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# SYNTHESIS AND NMR SPECTROSCOPY OF THE NEW IRIDIUM(I) AND RHODIUM(I) FIVE-COORDINATE TRICHLOROSTANNATE COMPLEXES (PPN)[M($SnCl_3$)$_2$(diolefin)($PR_3$)]

M. KRETSCHMER, P.S. PREGOSIN * and M. GARRALDA

*Laboratorium für Anorganische Chemie, ETH-Zentrum, Universitätstrasse 6, CH-8092 Zurich (Switzerland)*

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## Summary

The syntheses of the new five-coordinate trichlorostannate complexes (PPN)-[M($SnCl_3$)$_2$(1,5-COD)($PR_3$)] ($M = Rh$, Ir, $R = C_6H_5$, *p*-$ClC_6H_4$, *p*-$FC_6H_4$, *p*-$OCH_3C_6H_4$), (PPN)[Rh($SnCl_3$)$_2$(NBD)($PR_3$)] and [Ir($SnCl_3$)(CO)(1,5-COD)($PR_3$)] (PPN = bis(triphenylphosphino)imine) are reported, as well as their $^{119}Sn$ and $^{31}P$ NMR spectroscopic characteristics. The bis-$SnCl_3$ compounds show $^2J(^{119}Sn, ^{117}Sn)$ coupling constants in the range 891–3381 Hz, and these can vary by as much as a factor of three as a function of both the *para*-phosphine substituent and chelating olefin.

## Introduction

Mixtures of tin(II) chloride and platinum(II) salts have aroused considerable interest since early reports of their potential as catalysts in homogeneous hydrogenation and hydroformylation reactions [1]. We have been concerned with the synthesis and multinuclear NMR spectroscopy of the trichlorostannate complexes which are formed in such mixtures [2–12] and have recently shown that whereas mono- and tris-$SnCl_3^-$ complexes of palladium(II), platinum(II), rhodium(I) and iridium(I) are easily prepared, bis-$SnCl_3$ derivatives are somewhat scarcer [8,9]. Since all of our rhodium(I) and iridium(I) M($SnCl_3$) and M($SnCl_3$)$_3$ compounds were invariably associated with a five-coordinate metal [7–9], we thought it useful to determine which metals and ligands would permit easy access to complexes containing two trichlorostannate ligands, and we now report our results for some new complexes of rhodium(I) and iridium(I).

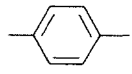
## Results and discussion

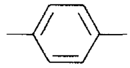
### *1. Preparation*

Our previous synthetic route to the dianionic complexes (PPN)$_2$[M($SnCl_3$)$_3$(diolefin)] (M = Rh, Ir; diolefin = 1,5-cyclooctadiene (COD) and norbornadiene(NBD); PPN = bis(triphenylphosphino)imine) involved the reaction of the dimeric complexes $[M(\mu\text{-Cl})(\text{diolefin})]_2$(I) with three equivalents of tin per metal. The tin was provided as one equivalent of $SnCl_2$ and two equivalents of $(PPN)(SnCl_3)$/metal [9]. We were unable to detect square planar intermediates but found the coordinatively saturated five-coordinate complexes to be stable isolable species. Since the metal seems to accept $SnCl_3^-$ ligands until the 18-electron rule is satisfied, we chose to prepare our bis-$SnCl_3$ molecules by first offering the metal a tertiary phosphine and afterwards the requisite number of tin ligands.

$$[M(\mu\text{-Cl})(1,5\text{-COD})]_2 + 2PR_3 \longrightarrow 2[MCl(1,5\text{-COD})(PR_3)] \quad (1)$$

$$[MCl(1,5\text{-COD})(PR_3)] + SnCl_2 + (PPN)SnCl_3 \longrightarrow (PPN)[M(SnCl_3)_2(1,5\text{-COD})(PR_3)] \quad (2)$$

(IIIa, M = Rh, R = —X, X = Cl, F, H, $OCH_3$;

IIIb, M = Ir, R = —X, X = Cl, F, H, $OCH_3$)

Starting from $[M(\mu\text{-Cl})(COD)]_2$, the arylphosphine complexes $[MCl(1,5\text{-COD})(PR_3)]$ (II) are readily prepared by cleavage of the halogen bridge in $CH_2Cl_2$ solution [13,14]. These square planar compounds can, but need not be, isolated, and react smoothly with one equivalent of $SnCl_2$ and one of $PPN(SnCl_3)$ to afford the complexes $(PPN)[M(SnCl_3)_2(1,5\text{-COD})(PR_3)]$ (III) in good yield (see eq. 1 and 2). Similar rhodium(I) complexes with NBD (IV) were also prepared, and a list of some of the new derivatives is shown in Table 1 with their microanalytical data. The

TABLE 1

MICROANALYTICAL DATA

| Complex | Analysis (found (calcd.) (%)) | | |
|---|---|---|---|
| | C | H | Cl |
| $(PPN)[Rh(SnCl_3)_2(COD)(PPh_3)]$ | 50.28 | 3.92 | 14.83 |
| | (50.93) | (3.93) | (14.55) |
| $(PPN)[Rh(SnCl_3)_2(COD)(p\text{-Cl})]$ | 47.01 | 3.45 | 20.02 |
| | (47.54) | (3.45) | (20.41) |
| $(PPN)[Rh(SnCl_3)_2(NBD)(PPh_3)]$ | 50.61 | 3.80 | 14.69 |
| | (50.66) | (3.69) | (14.71) |
| $(PPN)[Rh(SnCl_3)_2(NBD)(p\text{-Cl})]$ | 47.07 | 3.26 | 20.61 |
| | (47.26) | (3.23) | (20.63) |
| $(PPN)[Ir(SnCl_3)_2(COD)(PPh_3)]$ | 47.82 | 3.81 | 13.73 |
| | (47.99) | (3.70) | (13.71) |
| $(PPN)[Ir_2(SnCl_3)_2(COD)(p\text{-F})]$ | 45.90 | 3.38 | 13.51 |
| | (46.38) | (3.39) | (13.25) |
| $[Ir(SnCl_3)(CO)(COD)(PPh_3)]$ [a] | 40.06 | 3.43 | 13.21 |
| | (39.75) | (3.34) | (13.04) |
| $[Ir(SnCl_3)(CO)(COD)(p\text{-Cl})]\cdot 0.5(CH_3)_2CO$ | 36.24 | 2.79 | 22.32 |
| | (36.10) | (2.87) | (22.43) |

[a] $\nu$(CO) ($cm^{-1}$) for the 4 phosphine: p-H, 2000; p-$Ch_3O$, 2000, 1970; p-F, 2005; p-Cl, 2010.

TABLE 2

NMR DATA [a] FOR THE SnCl$_3$ COMPLEXES [b]

| Compound | $\delta(^{119}\mathrm{Sn})$ | $^2J(^{119}\mathrm{Sn},^{117}\mathrm{Sn})$ | $^1J(^{103}\mathrm{Rh},^{119}\mathrm{Sn})$ | $^2J(^{119}\mathrm{Sn},^{31}\mathrm{P})$ | $^1J(^{103}\mathrm{Rh},^{31}\mathrm{P})$ | $\delta(^{31}\mathrm{P})$ |
|---|---|---|---|---|---|---|
| (PPN)[Rh(SnCl$_3$)$_2$(COD)(PPh$_3$)] | 38.3 | 2747 | 674 | 350 | 117 | 40.6 |
| (PPN)[Rh(SnCl$_3$)$_2$(COD)(*p*-OCH$_3$)] | 34.8 | 3381 | 684 | 358 | 115 | 35.5 |
| (PPN)[Rh(SnCl$_3$)$_2$(COD)(*p*-F)] | 44.1 | 2649 | 671 | 346 | 118 | 38.1 |
| (PPN)[Rh(SnCl$_3$)$_2$(COD)(*p*-Cl)] | 39.1 | 3149 | 671 | 344 | 117 | 38.7 |
| (PPN)[Rh(SnCl$_3$)$_2$(NBD)(PPh$_3$)] [c] | 66.6 | 1270 | 757 | 349 | 129 | 45.5 |
| (PPN)[Rh(SnCl$_3$)$_2$(NBD)(*p*-OCH$_3$)] | 65.0 | 1624 | 757 | 352 | 128 | 40.9 |
| (PPN)[Rh(SnCl$_3$)$_2$(NBD)(*p*-F)] | 71.8 | 1074 | 757 | 349 | 129 | 43.0 |
| (PPN)[Rh(SnCl$_3$)$_2$(NBD)(*p*-Cl)] | 66.8 | 891 | 757 | 344 | 131 | 44.3 |
| (PPN)[Ir(SnCl$_3$)$_2$(COD)(PPh$_3$)] [d] | −217.6 | 1355 | | 280 | | 9.6 |
| (PPN)[Ir(SnCl$_3$)$_2$(COD)(*p*-OCH$_3$)] | −220.2 | 1831 | | 287 | | 3.6 |
| (PPN)[Ir(SnCl$_3$)$_2$(COD)(*p*-F)] | −210.1 | 1282 | | 273 | | 6.7 |
| (PPN)[Ir(SnCl$_3$)$_2$(COD)(*p*-Cl)] | −208.4 | 903 | | 271 | | 8.5 |
| [Ir(SnCl$_3$)(CO)(COD)(PPh$_3$)] | −204.0 | | | 196 | | 8.7 |
| [Ir(SnCl$_3$)(CO)(COD)(*p*-OCH$_3$)] | −208.4 | | | 209 | | 4.3 |
| [Ir(SnCl$_3$)(CO)(COD)(*p*-F)] | −198.4 | | | 199 | | 6.0 |
| [Ir(SnCl$_3$)(CO)(COD)(*p*-Cl)] | −196.6 | | | 186 | | 7.1 |

[a] Chemical shifts in ppm, ±0.1, coupling constants in Hz. ± 12 Hz for $^2J(^{119}\mathrm{Sn},^{117}\mathrm{Sn})$ and $^1J(^{103}\mathrm{Rh},^{119}\mathrm{Sn})$, ± 1.2 Hz for the others. [b] The abbreviations *p*-OCH$_3$, *p*-F and *p*-Cl represent *p*-CH$_3$OC$_6$H$_4$, *p*-FC$_6$H$_4$ and *p*-ClC$_6$H$_4$, respectively. The first 12 complexes were measured in acetone-$d_6$/acetone, 1/3, concentration = $3.3 \times 10^{-2}$ mol/l at 223 K. The last four in CDCl$_3$ at room temperature. [c] $\delta(^{13}\mathrm{C})$ olefin: 62.17, aliphatic: 48.00, 46.90, CDCl$_3$, room temperature. [d] $\delta(^{13}\mathrm{C})$ olefin: 68.48, $^2J(^{31}\mathrm{P},^{13}\mathrm{C})$ 39 Hz, $^2J(^{119,117}\mathrm{Sn},^{13}\mathrm{C})$ 67.0 Hz, $\delta(^{31}\mathrm{C})$ aliphatic: 33.20, $^3J(^{119,117}\mathrm{Sn},^{13}\mathrm{C})$ 49.0 Hz.

complexes are all air stable solids which are moderately soluble in acetone, methylene chloride and chloroform, but insoluble in benzene, diethyl ether and ethanol. The rhodium complexes are orange-red and the iridium yellow. The carbon monoxide derivatives [Ir(SnCl$_3$)(CO)(1,5-COD)(PR$_3$)] are prepared by reaction of the appropriate complexes (IIIb) with CO in acetone and served as useful comparison substances for the spectroscopic studies.

## 2. *NMR Spectroscopy*

The presence of two coordinated SnCl$_3^-$ ligands and one tertiary aryl phosphine was confirmed by $^{31}$P and $^{119}$Sn NMR spectroscopy. The $^{31}$P{$^1$H} spectra showed main-band resonances as well as satellite signals (due to the spin $I = 1/2$ isotopes $^{119}$Sn, 8.6%, and $^{117}$Sn, 7.6%) whose intensities were correct for two coordinated SnCl$_3$ ligands [15]. The rhodium complexes showed the expected $^{103}$Rh splitting. The $^{119}$Sn spectra consisted of doublets arising from the single $^{31}$P spin plus $^{117}$Sn satellites due to the isotopomeric anions. [M($^{119}$SnCl$_3$)($^{117}$SnCl$_3$)(diolefin)(PR$_3$)]$^-$. Once again the intensities of these $^{117}$Sn satellites were correct for bis-SnCl$_3$ complexes. For the compounds IIIa, coupling between $^{103}$Rh and $^{119}$Sn was also observed (see Fig. 1) and all the chemical shift and coupling constant data are tabulated in Table 2. These multiplicity data when combined with the microanalytical and $^{13}$C results support the formulation of III as five-coordinate complexes containing two coordinated SnCl$_3$ ligands. Inspection of the data reveals a number of interesting NMR spectroscopic details:

(a) The two-bond homonuclear coupling constant $^2J(^{119}\text{Sn},^{117}\text{Sn})$ falls in the range 891–3381 Hz and depends upon (i) the metal, (ii) the olefin with III > IV, and (iii) the *para*-substituent of the phosphine.

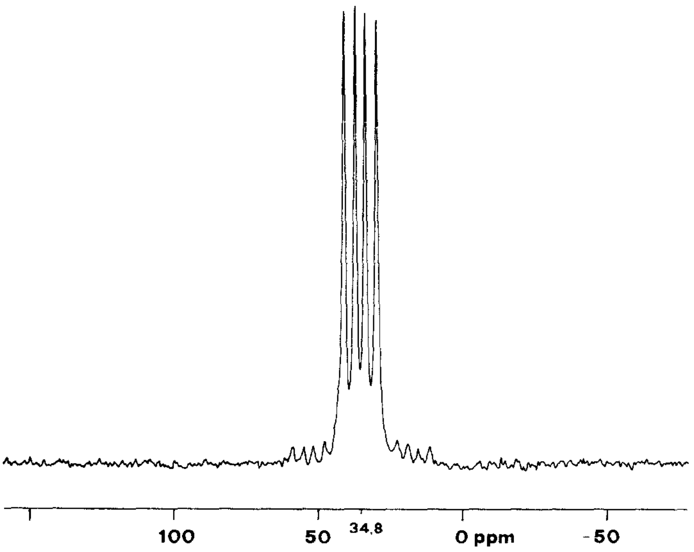


Fig. 1. $^{119}$Sn NMR spectrum (acetone-$d_6$) of (PPN)[Rh(SnCl$_3$)$_2$(COD)P($p$-OCH$_3$C$_6$H$_4$)$_3$] at 223 K. 1100 Hz/cm. The doublet of doublets arises from spin–spin coupling to $^{103}$Rh and $^{31}$P. The $^{117}$Sn satellites are also observable.

(b) $^1J(^{103}Rh,^{119}Sn)$ depends upon the olefin (it is 671–684 Hz for the 1,5-COD complexes and 757 Hz for the NBD derivatives) but not at all on the phosphine.

(c) $^2J(^{119}Sn,^{31}P)$ and $^1J(^{103}Rh,^{119}Sn)$ vary only slightly when compared to $^2J(^{119}Sn,^{117}Sn)$.

(d) $\delta(^{119}Sn)$ is not especially responsive to change in the aryl phosphine, although there is a moderate downfield shift ($<31$ ppm) on changing from III to IV. The usual effect of varying the metal is observed, with Ir complexes at much higher field ($\delta$ $-208$ to $-220$ ppm) than the Rh analogs ($\delta$ 38 to 72 ppm).

We find point (a) to be most interesting. We have shown that $^2J(^{119}Sn,^{117}Sn)$ can be as small as several hundred Hz or exceed 35000 Hz [8,9] and, consequently, it is not surprising that such a sensitive parameter reflects the subtle differences resulting from changing the *para*-substituent on the phosphine. In all 12 of our bis-$SnCl_3$ complexes the stronger donor (and more basic [16]) phosphines produce an increase in $^2J(^{119}Sn,^{117}Sn)$, with the change exceeding 100% for the iridium(I) compounds. To our knowledge, there are no previous examples of such a large change in a coupling constant as a function of the *para*-substituent on an aryl phosphine. It is possible that such empirical observations will prove useful in the future. Interestingly, when compared to the complex dianions $[M(SnCl_3)_3(diolefin)]^{2-}$ (V, 1,5-COD); VI, NBD), the changes in $^2J(^{119}Sn,^{117}Sn)$ are somewhat erratic. For V, $^2J(^{119}Sn,^{117}Sn)$ is 1681 Hz, less than the 2747–3381 Hz range found for III, but in VI, the value of 2411 Hz exceeds the 891–1624 Hz values found in IV. Obviously, subtle effects are quite important for this coupling constant.

### *3. Concluding remarks*

Five-coordinated anionic complexes containing two $SnCl_3$ ligands are easily accessible provided that the molecule contains a sufficient number of ligands such that a stable 16-electron chloro-rhodium or -iridium entity is available before addition of the tin containing ligands. In the light of the existence of mono- [17] and pentakis-$SnCl_3$ [18] complexes, and of our bis- and tris-molecules it would seem that poly-trichlorostannate complexes of rhodium(I) are generally stable isolable species, e.g., $[Rh(SnCl_3)_n(NBD)(PPh_3)_{(3-n)}]^{-n+1}$ are all known for $n = 1$–3. We do not know, as yet, whether our new complexes will demonstrate catalytic activity; however, since one $SnCl_3^-$ ligand is easily displaced by CO to form the neutral compounds $[M(SnCl_3)(CO)(1,5\text{-}COD)(PR_3)]$, additional ligands can gain access to the metal.

On the NMR spectroscopic side, these new tin containing molecules, provide further empirical evidence for the sensitivity of $^2J(^{119}Sn,^{117}Sn)$ to structural change. Unfortunately, these values do not seem to correlate with either $^1J(^{103}Rh,^{119}Sn)$ or $^1J(^{103}Rh,^{31}P)$, and consequently will probably not be directly relatable to the strength of these metal ligand interactions. Nevertheless, this two-bond coupling could be monitoring a higher lying molecular orbital, with relatively large *s*-coefficients at the tin atoms, which may be sensitive to the nature of the ligand.

## Experimental

The olefins and solvents were obtained from Fluka AG, Buchs, Switzerland, and were "pro analysi". All reactions were carried out at room temperature under an $N_2$ atmosphere. Rhodium complexes $[MCl(diolefin)(P(p\text{-}XC_6H_4)_3)]$ (M = Rh, Ir; diolefin = COD (1,5-cyclooctadiene), NBD (norbornadiene) and X = Cl, F, H and $OCH_3$) were prepared by literature methods [14] as was the bis(triphenylphosphinoimine)chloride, (PPN)Cl [19].

The NMR spectra were measured in 10 mm tubes (5 mm for $^1H$) using a Bruker WM 250 operating at 101.3 MHz for $^{31}P$, 93.3 MHz for $^{119}Sn$ and 62.9 MHz for $^{13}C$. Solvents, temperatures and experimental errors are given in the Tables. Chemical shifts are in ppm, coupling constants in Hz. References are: for $^{31}P$, external $H_3PO_4$; for $^{119}Sn$, $Me_4Sn$; for $^{13}C$, $Me_4Si$. Typically, pulse angles and acquisition times were: $^{31}P$; 35°, 0.8 sec. $^{119}Sn$; 50–70°, 0.08 sec. $^{13}C$; 45°, 0.6 sec. IR spectra were measured as KBr pellets using a Beckman IR 4250. Microanalytical data are from the ETH-Zentrum, Zürich.

### *Preparation of the complexes*

*(PPN)[Rh($SnCl_3$)$_2$(COD)P(p-X$C_6H_4$)$_3$] (X = Cl, F, H, $OCH_3$).* The following is representative for all four phosphines: Solid anhydrous tin(II) chloride (0.038 g, 0.2 mmol) was added to a suspension of [RhCl(COD)P(*p*-Cl$C_6H_4$)$_3$] (0.061 g, 0.1 mmol) in 3 ml acetone. Stirring for five minutes was followed by the addition of (PPN)Cl (0.057 g, 0.1 mmol). The resulting deep red solution was treated with 15 ml petroleum ether (30–60°C) and the product was filtered off and dried in vacuo (0.135 g, 86.3%).

The following complexes were prepared in an identical manner: (PPN)-[Rh($SnCl_3$)$_2$(NBD)P(*p*-X$C_6H_4$)$_3$] (X = Cl, F, H, $OCH_3$) yield 70–95% and (PPN)[Ir($SnCl_3$)$_2$(COD)P(*p*-X$C_6H_4$)$_3$] (X = Cl, F, H, $OCH_3$) yield 70–95%.

*Ir($SnCl_3$)(CO)(COD)P(p-X$C_6H_4$)$_3$] (X = Cl, F, H, $OCH_3$).* The following is representative for all four phosphines: A solution of (PPN)[Ir($SnCl_3$)$_2$(COD)($PPh_3$) (0.310 g, 0.2 mmol) in 4 ml acetone was treated with gaseous CO for 1 h. During this period a pale yellow crystalline material separated. This was filtered off and dried in vacuo (0.075 g, 46.1%). Prepared identically: [Ir($SnCl_3$)(CO)(COD)P(*p*-X$C_6H_4$)$_3$], X = Cl, F, H, $OCH_3$ yield 46–76%.

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