contrast to $^2J(^{119}Sn-^{117}Sn)$, $^2J(^{31}P-^{31}P)$ spin–spin coupling constants in metal phosphine complexes have been interpreted in terms of the Pople–Santry [22] expression by the extended-Hückel method.[23–25] Large $\pi(PP)_{trans}$ (positive) and small $\pi(PP)_{cis}$ (negative) ($\pi$ = polarisability) give rise to observation (1) and stem from the bonding properties of metal phosphine co-ordination such that the $p_\sigma$-type orbital is dominant for the *trans*-disposed ligands, whereas only the $d_\sigma$-type orbital is important for the *cis*-disposed ligands.[25] It would seem therefore that the qualitative aspects of our observed $^2J(^{119}Sn-^{117}Sn)$ are not new and it remains for us to understand the quantitative details.

## Experimental

*N.M.R. Measurements.*—$^{119}$Sn N.m.r. spectra of the trichlorostannate complexes were measured as solutions in 10-mm tubes using JEOL FX 60Q and Bruker WM-250 spectrometers operating at 22.30 and 93.27 MHz, respectively. Spectra were routinely measured using 90° (Fx 60 Q) and *ca.* 80° (WM-250) flip angles at ambient temperature. Chemical shifts were relative to external $SnMe_4$ as reference, with a negative sign indicating a shift to higher field.

*Preparation of the Complexes.*—Although the trichlorostannate complexes were stable to air, at least in the solid state, all of the preparations and procedures for measuring their n.m.r. spectra were carried out in an atmosphere of $N_2$. The compounds $RuCl_3\cdot3H_2O$, $K_2[OsCl_6]$, and $IrCl_3\cdot6H_2O$ were obtained from Johnson Matthey, and $SnCl_2\cdot2H_2O$ from Fluka (analytically pure grade).

$[PPh_4]_4[Ru(SnCl_3)_6]$. Hydrochloric acid (2 mol dm$^{-3}$, 10 cm$^3$) was added to a mixture of $RuCl_3\cdot3H_2O$ (0.5 g, 1.5 mmol) and $SnCl_2\cdot2H_2O$ (4.3 g, 19 mmol). The resulting dark brown solution was heated to 90 °C for 12 h during which time the solution colour changed successively to indigo-blue, dark green, brown, orange, and finally yellow. This solution was then treated dropwise with $PPh_4Cl$ (2.87 g, 7.6 mmol), dissolved in 2 mol dm$^{-3}$ HCl (25 cm$^3$). The yellow solid which precipitated was filtered off and washed successively with 2 mol dm$^{-3}$ HCl, EtOH, and $Et_2O$, and then dried *in vacuo* to afford the product (4.32 g, 81%) (Found: C, 40.9; H, 2.90; Cl, 22.85. $C_{96}H_{80}Cl_{18}P_4RuSn_6$ requires C, 41.05; H, 2.85; C, 22.7%).

$[PPh_4]_4[Os(SnCl_3)_6]$. A mixture of $K_2[OsCl_6]$ (0.24 g, 0.50 mmol) and $SnCl_2\cdot2H_2O$ (1.13 g, 5.0 mmol) was dissolved in 2 mol dm$^{-3}$ HCl (5 cm$^3$) and the dark brown solution heated at 100 °C for 5 d. The resulting pale yellow solution was then treated with $PPh_4Cl$ (0.75 g, 2.0 mmol), dissolved in 2 mol dm$^{-3}$ HCl (10 cm$^3$), and the yellow solid which precipitated was collected and washed as described above (1.25 g, 86%) (Found: C, 39.75; H, 2.75; Cl, 22.0. $C_{96}H_{80}Cl_{18}OsP_4Sn_6$ requires C, 39.8; H, 2.80; Cl, 22.0%).

$[PPh_4]_3[IrCl_2(SnCl_3)_4]$. A mixture of $IrCl_3\cdot6H_2O$ (0.08 g, 0.20 mmol) and $SnCl_2\cdot2H_2O$ (0.36 g, 1.6 mmol) suspended in 3 mol dm$^{-3}$ HCl (3 cm$^3$) was heated to 90 °C for 2 h. The resulting orange solution was then treated with $PPh_4Cl$ (0.25 g, 0.66 mmol) in 2 mol dm$^{-3}$ HCl (10 cm$^3$) after which the product precipitated as a yellow-orange powder. Filtration, washing successively with 2 mol dm$^{-3}$ HCl, EtOH, and then $Et_2O$, followed by recrystallization from $CH_2Cl_2$–$CH_3OH$ gave the product (0.37 g, 85%) (Found: C, 39.15; H, 2.80; Cl, 22.65. $C_{72}H_{60}Cl_{14}IrP_3Sn_4$ requires C, 39.65; H, 2.75; Cl, 22.75%).

*trans*-$[NMe_4]_4[RuCl_2(SnCl_3)_4]$. A mixture of $RuCl_3\cdot3H_2O$ (0.26 g, 1.0 mmol) and $SnCl_2\cdot2H_2O$ (0.46 g, 2.0 mmol) was dissolved in 3 mol dm$^{-3}$ HCl (3 cm$^3$) and stirred at room temperature for 0.5 h. The colour changed from brown to indigo-blue and finally dark green. The resulting solution was treated with $NMe_4Cl$ (0.4 g, 3.6 mmol) in 3 mol dm$^{-3}$ HCl (10 cm$^3$) to afford a dark brown precipitate. Filtration, washing successively with 3 mol dm$^{-3}$ HCl, EtOH, and then $Et_2O$ gave the product (Found: C, 13.9; H, 4.05; Cl, 36.9; N, 4.10. $C_{16}H_{48}Cl_{14}N_4RuSn_4$ requires C, 14.05; H, 3.55; Cl, 36.25; N, 4.10%).

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