^{1}H, ^{31}P and ^{119}Sn NMR Studies of Iridium Trichlorostannate Complexes

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The blue-green Ir(I) complexes resulting from the reaction of trans-$[IrCl(CO)P_2]$, $P = P(p\text{-}XC_6H_4)_3$, $X = H, F, Cl, OCH_3$, *with tin(II) chloride are discussed. The complexes are suggested to be isomers of composition* $[IrCl(CO)(SnCl_2)P_2]$ *which contain bridging halogen ligands, and are unusual in that the tin is not coordinated to iridium. Reaction of a mixture of these intermediates with either HCl or* H_2 *gives the expected* $[IrHCl(SnCl_3)(CO)P_2]$ *or* $[IrH_2(SnCl_3)(CO)P_2]$ *products. These Ir(III) complexes contain the Ir–Sn bond and show large* $^{2}J(^{119}Sn,^{1}H)_{trans}$ *coupling constants (>1200 Hz), which may be used to assign geometry. The products resulting from the reaction of Vaska's complex with tin(IV) chloride are suggested to be isomers involving five-coordinate tin and five-coordinate iridium.* ^{119}Sn, ^{31}P *NMR and* ^{1}H *data for all the complexes are reported, with the metal chemical shift encompassing a range of ~700 ppm. NMR spectroscopic data for the complexes* $[Ir(SnCl_3)(CO)_2P_2]$ *and* $[Ir(O_2)(SnCl_3)CO(PPh_3)_2]$ *are also reported.*

Introduction

We have been interested in the NMR spectroscopic properties of a variety of 'Pt–$SnCl_3$' complexes [1] in that these molecules are known to homogeneously catalyze the hydrogenation of olefins [2]. In all cases we observed the formation of the Pt–$SnCl_3$ moiety at either low or moderate temperatures. This is despite the fact that the $SnCl_3^-$ group can appear in other forms, *e.g.* anionic $SnCl_3^-$ [3] or $SnCl_2$ bridging an M–Cl bond [4]. Furthermore, although the ^{119}Sn (I = 1/2, natural abundance = 8.6%) chemical shift is well known for alkyl tin(IV) compounds, there is extremely little known for tin coordinated to transition metals [5] and specifically for the M–$SnCl_3$ case [6]. To increase our understanding of both the metal-trichlorostannate interaction and their ^{119}Sn NMR characteristics, we have begun a study of the reaction of tin(II) chloride, $SnCl_2$, with iridium complexes, and report here results for Vaska's complex *trans*-$[IrCl(CO)(PPh_3)_2]$ and some analogous $P(p\text{-}XC_6H_4)_3$ derivatives. Several studies have discussed Ir(III)–$SnCl_3$ chemistry [7–9] and a recent report concerns the five-coordinate $[Ir(SnCl_3)(diolefin)P_2]$ complexes [10]; however, none of these contain ^{119}Sn NMR data. Although [7] discusses the reaction of Vaska's complex with tin(IV) chloride, the structure of the product is uncertain.

Experimental

NMR spectra of the complexes were measured as solutions in 10 mm tubes (5 mm for ^{1}H) using a Bruker WM-250 operating at 250 MHz for ^{1}H, 101 MHz for ^{31}P and 93 MHz for ^{119}Sn. Spectra were routinely measured using ~45° flip angles and relatively short acquisition times (~3, 0.8 and 0.2 sec for ^{1}H, ^{31}P and ^{119}Sn, respectively). Solvents, temperatures and experimental errors are given in the Tables. IR spectra were measured as KBr pellets using a Beckman IR 4250. Microanalytical data stem from the ETH-Zentrum, Zurich.

Preparation of the Complexes

All operations were carried out under a nitrogen atmosphere using previously dried solvents.

Vaska's complex was prepared according to the literature [11], as was anhydrous tin(II) chloride [12]. Our experience with the latter preparation based on acetic anhydride is that traces of acetic acid are often present which lead to the formation of Ir(III) hydride complexes as impurities. The $ClCH_2CH_2Cl/CH_3CH_2OH$ method is preferable [12]. Tin(IV) chloride was freshly distilled under a nitrogen atmosphere, and directly employed in the syntheses.

$[IrCl(CO)(P(p\text{-}XC_6H_4)_3)_2(SnCl_2)]$, $X = Cl, F, H, OCH_3$

The following is representative for all four phosphines: solid $SnCl_2$ (25.4 mg; 0.15 mmol) was added to a solution of $[IrCl(CO)(P(p\text{-}FC_6H_4)_3)_2]$ (133 mg, 0.15 mmol) in 3 ml CH_2Cl_2 under a nitrogen atmosphere. The resulting blue-green solution was then slowly concentrated over a period of about 1 h using a stream of nitrogen gas. The deep blue residue was then dried overnight *i.v.* to afford 121 mg of product

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(75%) as a powder. In the solid state the material decomposes slowly in air. In solution the compound is very sensitive to both moisture and oxygen.

[IrHCl(SnCl$_3$)(CO)(P(p-FC$_6$H$_4$)$_3$)$_2$]

The procedure described above was employed using 4 ml of toluene rather than CH_2Cl_2. Instead of concentration, gaseous HCl was passed through the solution for ~3 min. (this may not be necessary as the solution color changes instantaneously from blue-green to yellow). Addition of 10 ml of petroleum ether (30–60°) induces precipitation of the product which was filtered and dried *i.v.* From 133 mg of the Vaska's derivative we obtain 145 mg (88%) of product. The same product can be obtained by addition of an 10 fold excess of $SnCl_2$ to a suspension of the Vaska's derivative in 10 ml acetone. The resulting yellow solution was evaporated to dryness and extracted with chloroform. Concentration to ~1 ml followed by the addition of ethanol induces precipitation of the pale yellow product which may be collected by filtration. From 150 mg starting phosphine complex we obtain 170 mg (90%) of product. The failure to observe the blue-green color is related to the quality (relatively wet) of the acetone. The two methods (toluene as opposed to acetone) differ in that the latter gives pure $[IrHCl(SnCl_3)(CO)(P(p\text{-}FC_6H_4)_3)_2]$ whereas with the former we find $[IrHCl_2(CO)(P(p\text{-}FC_6H_4)_3)_2]$ as an impurity.

[IrH$_2$(SnCl$_3$)(CO)(P(p-FC$_6$H$_4$)$_3$)$_2$]

The procedure described for $[IrCl(CO)(SnCl_2)(P(p\text{-}FC_6H_4)_3)_2]$ was followed using 4 ml toluene as solvent. Instead of concentration, the blue-green solution was treated with dihydrogen for 20 min. The resulting yellow solution was concentrated to half its original volume and then treated with 10 ml of petroleum ether (30–60°). The product precipitates and may be collected and dried. From 133 mg of phosphine complex we obtain 99 mg (65%) of pure product.

[Ir(SnCl$_3$)(CO)$_2$(P(p-FC$_6$H$_4$)$_3$)$_2$]

The same procedure as that described for $[IrH_2(SnCl_3)(CO)(P(p\text{-}FC_6H_4)_3)_2)]$ was followed except that the solution was treated with gaseous CO for 30 min. During this period a pale yellow crystalline material precipitates. This may be collected by filtration and dried *i.v.* to afford the product. From 200 mg of phosphine complex and 43 mg $SnCl_2$ we obtain 162 mg (65%) of pure product.

[IrCl(CO)(P(p-FC$_6$H$_4$)$_3$)$_2$(SnCl$_4$)]

To a solution of $[IrCl(CO)(P(p\text{-}FC_6H_4)_3)_2]$ (89 mg, 0.10 mmol) in 3 ml toluene was injected a solution of freshly distilled $SnCl_4$ (0.1 mmol) in 1 ml toluene. The resulting pale yellow solution was concentrated to ~1 ml and then treated with 10 ml petroleum ether (30–60°). The precipitate which results was collected by filtration and dried *i.v.* (106 mg, 92%).

Results and Discussion

a) Iridium(I)–Tin

Reaction of *trans*-$[IrCl(CO)(P(p\text{-}XC_6H_4)_3)_2]$, X = OCH_3, H, Cl, F, with one equivalent of anhydrous tin(II) chloride, $SnCl_2$, in dry solvents, leads to deeply colored solutions from which it is possible to isolate blue-green complexes as powders. These molecules are both air and moisture sensitive in solution. Their IR spectra show two bands in the region 1945–1960 cm^{-1} and 2020–2050 cm^{-1} which we attribute to carbonyl stretches. For our blue-green solutions in CH_2Cl_2/C_6D_6(4:1) the $^{31}P(^1H)$ spectra reveal only broad resonances at room temperature, suggesting dynamic behavior on the NMR time scale. At 193 K we observe *red* solutions* which give sharp signals due to two complexes, I and II, both with tin satellites (see Fig. 1). One of the two compounds (I) has equivalent phosphorus atoms, whereas II reveals an AB pattern with $^2J(^{31}P,^{31}P) = 325–330$ Hz. The magnitude of this coupling places the two phosphorus nuclei in a *trans* orientation [13]. Furthermore, the relative abundance of the two components is phosphine dependent (see Table I) with increasing quantities of II favored by electron withdrawing groups.

The ^{119}Sn NMR spectra also show the presence of two complexes at very *low* field, $\delta = 206–241$ and $\delta = 147–154$, which may be assigned to I and II, respectively. Low temperature ^1H spectra show no resonances attributable to hydride ligands, with the aromatic protons being complicated by the mixture as well as by the non-equivalence of the aryl phosphines. Interestingly, at –80 ℃ for $P(p\text{-}FC_6H_4)_3$ we observe a relatively sharp triplet which appears at $\delta = 5.84$. Since at room temperature there are no signals below $\delta = 7.14$, we have a new situation in which one proton environment is markedly shielded. As high field shifts of *ortho* protons in $[Ir(Ph_2PCH_2CH_2PPh_2)_2]^+$ [14] are known, and attributed to close contacts between the metal and phenyl ring, the significance of our observation remains uncertain.

At this point a comment on the values $^2J(^{119}Sn,^{31}P)_{cis}$ is relevant. In all of our Ir(I) and Ir(III) complexes containing the iridium–tin bond, the magnitude of this two-bond coupling constant varies from 128–198 Hz (see Table II). In square planar platinum complexes the values are generally larger, ≃225–268 Hz (and >4KHz for $^2J(^{119}Sn,^{31}P)_{trans}$ [1]).

For both of the components of our mixture we observe relatively small tin phosphorus coupling con-

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*This color change is reversible with temperature.

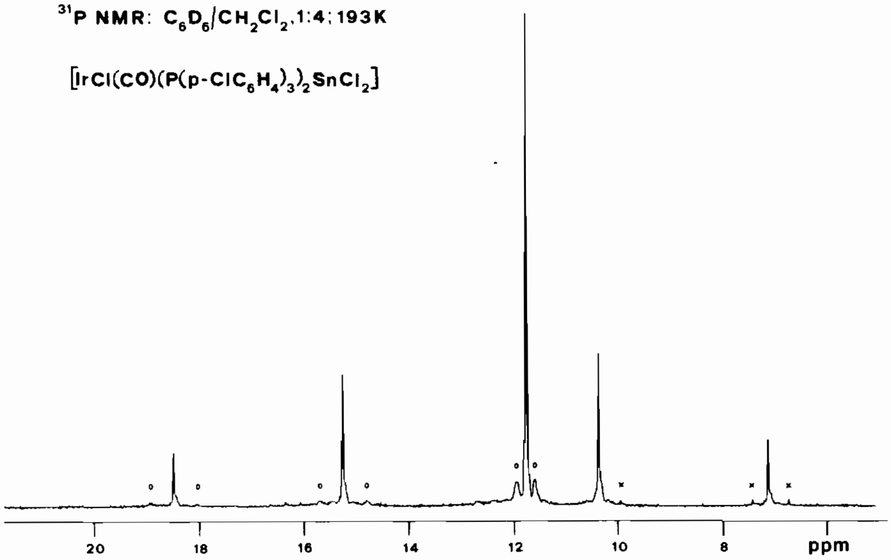


Fig. 1. $^{31}P\{^1H\}$ NMR Spectrum of $[IrCl(CO)(P(p\text{-}ClC_6H_4)_3)_2(SnCl_2)]$ (193 K, C_6D_6/CH_2Cl_2 1:4). The circles indicate the satellites whereas the crosses stem from an impurity.

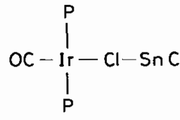
TABLE I. NMR Data[a] for the Complexes.

Complex	$\delta^{119}Sn$	$\delta^{31}P$	$\delta^{31}P$(AB System)	$^2J(^{31}P,^{31}P)$	$J(^{117,119}Sn,^{31}P)$	$J(^{117,119}Sn,^{31}P$ AB)	I/II
$[IrCl(CO)(P(p\text{-}XC_6H_4)_3)_2(SnCl_2)]$							
X=H	223.1	13.0	10.1, 18.9	325	32	–	1:01
OCH_3	241.1, 146.9	9.7	7.7, 15.0	326	~30	81	1:05
Cl	205.5, 154.7	11.8	9.1, 16.5	330	39	89	1:2
F	214.8, 154.2	11.0	7.8, 16.2	330	33	87	1:1

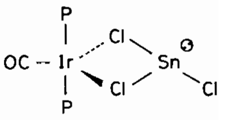
[a] In C_6D_6/CH_2Cl_2 1:4, 193K.

stants of ~32–39 Hz for I, and 80–89 Hz and <30 Hz* for II, suggesting that these have a different type of tin coordination.

Treatment of these solutions with HCl or H_2 gives excellent yields of the Ir(III) complexes $[IrHCl(SnCl_3)(CO)P_2]$ (III)** and $[IrH_2(SnCl_3)(CO)P_2]$, IV, respectively (P will always refer to a tertiary aryl phosphine) whereas reaction with CO affords the five-coordinate iridium(I) complexes $[Ir(SnCl_3)(CO)_2P_2]$, V. A summary of this chemistry is given in the Scheme. The smooth oxidative addition reactions as well as the isolation of the bis-carbonyl compounds, V, suggest that our unknown complexes contain iridium in the +1 oxidation state. This information taken together with the small $J(^{119}Sn,^{31}P)$ values prompts us to suggest the bridged structures shown below for I and II.



(I)



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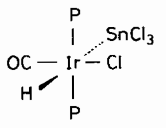

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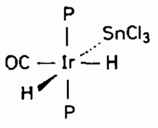

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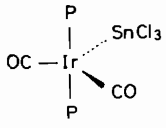

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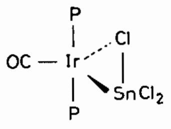

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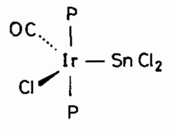

(VII)

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*We have not observed a coupling to one partner of the AB pattern.

**For this complex we find an 87% yield of 'Ir(III)' of which ~70% is $[IrHCl(SnCl_3)(CO)P_2]$ and 30% $[IrHCl_2(CO)P_2]$.

TABLE II. IR and Microanalytical Data for the Complexes.

Complex	IR Data[a]			Microanalytical Data: Calcd (Found)	
	ν(C≡O)	ν(Ir–H)	ν(Sn–Cl)	C	H
$[IrHCl(SnCl_3)(CO)(P(p\text{-}XC_6H_4)_3)_2]$					
X=H	2055	2130	330,300	44.13(44.27)	3.08(3.32)
OCH_3	2050	2125	315,290	43.51(43.23)	3.63(3.51)
Cl	2060	2100	~300	36.61(36.46)	2.06(2.12)
F	2070	2140	335,310	39.86(38.17)	2.24(2.17)
$[IrH_2(SnCl_3)(CO)(P(p\text{-}XC_6H_4)_3)_2]$					
X=H	2025	2100,2005	~300	45.70(44.15)	3.29(3.13)
OCH_3	2065	2110,2010	330,295	44.80(44.57)	3.82(3.98)
Cl	2055	2105,2010	320,295	37.68(37.50)	2.21(2.34)
F	2070	2120,2025	332,310	41.13(40.48)	2.41(2.75)
$[Ir(SnCl_3)(CO)_2(P(p\text{-}XC_6H_4)_3)_2]$					
X=H	2020,1970		~300	45.70(45.88)	3.02(3.41)
OCH_3	2020,1970		~300	44.84(44.49)	3.57(3.47)
Cl	2030,1975		295	37.86(38.30)	1.99(2.23)
F	2030,1980		~300	41.25(40.87)	2.17(2.25)
$[IrCl(CO)(P(p\text{-}XC_6H_4)_3)_2(SnCl_4)]$[b]					
	major minor				
X=H	2085,2038		~325	42.68(43.46)	2.88(3.15)
OCH_3	2078,2020		~330	42.28(42.53)	3.44(3.48)
Cl	2083,2040		~330	35.59(35.23)	1.92(2.08)
F	2080,2030		~340,320	38.66(38.52)	2.09(2.18)
$[Ir(SnCl_3)(O_2)(CO)(PPh_3)_2]$	2080		335	44.30(44.59)	2.99(3.12)
$[IrCl(CO)(P(p\text{-}XC_6H_4)_3)_2(SnCl_2)]$					
X=H	2052,1960				
OCH_3	2050,1945				
Cl	2050,1960				
F	2040,1960				

[a]Measured as KBr disks. [b]Two components. The ratio major/minor is solvent dependent.

Scheme

Chemistry of the Blue-Green Intermediates $[IrCl(CO)(SnCl_2)P_2]$.

$$\begin{tikzcd}
 & {[IrCl(CO)P_2]} \arrow[d, "SnCl_2"] & \\
 & {[IrCl(CO)(SnCl_2)P_2]} \arrow[dl, "H_2"'] \arrow[d, "HCl"'] \arrow[dr, "CO"] & \\
{[IrH_2(SnCl_3)(CO)P_2]} & {[IrHCl(SnCl_3)(CO)P_2]} & {[Ir(SnCl_3(CO)_2P_2]}
\end{tikzcd}$$

In I, the tin is coordinated to the chloride, such as in that found for $[Ag(SnCl_3)(PP)]$, PP = bis-diphenylphosphinobenzo[c]phenanthrene [15] or, put in a different way, the halogen bridges the iridium and tin metals. We cannot differentiate between I and structures such as VI, which has been observed for $[Mo(\mu\text{-}Cl)(SnCl_2CH_3)(2\text{-}2'\text{-bipyridyl})(CO)_3]$ [4], or a five-coordinate such as VII*, but feel that the 31–39 Hz tin–phosphorus coupling is more consistent with I than either of these. In II the iridium is five-coordinate with the two metals separated by two bridging chlorine atoms. For slow inversion of the

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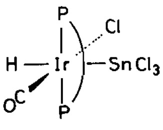
*This might also have a square pyramidal structure.

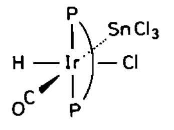
pyramidal tin, we expect and observe non-equivalent axial phosphines. The markedly different J(^{119}Sn,-^{31}P) values, ≃80–90 Hz and <30 Hz**, are reasonable for a lone-pair effect [16]. We note that a blue-green color has been recently observed in hydroxy bridged dimers of Ir(I) [17], related to Vaska's complex, and take this as further support that bridging halogens are involved in our complexes. The identification of a structure such as II is important to our understanding of how $SnCl_2$ attacks metal–halogen bonds.

b) Iridium(III)–Tin

As noted above, oxidative addition of HCl to a mixture of Vaska's complex and tin(II) chloride leads to the mono hydride complexes *trans*-[IrHCl($SnCl_3$)-(CO)P_2]. We had previously noted that $^2J(^{119}Sn,^1H)$ in [IrHCl($SnCl_3$)(CO)($Et_2\widehat{PP}Et_2$)], VII $Et_2\widehat{PP}Et_2$ = bis-diethylphosphinobenzo[c]phenanthrene which contains a *trans* chelating phosphine [18] was rather large, at 1570 Hz. Since $^2J(X,Y)_{trans}$ is often much greater than $^2J(X,Y)_{cis}$ it was conceivable that ^2J-(^{119}Sn,^{1}H) would provide a useful probe for the geometric arrangement of the tin and hydride ligands, thus allowing a distinction between VIIIa and VIIIb. Consequently, we have prepared and studies several triaryl phosphine complexes as models and give microanalytical IR and ^{1}H, ^{31}P and ^{119}Sn NMR data for these in the Tables.



(VIII a)

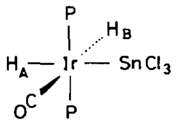


(VIII b)

The IR spectra show both metal–hydride and metal–carbonyl stretches, in agreement with the literature [8]. The ^{1}H NMR spectrum of the PPh_3 complex shows a hydride resonance at $\delta = -9.94$ split by equivalent phosphorus spins and accompanied by both ^{117}Sn and ^{119}Sn tin satellites. The $^{31}P\{^1H\}$ spectrum is a singlet at $\delta = -2.1$, also flanked by the appropriate tin satellites. The ^{119}Sn spectrum *with* ^{1}H coupling is a doublet of triplets arising from the equivalent ^{31}P atoms and the single hydride (see Fig. 2). The value of $^2J(^{119}Sn,^1H)$ at 1601 Hz is in good agreement (as are the other values) with that found for VIII. Obviously the geometric arrangement of the ligands is the same in both the monodentate and chelating phosphine complexes. The assignment of VIIIa as the correct isomer follows from the complexes *trans*-[IrH_2($SnCl_3$)(CO)P_2].

$IrH_2(SnCl_3)(CO)P_2$

Addition of $SnCl_2$ to Vaska's complex followed by the addition of molecular hydrogen affords the Ir(III) complexes, IX in which we have two distinct hydride ligands, H_A & H_B. This and the analogous *para* substituted phosphine compounds have also been characterized as described above (see Tables). The geometric orientation of the hydride and tin ligands is provided by a combination of ^{1}H, ^{119}Sn and ^{31}P NMR. The former reveals ^{1}H resonances at $\delta = -9.67$ to -10.02 and -12.57 to -12.60 (see Fig. 3) with triplet structure, arising from the phosphines, a doublet splitting of 3Hz due to $^2J(H_A,H_B)$ and ^{117}Sn and ^{119}Sn satellites. As expected, one of the two $^2J(^{119}Sn,H)$ values is substantially larger than the other, ^2J = 125–134 Hz and 1160–1223 Hz, with the latter in fair agreement with what we find for the mono hydride complexes.



(IX)

The much smaller tin–proton coupling is reasonable for a *cis* coupling since it is often found that $^2J(A,B)_{trans}$ is five to ten times larger than $^2J(A,B)_{cis}$ when coupling pathway proceeds through a transition metal [13]. The ^{119}Sn resonances at δ −232 to −252 are doublets of doublets, further coupled to the ^{31}P spins, thereby reflecting the two different tin–proton interactions. The $^{31}P\{^1H\}$ spectrum shows the expected singlet, plus tin satellites, due to

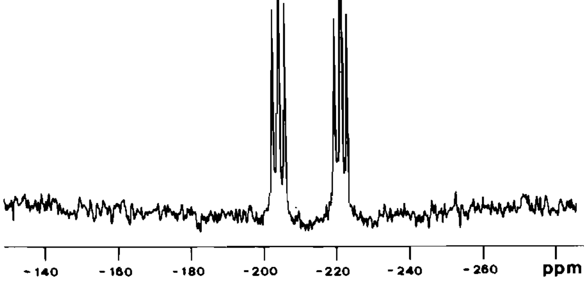


Fig. 2. ^{119}Sn NMR Spectrum of [IrHCl($SnCl_3$)(CO)(PPh_3)$_2$]. The large doublet spacing represents $^2J(^{119}Sn,^1H)$.

** ^{119}Sn line widths in $SnCl_3$ complexes are routinely between 25 and 50 Hz thus complicating the observation of small $^2J(^{119}Sn,^{31}P)$ values.

TABLE III. NMR Data[a] for the Complexes.

Complex	δ^{119}Sn	δ^{31}P	J(^{119}Sn,^{31}P)	δ^{1}H	^{2}J(^{119}Sn,H)	^{2}J(^{31}P,H)
$[IrHCl(SnCl_3)(CO)(P(p\text{-}XC_6H_4)_3)_2]$[b]						
X=H	−212.5	−2.1	157	−9.94	1601	10.9
OCH_3	−214.6	−7.1	157	−10.15	1609	10.2
Cl	−193.7	−4.4	163	−9.92	1545	10.2
F	−198.9	−5.6	163	−9.98	1554	10.2
$[IrH_2(SnCl_3)(CO)(P(p\text{-}XC_6H_4)_3)_2]$[c]						
X=H	−249.0	7.0	155	−9.71,−12.57	131,1209	16
OCH_3	−251.8	0.9	154	−9.67,−12.65	134,1223	16
Cl	−232.3	5.0	163	−10.02,−12.67	125,1160	16
F	−237.6	3.4	157	−9.91,−12.66	128,1171	14
$[Ir(SnCl_3)(CO)_2(P(p\text{-}XC_6H_4)_3)_2]$[b]						
X=H	−138.7	1.0	184			
OCH_3	−144.0	−4.5	194			
Cl	−131.0	−4.4	197			
F	−132.0	−2.0	198			
$[IrCl(CO)(P(p\text{-}XC_6H_4)_3)_2(SnCl_4)]$[d]						
X=H	−473.0	−18.5	138			
OCH_3	−492.0	−20.1	137			
Cl	−440.0	−21.4	138			
F	−448.0	−22.2	137			
F[e]	−525.0,−415.0	−6.9,−27.2	128,140			

[a] Coupling constants are in Hz, chemical shifts in ppm relative to: $^{119}SnMe_4$, $H_3{}^{31}PO_4$ and TMS, respectively. For J values, ^{1}H; ±0.7, ^{31}P ± 2.5; ^{119}Sn; ±12. For δ values, ^{1}H: ±0.01; ^{31}P: ±0.1; ^{119}Sn: ±0.1 ppm. [b] In $CDCl_3$, room temperature. [c] ^{2}J(H, H) values for all phosphine derivatives: ⩽3 Hz. [d] In C_6D_6/CH_2Cl_2 1:4, room temperature. [e] In C_6D_6/CH_2Cl_2 1:4; 163 K.

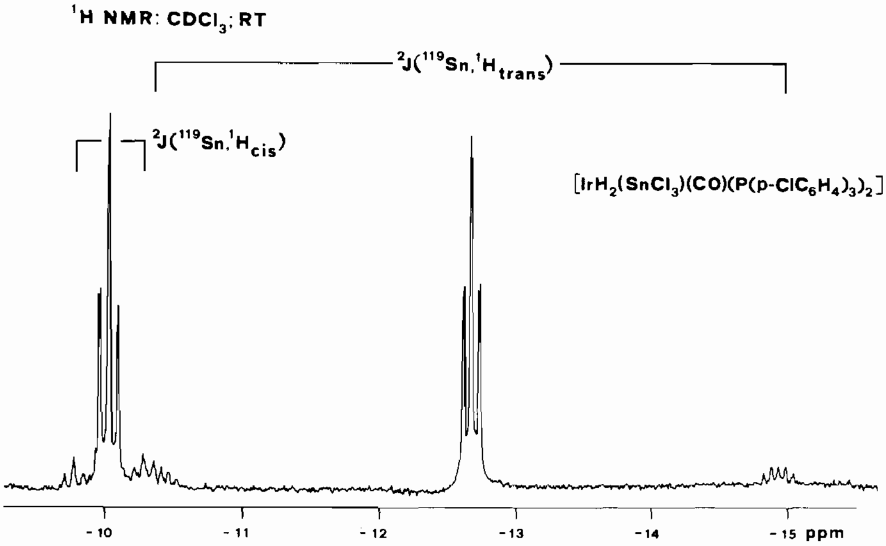


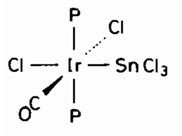
Fig. 3. ^{1}H NMR Spectrum of $[IrH_2(SnCl_3)(CO)(P(p\text{-}ClC_6H_4)_3)_2]$; hydride region showing the two very different ^{2}J(^{119,117}Sn, ^{1}H) coupling constants.

the equivalent phosphines. Clearly the spectroscopic data are consistent with IX and provide supporting evidence for *trans* assignment of the hydride and trichlorostannate ligands in VIII and its monodentate analogs. It is interesting to note the high field position of the tin resonances in these Ir(III) complexes, δ = −194 to −252, relative to the low field tin shifts, δ = 147 to 241, for I and II.

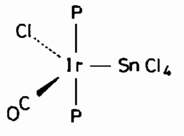
Having shown that tin(II) chloride can react in several ways with Vaska's complex we chose to investigate its reaction with tin(IV) chloride as shown in eqn. *1*.

$$\mathrm{IrCl(CO)(PPh_3)_2 + SnCl_4 \rightarrow [IrCl(CO)(PPh_3)_2(SnCl_4)]} \qquad (1)$$

This route was attractive since we had hoped (but were unable) to prepare X (or its isomers) via reaction of $[\mathrm{IrCl_3(CO)(PPh_3)_2}]$ with $\mathrm{SnCl_2}$. Conceivably, the oxidative addition of $\mathrm{SnCl_4}$ might afford X directly. Furthermore, there is a report suggesting that a five-coordinate complex, similar to XI, is indeed the product of this reaction [7]. In our hands, reaction (*1*) affords yellow products which show two stretches in the carbonyl region, but at room temperature only one ^{31}P signal, with tin satellites. Since the vibrational spectroscopic time scale is faster than that for NMR, we have measured ^{31}P and ^{119}Sn NMR spectra at reduced temperatures. For the $\mathrm{P(}p\mathrm{\text{-}FC_6H_4)_3}$ complex, the ^{31}P singlet broadens and eventually splits into two components which at −110 °C are static on NMR time scale. The magnitude of $^2J(^{119}\mathrm{Sn}, {}^{31}\mathrm{P})$, 128 and 140 Hz, together with the very high field position of the tin resonances, $\delta = -525$ and -415 ppm as compared to $\delta = +206$ to $+241$ and $\delta = +147$–155 for I and II, respectively, suggests that the tin is coordinated to iridium. Moreover, the low activation energy for conversion of one isomer into another (the microanalytical data are reasonable for the composition $[\mathrm{IrCl(CO)P_2(SnCl_4)}]$) is not compatible with isomerization processes leading to isomers of X, but is fully consistent with what is known about the molecular dynamics of five-coordinate complexes [19]. Unfortunately we cannot contribute more to this structural chemistry other than saying that the phosphines remain equivalent. It is even conceivable that one of the two components has five-coordinate Ir(III) whereas the other has the iridium in an octahedral environment. A single crystal X-ray structure would be of value.



(X)



(XI)

^{119}*Sn Chemical Schifts*

We should like to note that, whatever the reason, we have observed changes in $\delta\,^{119}$Sn which exceed 700 ppm. This approaches the entire range for routine tin compounds [20] and is roughly equal to the changes in chemical shift observed for the $\mathrm{SnMe_3}$ ligand bound to more than a dozen different transition metals [5]. An even larger range has been observed recently in the polytrichlorostannates of Rh(III) [2], and when these latter are combined with results for Rh(I) five-coordinate complexes [22], a range of >1100 ppm is known for the tin chemical shift of the Rh–$\mathrm{SnCl_3}$ unit. We cannot be certain that all bridging halogen complexes will appear at very low field or that five-coordinate tin must come at very high field (note that for the known $[\mathrm{Ir(O_2)(SnCl_3)(CO)(PPh_3)_2}]$, $\delta = -477$); however, it appears that ^{119}Sn NMR will prove a sensitive probe for the structural tin chemistry of trichlorostannate complexes once more data becomes available.

Conclusions

We have shown that tin(II) chloride reacts with Vaska's complex to form chloride bridged compounds. These may well be intermediates on the reaction pathway which begins with electrophilic attack of tin on chloride and ends with either halogen abstraction, to form the $\mathrm{SnCl_3^-}$ anion, or the eventual formation of an iridium–tin bond. Both ^{1}H and ^{119}Sn NMR spectroscopy are valuable structural tools, with the former especially useful for probing the geometric orientation of the hydride and tin ligands. The ^{119}Sn chemical shift seems to be of promising value, but will require further study.

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