▮ Inorganic Chemistry

Stannyl Complexes of Rhodium and Iridium: Preparation of Mono- and Bis(trihydridestannyl) Derivatives

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Mono- and bis(trichlorostannyl) complexes [MCl(SnCl$_3$)(η^5-C$_5$Me$_5$){P(OR)$_3$}] (**1**, **2**) and [M(SnCl$_3$)$_2$(η^5-C$_5$Me$_5$){P(OR)$_3$}] (**3**, **4**) (M = Rh, Ir; R = Me, Et) were prepared by allowing chloro compounds MCl$_2$(η^5-C$_5$Me$_5$)[P(OR)$_3$] to react with anhydrous SnCl$_2$ in refluxing 1,2-dichloroethane. Treatment of trichlorostannyl complexes of iridium **2** and **4** with NaBH$_4$ in ethanol afforded hydride-trihydridestannyl derivatives [IrH(SnH$_3$)(η^5-C$_5$Me$_5$){P(OR)$_3$}] (**5**) and bis(trihydridestannyl) [Ir(SnH$_3$)$_2$(η^5-

C$_5$Me$_5$){P(OR)$_3$}] (**6**), the reaction of which with methylpropiolate HC≡CCOOMe led to trivinylstannyl derivatives [IrH{Sn[C(COOMe)=CH$_2$]$_3$}(η^5-C$_5$Me$_5$){P(OMe)$_3$}] (**7a**) and [Ir{Sn[CH=C(H)COOMe]$_3$}$_2$(η^5-C$_5$Me$_5$){P(OMe)$_3$}] (**8a**). The complexes were characterised spectroscopically (IR and ^{1}H, ^{31}P, ^{13}C, ^{119}Sn NMR) and by X-ray crystal structure determination of [Ir(SnCl$_3$)$_2$(η^5-C$_5$Me$_5$){P(OMe)$_3$}] (**4a**).

Introduction

The chemistry of inorganic and organometallic complexes containing metal-main group metal bonds has shown a resurgence of interest in recent years.[1–5] In particular, complexes containing stannyl groups of the type SnX$_3$, SnR$_3$ and SnH$_3$ as ligands, which display novel reactivity, played a prominent role in such renaissance.

We have a long-standing interest in the chemistry of stannyl complexes of transition metals[5,6] and have reported the synthesis and reactivity of trihydride M–[SnH$_3$] and triorganostannyl M–[SnR$_3$] derivatives of both the Mn and Fe triads. The interesting properties shown, in particular, by the trihydridestannyl ligand SnH$_3$[5] prompted us to extend our study to the Rh and Ir central metals[7] to test whether tin trihydride compounds can be prepared and how the reactivity of the stannyl groups is influenced by the metal fragments. The results of these studies, which include the preparation of the first tin trihydride complexes of iridium, are reported here.

Results and Discussion

Preparation of stannyl complexes. Dichloro complexes [MCl$_2$(η^5-C$_5$Me$_5$){P(OR)$_3$}] react with equimolar amounts of SnCl$_2$ to give the trichlorostannyl derivatives [MCl(SnCl$_3$)(η^5-C$_5$Me$_5$){P(OR)$_3$}] (**1**, **2**) in good yields. In the presence of an excess of SnCl$_2$, instead, the reaction affords bis(trichlorostannyl) derivatives [M(SnCl$_3$)$_2$(η^5-C$_5$Me$_5$){P(OR)$_3$}] (**3**, **4**), as shown in Scheme 1.
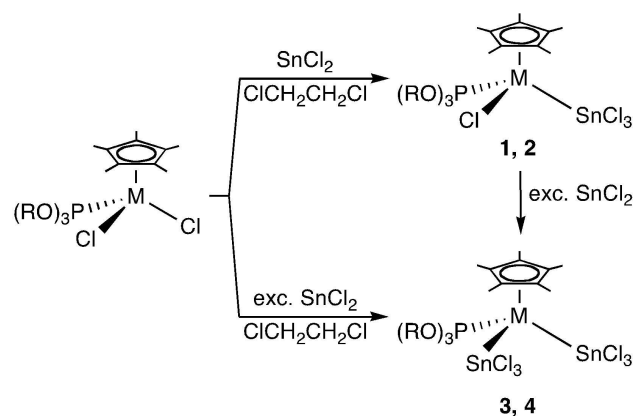
Scheme 1. Preparation of complexes **1–4**. M = Rh (**1**, **3**), Ir (**2**, **4**); R = Me (**a**), Et (**b**).

Indeed, treatment of monostannyl complexes **1** and **2** with an excess of SnCl$_2$ in refluxing 1,2-dichloroethane afforded the bis(stannyl) derivatives **3** and **4**.

The reaction proceeds with the insertion of SnCl$_2$ into the M–Cl bond to give monostannyl complexes **1** and **2**, which can undergo a second insertion affording the bis(trichlorostannyl) derivatives **3** and **4** as final products. Both the first and second insertion have slow rate and need refluxing conditions in 1,2-dichloroethane to afford pure samples of compounds **1–4** in a reasonable time. It is worth also noting that the use of SnCl$_2$•H$_2$O in ethanol instead of SnCl$_2$ in the reaction of [MCl$_2$(η^5-C$_5$Me$_5$){P(OR)$_3$}] did not afford trichlorostannyl complexes like **1–4** but intractable mixtures of compounds. Only the use of anhydrous SnCl$_2$ in 1,2-dichloroethane allows to prepare mono- and bis(trichlorostannyl) complexes of rhodium and iridium stabilised by our pentamethylcyclopentadienyl half-sandwich fragments.

The reactivity of chlorostannyl complexes **1–4** with NaBH$_4$ was studied and the results are shown in Scheme 2. While both

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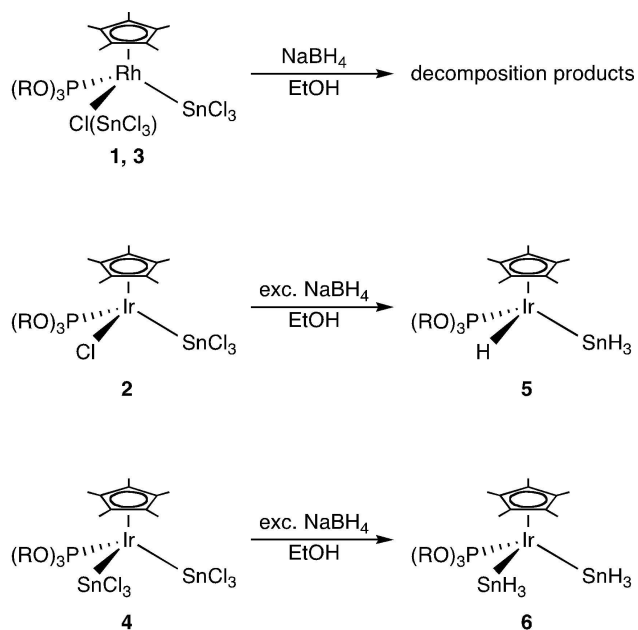
Scheme 2. Preparation of complexes 5 and 6. R = Me (a), Et (b).

confirmed by X-ray crystal structure determination of [Ir (SnCl$_3$)$_2$(η^5-C$_5$Me$_5$){P(OMe)$_3$}] (4a), the ORTEP[9] of which is shown in Figure 1.
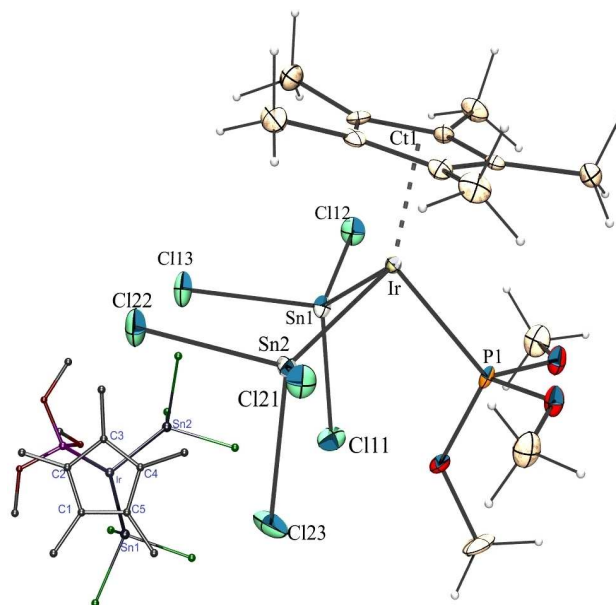

Figure 1. ORTEP scheme of the molecular structure of 4a. The small inset on the left represents the compound drawn perpendicular to the Ir–Ct vector.

the mono- and bis(trichlorostannyl) complexes of rhodium 1 and 3 react with NaBH$_4$ affording, in all conditions, decomposition products, the iridium derivatives 2 and 4 quickly react with NaBH$_4$ in ethanol affording trihydridestannyl derivatives [IrH(SnH$_3$)(η^5-C$_5$Me$_5$){P(OR)$_3$}] (5) and [Ir(SnH$_3$)$_2$(η^5-C$_5$Me$_5$){P(OR)$_3$}] (6), respectively, which were isolated as yellow-orange solids and characterised. The reaction proceeds in any case with the substitution of all chloro groups, bonded either to Sn or to Ir, affording hydride-trihydridestannyl 5 and bis(trihydridestannyl) 6 derivatives in good yields.

The use of NaBH$_4$ as a reagent to prepare tin trihydride complexes turns out to be an interesting synthetic method in tin chemistry that we had previously used to synthesise several [M]–SnH$_3$ derivatives.[5a,b,c,e,6c,d,f] In the present study, this route allowed the preparation of the first iridium complexes containing tin trihydride as a ligand. As observed with other stannyl derivatives,[5a,b,6d,f] the nature of the central metal and the ancillary ligands seem to be crucial for stabilising tin trihydride complexes. The pentamethylcyclopentadienyl half-sandwich fragment with phosphite ligand is able to stabilise both mono- and bis(tin trihydride) derivatives, but only with iridium. In the case of rhodium, only trichlorostannyl complexes were prepared, resulting the related trihydride species very unstable and not isolable. In addition, it is worth noting that metal complexes containing two tin trihydride groups are very rare and only two examples of Ru and Os, reported by us,[6c] were known until now. The use of the [Ir(η^5-C$_5$Me$_5$){P(OR)$_3$}] fragment afforded a new example of this class of compounds.

Good analytical data were obtained for all the stannyl complexes 1–6, which were isolated as yellow or orange solids stable in air and in solution of common organic solvents, where they behave as non-electrolytes.[8] Infrared and NMR data (^{1}H, ^{31}P, ^{119}Sn) support the proposed formulation, which was further

The structure of complex 4a contains an iridium atom η^5-coordinated to a pentamethylcyclopentadienyl ligand (Cp*) [ring-slippage 0.039 Å] and to three monodentate ligands, leading to the formation of a "three-legged piano stool" structure. These ligands are one P(OMe)$_3$ phosphite ligand and two monodentate trichlorostannyl ligands. The geometry of the complex is pseudo-octahedral with the Cp* ligand occupying three coordination positions and is marked by near-90° values for the angles among the legs (Table 1) between 90.780(15) and 92.74(3)°. The remaining angles between the Cp* centroid and the donor atoms (expected 125.3°) are between 121.92(12) and 126.32(8)°, bigger than the CT–Ir-P one as occurs in a related Rh compound with triphenylphosphine [Cp*Rh(PPh$_3$)(SnCl$_3$)$_2$].[10]

The centroid of Cp* ligand is situated at 1.875(2) Å from the iridium atom, and the average Ir–C bond distances for the Cp* ligand is 2.238 Å, being both values similar to those found in the literature, as for example in the cations [Cp*IrCl(NH$_2$NH$_2$){P(OEt)$_3$}]$^+$,[11a] and [Cp*IrCl(CH$_3$NHNH$_2$){P(OEt)$_3$}]$^+$,[11a] or in [Cp*Ir{η^1-C$_6$H$_5$(H)C≡N–N≡C(H)(C$_6$H$_5$)} {P(OMe)$_3$}]$^+$,[11b] or also in [Ir(η^5-C$_5$Me$_5$)(N≡CNEt$_2$)$_2${P(OMe)$_3$}]$^{2+}$.[11c] However, it is noteworthy the wide range of the Ir–C bonds, from 2.213(5) to 2.263(5) Å, longest values, Ir–C(4) and Ir–C(5), quasi-trans to the phosphite ligand, as can be seen in the small inset in Figure 1. The Ir–P [2.2558(12) Å] bond length is also similar to those in the above-mentioned cation complexes.[11]

The two Ir–Sn distances, 2.5709(4) and 2.5734(5) Å, are only slightly longer than those found in the [Cp*Ir(SnCl$_3$)$_3$]$^-$ anion,

Table 1. Selected bond lengths [Å] and angles [°] for **4a**			
Ir–CT1	1.875(2)	Ir–P(1)	2.2558(12)
Ir–Sn(1)	2.5709(4)	Ir–Sn(2)	2.5734(5)
Ir–C(1)	2.227(5)	Ir–C(4)	2.258(5)
Ir–C(2)	2.228(4)	Ir–C(5)	2.263(5)
Ir–C(3)	2.213(5)	Ir–C$_{av}$	2.238
Sn(1)–Cl(11)	2.3595(13)	Sn(2)–Cl(21)	2.3735(13)
Sn(1)–Cl(12)	2.3718(13)	Sn(2)–Cl(22)	2.3608(13)
Sn(1)–Cl(13)	2.3586(13)	Sn(2)–Cl(23)	2.3540(14)
CT1-Ir–P(1)	126.32(8)	CT1-Ir–Sn(1)	123.92(15)
CT1-Ir–Sn(2)	121.92(12)	Sn(1)-Ir–Sn(2)	90.780(15)
P(1)-Ir–Sn(1)	91.45(3)	P(1)-Ir–Sn(2)	92.74(3)
Cl(13)-Sn(1)-Cl(11)	98.31(5)	Cl(23)-Sn(2)-Cl(22)	97.71(5)
Cl(13)-Sn(1)-Cl(12)	96.22(5)	Cl(23)-Sn(2)-Cl(21)	98.38(5)
Cl(11)-Sn(1)-Cl(12)	96.73(5)	Cl(22)-Sn(2)-Cl(21)	94.39(5)
Cl(13)-Sn(1)-Ir	117.73(3)	Cl(21)-Sn(2)-Ir	117.85(3)
Cl(12)-Sn(1)-Ir	118.78(4)	Cl(22)-Sn(2)-Ir	120.43(4)
Cl(11)-Sn(1)-Ir	123.55(3)	Cl(23)-Sn(2)-Ir	122.33(4)
Cl(11)-Sn(1)-Ir	123.55(3)	Cl(23)-Sn(2)-Ir	122.33(4)

between 2.5582(7) Å and 2.5592(5) Å.[12] The Sn–Ir-Sn angle, 90.780(15)°, is the acutest among donors in the legs. The Sn–Cl distances are between 2.3540(14) and 2.3735(13) Å. This range is slightly narrower than that found in the [Cp*Ir(SnCl$_3$)$_3$]⁻ anion or in [Cp*Ir{(SnCl$_2$(H$_2$O)$_2$}(SnCl$_3$)$_2$]. An interesting feature is that in both SnCl$_3$ ligands one of the Sn–Cl distances is slightly longer than the other two, a structural parameter previously observed[11,13] and apparently an usual behaviour for this kind of ligand.

The Ir–Sn-Cl angles between 117.73(3) and 123.55(3)° and Cl–Sn-Cl angles around 96.9° (average) show high distortion around tin atoms, far from a tetrahedral disposition usual for trichlorostannyl ligands.[11-14]

The ¹H NMR spectra of mono- and bis(trichlorostannyl) complexes of rhodium **1** and **3** show the characteristic signals of the ancillary ligands C$_5$Me$_5$ and P(OR)$_3$ whereas the ³¹P ones appear as doublets due to the presence of the ¹⁰³Rh nuclei ($J_{31P103Rh}$ = 220–208 Hz), with their characteristic satellites due to coupling with the ¹¹⁷Sn and ¹¹⁹Sn nuclei of the SnCl$_3$ groups. However, the presence of this stannyl ligand is confirmed by the ¹¹⁹Sn NMR spectra, which show a multiplet centred at -75.32 to -76.54 ppm for **1** and at 1–5 ppm for **3**, which can be simulated using an AMX model (A = ³¹P, X = ¹⁰³Rh) with the parameters reported in the Experimental section (see S.I.). The good fit between the calculated and experimental spectra supports the proposed formulation for the rhodium derivatives.

The ³¹P NMR spectra of the trichlorostannyl derivatives of iridium **2** and **4** show a sharp singlet with the characteristic satellites due to coupling with the ¹¹⁷Sn and ¹¹⁹Sn nuclei of the SnCl$_3$ ligand. The ¹¹⁹Sn NMR spectra confirm its presence showing a doublet at -347.0 to -342.0 ppm for monostannyl **2** and at -312.6 to -320.4 ppm for bis(stannyl) **4** derivatives, due to coupling with the ³¹P nuclei, in agreement with the proposed formulation.

The IR spectra of the hydride-trihydridestannyl complexes [IrH(SnH$_3$)(η⁵-C$_5$Me$_5$){P(OR)$_3$}] (**5**) show one medium-intensity band at 2113–2134 cm⁻¹ attributed to the ν$_{Ir-H}$ of the hydride and another one, of strong intensity and rather broad, at 1771–

1755 cm⁻¹ attributed to the stretching of the Sn–H bond of the SnH$_3$ ligand. However, two ν$_{Sn-H}$ bands are expected for the metal-bonded SnH$_3$ group, as had been observed in related Os and Re complexes.[5a,b] Probably, the difference of the stretching values of the two bands is too small to allow resolution by our instrument and therefore the spectra display only a single enlarged absorption.

Besides the signals of the ancillary ligands, the ¹H NMR spectra of **5** show a doublet near -17 ppm due to the hydride and a slightly broad singlet at 2.93–2.94 ppm, with the characteristic satellites (see S.I., Fig. S1) due to coupling with the ¹¹⁷Sn and ¹¹⁹Sn nuclei and attributed to the SnH$_3$ ligand. The proton-coupled ¹¹⁹Sn NMR spectra of **5** appear as quartets of multiplets at -491 to -489 ppm due to coupling not only with the hydride hydrogen atoms IrH and SnH$_3$ and with the ³¹P nuclei, but also with the methyl hydrogen atoms of the C$_5$Me$_5$ ligand. These multiplets were simulated using an AMX$_3$Y$_{15}$Z model (A = ³¹P, M = ¹¹⁹Sn, X, Z = ¹H hydride, Y = ¹H C$_5$Me$_5$) with the parameters reported in the Experimental section (see S.I., Fig. S2) and the good fit between the experimental and calculated spectra strongly supports the proposed formulation for the hydride-trihydridestannyl derivatives **5**.

The IR spectra of the bis(tin trihydride) complexes [Ir (SnH$_3$)$_2$(η⁵-C$_5$Me$_5$){P(OR)$_3$}] (**6**) show two strong bands at 1733–1765 (**6a**) and at 1767–1798 cm⁻¹ (**6b**) attributed to the ν$_{SnH}$ of the SnH$_3$ group. However, diagnostic for the presence of the SnH$_3$ ligand are both the ¹H and ¹¹⁹Sn NMR spectra. A slightly broad singlet, with the characteristic satellites due to coupling with the ¹¹⁷Sn and ¹¹⁹Sn nuclei, was observed in the proton spectra between 3.05 and 3.10 ppm and attributed to the SnH$_3$ group. In addition, the proton-coupled ¹¹⁹Sn NMR spectra of **6a** and **6b** appear as quartets of doublets of multiplets due to coupling with the hydride, the phosphorus nuclei of the phosphite and the fifteen hydrogens of the pentamethylcyclopentadienyl ligand. These spectra can be simulated with an AMX$_6$Y$_{15}$ model (A = ³¹P, M = ¹¹⁹Sn, X, Y = ¹H) with the parameters reported in the Experimental section (see S.I.) and

the good fit between the experimental and calculated spectra strongly support the proposed formulation for the complexes.

Reactions with alkynes. Methylpropiolate $HC\equiv CCOOMe$ reacts with both the trihydridestannyl complexes $[IrH(SnH_3)(\eta^5\text{-}C_5Me_5)\{P(OMe)_3\}]$ (**5a**) and $[Ir(SnH_3)_2(\eta^5\text{-}C_5Me_5)\{P(OMe)_3\}]$ (**6a**) to give the trivinylstannyl derivatives $[IrH\{Sn[C(COOMe)=CH_2]_3\}(\eta^5\text{-}C_5Me_5)\{P(OMe)_3\}]$ (**7a**) and $[Ir\{Sn[CH=C(H)COOMe]_3\}_2(\eta^5\text{-}C_5Me_5)\{P(OMe)_3\}]$ (**8a**), which were isolated as yellow oils and characterised (Scheme 3).
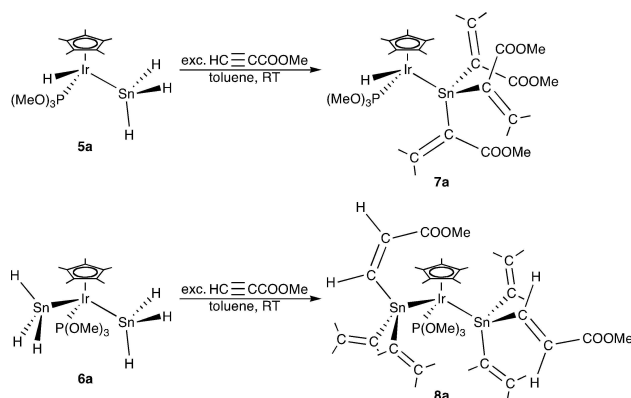
Scheme 3. Preparation of complexes **5** and **6**.

The reaction involves the addition of three Sn–H bonds to three alkynes affording the trivinylstannyl derivatives **7a** and **8a**. It probably proceeds by sequential addition of $HC\equiv CCOOMe$ to the Sn–H bonds but it is too fast to allow the isolation from **5a** of mono- and bis(vinyl) intermediates $[Ir]\text{-}SnH_2\{C(COOMe)=CH_2\}$ and $[Ir]\text{-}SnH\{C(COOMe)=CH_2\}_2$. Although only trivinylstannyl complexes are formed with an excess of alkyne, with a ratio $HC\equiv CCOOMe:[Ir]\text{-}SnH_3$ or $[Ir]\text{-}(SnH_3)_2$ lower than 3 or 6, the products were always mixtures of mono-, di- and trivinyl complexes, which were not separated. Moreover, it is worth noting that no addition of the Ir–H bond to alkyne was observed, resulting this hydride ligand always present in the final monotrivinylstannyl complex **7a**.

In addition, depending on the nature of the starting complex **5a** and **6a**, the addition of the Sn–H bond to $HC\equiv CCOOMe$ affords different vinylstannyl derivatives **7a** and **8a** probably owing to the steric requirements of the bis(trivinyl-stannyl) derivative **8a**.

Phenylacetylene was also reacted with the trihydridestannyl precursors **5a** and **6a** but in this case a mixture of products was obtained, the NMR spectra of which indicate the formation of some vinyl species. However, these species are rather unstable and decomposed in any attempt of separation. It seems therefore that only activated alkynes such as methyl-propiolate can undergo addition of the Sn–H bond affording stable and isolable trivinylstannyl derivatives.

Although the addition of organotin hydrides R_nSnH_{4-n} (n = 1–3) to terminal acetylene $RC\equiv CH$ is a well-known reaction,[15] the cases of coordinated SnH_3 groups to a transition metal are very rare and only two examples are reported in the literature

involving Re and Os derivatives.[5d,6d] The reaction of our trihydridestannyl derivatives **5** and **6** represents a new example of such a type of reaction, affording the first trivinylstannyl derivatives of iridium.

The complexes $[IrH\{Sn[C(COOMe)=CH_2]_3\}(\eta^5\text{-}C_5Me_5)\{P(OMe)_3\}]$ (**7a**) and $[Ir\{Sn[CH=C(H)COOMe]_3\}_2(\eta^5\text{-}C_5Me_5)\{P(OMe)_3\}]$ (**8a**) were isolated as oils that we were not able to transform into solids. However, their spectroscopic properties (IR and ^{1}H, ^{13}C, ^{31}P, ^{119}Sn NMR) strongly support the proposed formulations. The IR spectrum of **7a** shows a medium-intensity band at 2111 cm^{-1} attributed to the ν_{Ir-H} of the hydride and a strong one at 1700 cm^{-1} attributed to the ν_{CO} of the ester group of the $C(COOMe)=CH_2$. The presence of vinylstannyl ligand is confirmed by the ^{1}H, ^{13}C and ^{119}Sn NMR spectra. The proton spectrum shows an AB quartet between 7.04 and 6.17 ppm with the characteristic satellites due to coupling with the ^{117}Sn and ^{119}Sn nuclei and attributed to the H_x and H_y vinyl protons (Figure 2).
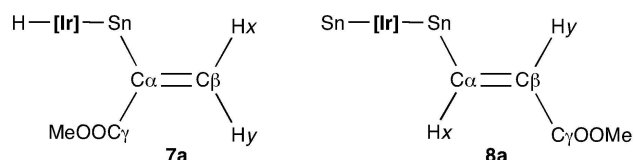

Figure 2. Trivinylstannyl ligand forms in complexes **7a** and **8a**.

The $^2J_{HH}$ value of 3.5 Hz is characteristic of the geminal position of the two vinyl protons. The spectrum also shows a singlet at 3.50 ppm of the methyl group pf the substituent COOMe and a doublet at -17.55 ppm of the hydride ligand, in agreement with the presence of both the vinyl and hydride groups. Besides the signals of the ancillary ligands $P(OMe)_3$ and C_5Me_5, the ^{13}C NMR spectrum shows two signals at 171.62 and 135.98 ppm, each with the ^{117}Sn and ^{119}Sn satellites, attributed to the $C\gamma$ and $C\beta$ carbon resonances of the $C\alpha(C\gamma OOMe)=C\beta H_2$ group. This attribution was confirmed by HMQC and HMBC experiments and by the $J_{13C119Sn}$ values, which range from 21 Hz for $C\gamma$ to 32 Hz for $C\beta$; the resonance for $C\alpha$ was not unambiguously attributed. The ^{119}Sn$\{^1$H$\}$ NMR spectrum of **7a** confirms the presence of the stannyl ligand showing a doublet at -203.4 ppm due to coupling with the ^{31}P nucleus of the phosphite. The ^{31}P NMR spectrum appears as a singlet at 101.4 ppm with the characteristic satellites, in agreement with the proposed formulation for the complex.

The IR spectrum of the bis(trivinylstannyl) derivative $[Ir\{Sn[CH=C(H)COOMe]_3\}_2(\eta^5\text{-}C_5Me_5)\{P(OMe)_3\}]$ (**8a**) shows a strong band at 1719 cm^{-1} due to the ν_{CO} of the ester groups $CH=C(H)$COOMe. The ^{1}H NMR spectrum shows an AB quartet at 7.80 and 6.17 ppm, with the ^{117}Sn and ^{119}Sn satellites and attributed to the H_x and H_y vinyl protons (Figure 2). The $^2J_{HH}$ value of 19 Hz suggests a *trans* position of the two vinyl protons. A singlet at 3.47 ppm due to the methyl group of $CH=C(H)$COOMe is also present in the ^{1}H NMR spectrum, matching the presence of the vinyl group. Further support came from the ^{13}C NMR spectrum

which, besides the signals of the ancillary ligands $P(OMe)_3$ and C_5Me_5, shows three signals at 165.39, 155.54 and 135.21 ppm, each with the ^{117}Sn and ^{119}Sn satellites, attributed to the Cγ, Cα and Cβ, respectively, carbon resonances of the Cα(H)=Cβ(H)CγOOMe group. This attribution was confirmed by HMQC and HMBC experiments and by the $J_{13C119Sn}$ value ranging from 295 Hz for Cα to 119 Hz for Cβ and 17.5 Hz for Cγ.

The $^{119}Sn\{^1H\}$ NMR spectrum of **8a** appears as a doublet at -290.96 ppm due to coupling with the ^{31}P nucleus of the phosphine, whereas the ^{31}P spectrum is a singlet at 79.61 ppm with the characteristic ^{117}Sn and ^{119}Sn satellites, fitting the proposed formulation.

Conclusions

In this paper we report that the pentamethylcyclopentadienyl fragment $MCl_2(\eta^5\text{-}C_5Me_5)[P(OR)_3]$ stabilises both mono- and bis(trichlorostannyl) derivatives of rhodium and iridium. Reaction with $NaBH_4$ of these compounds allows the synthesis of the first trihydridestannyl derivatives of iridium $[IrH(SnH_3)(\eta^5\text{-}C_5Me_5)\{P(OMe)_3\}]$ and $[Ir(SnH_3)_2(\eta^5\text{-}C_5Me_5)\{P(OMe)_3\}]$. Among the properties shown by the $[M]–SnH_3$ fragments there is the insertion of methylpropiolate into the Sn–H bond yielding trivinylstannyl derivatives $[Ir]–(H)\{Sn[C(COOMe)=CH_2]_3\}$ and $[Ir]–\{Sn[CH=C(H)COOMe]_3\}_2$.

Supporting information Summary

Complete Experimental section including details of crystal data and structure refinement (Table S1); ^1H and ^{119}Sn NMR spectra of compound **5b** (Fig. S1, S2, pdf).

Conflict of Interest

The authors declare no conflict of interest.

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