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Trichlorostannyl complexes of iridium with both P-donor and N-donor ligands: Preparation and activity as hydrogenation catalysts

Gabriele Albertin *, Stefano Antoniutti, Stefano Paganelli

Dipartimento di Chimica, Università Ca' Foscari Venezia, Dorsoduro 2137, 30123 Venezia, Italy

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ABSTRACT

Bis(trichlorostannyl) complex $IrH(SnCl_3)_2(PPh_3)_2$ (**1**) was prepared by allowing the chloro-derivative $IrHCl_2(PPh_3)_3$ to react with $SnCl_2{\cdot}2H_2O$ in ethanol. Instead, treatment of phosphite complexes $IrHCl_2P_3$ [P = $P(OEt)_3$ and $PPh(OEt)_2$] with $SnCl_2{\cdot}2H_2O$ gave stannyl derivatives $IrCl_2(SnCl_3)P_3$ (**2**). Pyrazole–trichlorostannyl complexes $IrHCl(SnCl_3)(HRpz)P_2$ (**3**, **4**) (R = H, 3-Me; P = PPh_3, P^iPr_3) were prepared by allowing chloro-derivatives $IrHCl_2(HRpz)P_2$ to react with $SnCl_2{\cdot}2H_2O$. 1,2-Bipyridine-trichlorostannyl complexes $IrHCl(SnCl_3)(bpy)P$ (**5**) (P = PPh_3, P^iPr_3) were also prepared. Complexes **1**–**5** were characterised spectroscopically (IR, ^1H, ^{31}P, ^{119}Sn NMR) and a geometry in solution was also established. The trichlorostannyl iridium complexes were evaluated as catalyst precursors for the hydrogenation of 2-cyclohexen-1-one and cinnamaldehyde. The influence of the stannyl group, as well as the steric hindrance of both N-donor and P-donor ligands in the catalytic activity of the complexes is discussed.

1. Introduction

Stannyl complexes [M]–SnX_3 and [M]–SnR_3 (X = halogen, R = alkyl or aryl group) of transition metals have been extensively studied in recent years [1–3], both for the variety of reactions they may undergo, including ligand-substitution at both metal and tin centres, and because the introduction of a stannyl ligand may modify the properties of complexes and often improve their catalytic activity [4].

However, despite the large number of stannyl complexes prepared, relatively few involve iridium as a metal centre [5], although several complexes of this metal have shown interesting catalytic properties.

We are interested in the chemistry of stannyl complexes of transition metals and have recently reported [6] the synthesis and reactivity of chloro-, hydride- and organo-stannyl complexes of Mn(I), Re(I), Ru(II) and Os(II) of the type $M(SnR_3)(CO)_nL_{5-n}$ (M = Mn, Re; n = 2, 3), $M(SnR_3)(Tp)L(PPh_3)$ and $M(SnR_3)(Cp)L(PPh_3)$ (M = Ru, Os; R = Cl, H, Me, ArC≡C; L = phosphite). We have now extended these studies to iridium(III) in order to test whether new stannyl complexes can be prepared and how the introduction of a stannyl group can change their catalytic properties. The synthesis of mixed-ligands stannyl complexes of Ir(III) and some studies on their catalytic activity in the hydrogenation of 2-cyclohexen-1-one and cinnamaldehyde are reported in this paper.

2. Experimental

2.1. General comments

All synthetic work was carried out in an appropriate atmosphere (Ar) using standard Schlenk techniques or an inert atmosphere dry-box. Once isolated, the complexes were found to be relatively stable in air, but were stored under nitrogen at −25 °C. All solvents were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. $IrCl_3{\cdot}3H_2O$ was a Pressure Chemical Co. (USA) product, used as received. Phosphite $PPh(OEt)_2$ was prepared by the method of Rabinowitz and Pellon [7]. Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on Nicolet Magna 750 or Perkin–Elmer Spectrum-One FT-IR spectrophotometers. NMR spectra (^1H, ^{31}P, ^{119}Sn) were obtained on AC200 or AVANCE 300 Bruker spectrometers at temperatures between −90 and +30 °C, unless otherwise noted. ^1H spectra are referred to internal tetramethylsilane; $^{31}P\{^1H\}$ chemical shifts are reported with respect to 85% H_3PO_4, and ^{119}Sn with respect to $Sn(CH_3)_4$, and in both cases downfield shifts are considered positive. COSY, HMQC and HMBC NMR experiments were performed with standard programs. The SWAN-MR and INMR software packages [8] were used to treat NMR data. The conductivity of 10^{-3} mol dm^{-3} solutions of the complexes in CH_3NO_2 at 25 °C was measured on a Radiometer CDM 83. Elemental analyses were determined in the Microanalytical Laboratory of the Dipartimento di Scienze Farmaceutiche, University of Padova (Italy).

* Corresponding author. Fax: +39 041 234 8917.
E-mail address: albertin@unive.it (G. Albertin).

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2.2. Synthesis of precursor compounds

The chlorocomplex precursors *mer*- and *fac*-$IrHCl_2(PPh_3)_3$, $IrHCl_2(P^iPr_3)_2$, $IrHCl_2(HRpz)P_2$ (P = PPh_3, P^iPr_3; R = H, 3-Me), $IrHCl_2P_3$ [P = $P(OEt)_3$, $PPh(OEt)_2$] and the aryltriazenide $IrHCl(\eta^2$-1,3-PhNNNPh)$(PPh_3)_2$ were prepared following previously reported methods [9–13].

2.2.1. $IrHCl_2(bpy)P$ (P = PPh_3, P^iPr_3)

In a 50-mL three-necked round-bottomed flask were placed 0.68 mmol of the appropriate precursor $IrHCl_2P_3$, an excess of 2,2'-bipyridine (1.0 mmol, 0.16 g) and 15 mL of 1,2-dichloroethane. The resulting solution was refluxed for 3 h and then the solvent removed under reduced pressure. The oil obtained was triturated with ethanol (3 mL) giving a yellow solid which was filtered and crystallised from CH_2Cl_2 and ethanol; yield ⩾30% for P = PPh_3, ⩾75% for P = P^iPr_3. $IrHCl_2(bpy)(PPh_3)$: Anal. Calc. for $C_{28}H_{24}Cl_2IrN_2P$: C, 49.27; H, 3.54; Cl, 10.39; N, 4.10. Found: C, 49.49; H, 3.63; Cl, 10.12; N, 4.05%. ^{1}H NMR (CD_2Cl_2, 25 °C) δ (ppm): 9.45–7.35 (m, 23H, Ph+bpy), −19.73 (d, 1H, J_{HP}^{31} = 18 Hz, IrH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ (ppm): 6.7 (s). $IrHCl_2(bpy)(P^iPr_3)$: Anal. Calc. for $C_{19}H_{30}Cl_2IrN_2P$: C, 39.31; H, 5.21; Cl, 12.21; N, 4.83. Found: C, 39.54; H, 5.13; Cl, 12.45; N, 4.70%. IR (KBr, cm^{-1}): 2229 (s) ν_{IrH}. ^{1}H NMR (CD_2Cl_2, 25 °C) δ (ppm): 9.47–7.48 (m, 8H, bpy), 2.70 (m, 3H, CH), 1.41, 1.37 (d, 18H, CH_3), −25.25 (d, 1H, $J_{^1H^{31}P}$ = 18 Hz, IrH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ (ppm): 1.20 (s).

2.3. Synthesis of complexes

2.3.1. $IrH(SnCl_3)_2(PPh_3)_2$ (**1**)

In a 25-mL three-necked round-bottomed flask were placed 0.30 g (0.29 mmol) of $IrHCl_2(PPh_3)_3$, 0.65 g of $SnCl_2{\cdot}2H_2O$ (2.9 mmol) and 25 mL of ethanol. The resulting suspension was refluxed for 3 h and then the volume was reduced to about 10 mL by evaporation of the solvent under reduced pressure. The pale yellow solid formed was filtered and crystallised from CH_2Cl_2 and ethanol; yield ⩾75%. Anal. Calc. for $C_{36}H_{31}Cl_6IrP_2Sn_2$: C, 37.02; H, 2.68; Cl, 18.21. Found: C, 37.24; H, 2.80; Cl, 18.46%. IR (KBr, cm^{-1}): 2126 (m) ν_{IrH}. ^{1}H NMR (CD_2Cl_2, 25 °C) δ (ppm): 7.44–6.95 (m, 30H, Ph), −12.86 (t, 1H, IrH); (−70 °C) ABX spin syst, δ_M −12.64, J_{AX} = 9.5, J_{BX} = 10.0, $J_{^1H^{119}Sn1}$ = 97.1, $J_{^1H^{119}Sn2}$ = 960.8, $J_{^1H^{117}Sn}$ = 92.0, $J_{^1H^{117}Sn}$ = 917.7 Hz. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C,) δ (ppm): −3.29 s, br; (−70 °C) AB, δ_A −1.39, δ_B -5.66, J_{AB} = 13.2. $^{119}Sn\{^1H\}$ NMR (CD_2Cl_2, -70 °C) δ (ppm): ABM1, δ_{M1} -395.8, J_{AM1} = 2564.5, J_{BM1} = 295.0; ABM2, δ_{M2} −421.7, J_{AM2} = 183.0, J_{BM2} = 2526.0.

2.3.2. $IrCl_2(SnCl_3)P_3$ (**2**) [P = $P(OEt)_3$ (**a**), $PPh(OEt)_2$ (**b**)]

In a 25-mL three-necked round-bottomed flask were placed 0.2 mmol of the appropriate hydride $IrHCl_2P_3$, an excess of $SnCl_2{\cdot}2H_2O$ (2.0 mmol, 0.45 g) and 10 mL of ethanol. The resulting solution was stirred at room temperature for 3 h and the yellow solid formed was filtered and crystallised from CH_2Cl_2 and ethanol; yield ⩾90%. Anal. Calc. for $C_{18}H_{45}Cl_5IrO_9P_3Sn$ (**2a**): C, 21.91; H, 4.60; Cl, 17.97. Found: C, 21.76; H, 4.52; Cl, 17.75%. IR (polyethylene, cm^{-1}): 333, 310 (m) ν_{IrCl}. ^{1}H NMR (CD_2Cl_2, 25 °C) δ (ppm): 4.33 (m, 18H, CH_2), 1.34, 1.33 (t, 27H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ (ppm): A_2B spin syst, δ_A 56.6, δ_B 45.9, J_{AB} = 34.3, $J_{^{31}H^{119}Sn}$ = 360.1, $J_{^{31}H^{117}Sn}$ = 342.6, $J_{^{31}H^{119}Sn}$ = 6107.0, $J_{^{31}H^{117}Sn}$ = 5839.2 Hz. Anal. Calc. for $C_{30}H_{45}Cl_5IrO_6P_3Sn$ (**2b**): C, 33.28; H, 4.19; Cl, 16.37. Found: C, 33.40; H, 4.33; Cl, 16.55%. ^{1}H NMR (CD_2Cl_2, 25 °C) δ (ppm): 7.92–6.87 (m, 15H, Ph), 4.32–3.96, 3.73–3.43 (m, 12H, CH_2), 1.33, 1.14 (t, 18H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ (ppm): A_2B, δ_A 83.9, δ_B 74.2, J_{AB} = 24.8, $J_{^{31}H^{117}Sn}$ = 280.8, $J_{^{31}H^{117}Sn}$ = 4948.0. $^{119}Sn\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ (ppm): A_2BM, δ_M −535.0, J_{AM} = 293.8, J_{BM} = 5177.6.

2.3.3. $IrHCl(SnCl_3)(HRpz)P_2$ (**3, 4**) [R = H (**a**), 3-Me (**b**); P = PPh_3 (**3**), P^iPr_3 (**4**)]

In a 50-mL three-necked round-bottomed flask were placed 0.5 mmol of the appropriate chlorocomplex $IrHCl_2(HRpz)P_2$, an excess of $SnCl_2{\cdot}2H_2O$ (5 mmol, 1.13 g) and 25 mL of ethanol. The resulting suspension was refluxed for 3 h and then the volume was reduced to about 10 mL by evaporation of the solvent under reduced pressure. The pale yellow solid formed was filtered and crystallised from CH_2Cl_2 and ethanol; yield ⩾75%. Anal. Calc. for $C_{39}H_{35}Cl_4IrN_2P_2Sn$ (**3a**): C, 44.76; H, 3.37; Cl, 13.55; N, 2.68. Found: C, 44.54; H, 3.23; Cl, 13.77; N, 2.55%. IR (KBr, cm^{-1}): 3265 (m) ν_{NH}, 2308 (w) ν_{IrH}. ^{1}H NMR (CD_2Cl_2, 25 °C) δ (ppm): 10.70 (s, br, 1H, NH), 7.70–7.31 (m, 30H, Ph), 7.15 (s, br, 1H, H5 Hpz), 6.48 (s, br, 1H, H3 Hpz), 5.92 (t, 1H, H4 Hpz), −20.58 (t, 1H, $J_{^1H^{31}P}$ = 11.1, $J_{^1H^{119}Sn}$ = 197.1, $J_{^1H^{117}Sn}$ = 189.1 Hz, IrH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ (ppm): A_2, −0.14 (s, $J_{^{31}H^{117}Sn}$ = 228.0). $^{119}Sn\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ (ppm): A_2M, δ_M -651.9, J_{AM} = 239.5. Anal. Calc. for $C_{40}H_{37}Cl_4IrN_2P_2Sn$ (**3b**): C, 45.31; H, 3.52; Cl, 13.37; N, 2.64. Found: C, 45.49; H, 3.42; Cl, 13.22; N, 2.76%. IR (KBr, cm^{-1}): 3270 (m) ν_{NH}, 2153 (m) ν_{IrH}. ^{1}H NMR (CD_2Cl_2, 25 °C) δ (ppm): 10.23 (s, br, 1H, NH), 7.70–7.27 (m, 30H, Ph), 6.97 (s, br, 1H, H5 Hpz), 5.68 (s, br, 1H, H4 Hpz), 1.55 (s, 3H, CH_3), −20.52 (t, 1H, $J_{^1H^{31}P}$ = 11.1, $J_{^1H^{119}Sn}$ = 195.3, $J_{^1H^{117}Sn}$ = 187.2, IrH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C,) δ (ppm): A_2, −0.89 (s, $J_{^{31}H^{117}Sn}$ = 227.5). $^{119}Sn\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ (ppm): A_2M, δ_M −645.6, J_{AM} = 237.0. Anal. Calc. for $C_{21}H_{47}Cl_4IrN_2P_2Sn$ (**4a**): C, 29.94; H, 5.62; Cl, 16.84; N, 3.33. Found: C, 29.83; H, 5.75; Cl, 16.70; N, 3.26%. IR (KBr, cm^{-1}): 3285 (m) ν_{NH}, 2071 (m) ν_{IrH}. ^{1}H NMR (CD_2Cl_2, 25 °C) δ (ppm): 10.20 (s, br, 1H, NH), 7.12 (s, br, 1H, H5 Hpz), 6.50 (m, 2H, H4+H3 Hpz), 2.75 (m, 6H, CH phos), 1.54, 1.48 (d, 36H, CH_3), −14.17 (t, 1H, $J_{^1H^{31}P}$ = 16.0, $J_{^1H^{119}Sn}$ = 49.0, $J_{^1H^{117}Sn}$ = 47.5, IrH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C,) δ (ppm): A_2, 31.8 (s, $J_{^{31}P^{117}Sn}$ = 173.5). $^{119}Sn\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ (ppm): A_2M, δ_M −400.6, J_{AM} = 182.0.

2.3.4. $IrHCl(SnCl_3)(bpy)P$ (**5**) [P = PPh_3 (**a**), P^iPr_3 (**b**)]

In a 50-mL three-necked round-bottomed flask were placed 0.42 mmol of the appropriate complex precursor $IrHCl_2(bpy)P$ (P = PPh_3, P^iPr_3), an excess of $SnCl_2{\cdot}2H_2O$ (6.0 mmol, 1.35 g) and 40 mL of ethanol. The resulting suspension was refluxed for 4 h and then the volume reduced to about 15 mL by evaporation of the solvent under reduced pressure. An orange solid separated out which was filtered and crystallised from CH_2Cl_2 and ethanol; yield ⩾70%. Anal. Calc. for $C_{28}H_{24}Cl_4IrN_2PSn$ (**5a**): C, 38.56; H, 2.77; Cl, 16.26; N, 3.21. Found: C, 38.73; H, 2.65; Cl, 16.07; N, 3.32%. IR (KBr, cm^{-1}): 2186 (m) ν_{IrH}. ^{1}H NMR (CD_2Cl_2, 25 °C) δ (ppm): 9.42–7.21 (m, 23H, Ph+bpy), -19.45 (d, 1H, $J_{^1H^{31}P}$ = 21.0, $J_{^1H^{119}Sn}$ = 102.7, $J_{^1H^{117}Sn}$ = 98.6 Hz, IrH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ (ppm): A, −2.20 (s, $J_{^{31}H^{117}Sn}$ = 198.0). $^{119}Sn\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ (ppm): AM, δ_M −328.4, J_{AM} = 206.0. Anal. Calc. for $C_{19}H_{30}Cl_4IrN_2PSn$ (**5b**): C, 29.63; H, 3.93; Cl, 18.41; N, 3.64. Found: C, 29.45; H, 3.89; Cl, 18.64; N, 3.53%. IR (KBr, cm^{-1}): 2148 (m) ν_{IrH}. ^{1}H NMR (CD_2Cl_2, 25 °C) δ (ppm): 9.74–7.31 (m, 8H, bpy), 2.28 (m, 3H, CH phos), 1.22, 1.17, 0.94 0.90 (d, 18H, CH_3), −18.44 (d, 1H, $J_{^1H^{31}P}$ = 15.8, $J_{^1H^{119}Sn}$ = 114.6, $J_{^1H^{117}Sn}$ = 110.7, IrH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C,) δ (ppm): A, 14.3 (s, $J_{^{31}P^{117}Sn}$ = 3475). $^{119}Sn\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ (ppm): AM, δ_M −280.3, J_{AM} = 3637.

2.3.5. General procedure for hydrogenation experiments

A 150-mL stainless steel reaction vessel was charged, under a nitrogen purge, with 5.2 mmol of substrate, 0.0104 mmol of the catalytic precursor and 5 mL of solvent. The reactor was then pressurised with 50 atm of hydrogen, heated at 80–100 °C for the due time (see Tables 1 and 2), cooled to room temperature and the gas allowed to vent off. For analytical purposes, the target products were recovered from the reaction mixture by flash silica gel chromatography (*n*-hexane/ether, 8/2).

Table 1
Hydrogenation of 2-cyclohexen-1-one catalysed by iridium complexes.

Run	Cat.	T (°C)	Conv. (%)	**B** yield (%)
1	$IrHCl_2(Hpz)(PPh_3)_2$	80	100	100
2	$IrHCl(SnCl_3)(Hpz)(PPh_3)_2$ (**3a**)	80	69.0	69.0
3	$IrHCl(SnCl_3)(Hpz)(PPh_3)_2$ (**3a**)	100	94.6	94.6
4	$IrHCl_2(Hpz)(P^iPr_3)_2$	80	5.6	5.6
5	$IrHCl(SnCl_3)(Hpz)(P^iPr_3)_2$ (**4a**)	80	–	–
6	$IrHCl(SnCl_3)(Hpz)(P^iPr_3)_2$ (**4a**)	100	1.0	1.0
7	$IrHCl_2$(H-3-Mepz)$(PPh_3)_2$	80	–	–
8	$IrHCl(SnCl_3)$(H-3-Mepz)$(PPh_3)_2$ (**3b**)	80	–	–
9	$IrHCl(SnCl_3)$(H-3-Mepz)$(PPh_3)_2$ (**3b**)	100	4.4	4.4
10	$IrCl_2(SnCl_3)[P(OEt_3)]_3$ (**2a**)	80	57.5	57.5

2-Cyclohexen-1-one = 5.2 mmol; catalyst = 0.0104 mmol; substrate/catalyst (molar ratio) = 500/1; toluene = 5 mL; $p(H_2)$ = 50 atm; reaction time = 22 h.

3. Results and discussion

3.1. Preparation of complexes

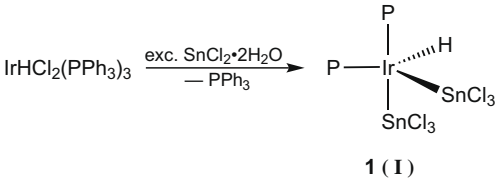
Both *mer*- and *fac*-iridium(III) complexes $IrHCl_2(PPh_3)_3$ [9] react with $SnCl_2{\cdot}2H_2O$ to give hydride-bis(trichlorostannyl) derivative $IrH(SnCl_3)_2(PPh_3)_2$ (**1**), which was isolated in good yield and characterised (Scheme 1).

The reaction proceeds with the insertion of $SnCl_2$ into both Ir–Cl bonds of the starting complex and concurrent loss of one triphenylphosphine, to yield pentacoordinate final derivative **1**.

Related hydride complexes $IrHCl_2P_3$ [12] [P = $P(OEt)_3$ and $PPh(OEt)_2$] also react with $SnCl_2{\cdot}2H_2O$, but in this case the reaction gives exclusively dichloro(trichlorostannyl) complexes $IrCl_2(SnCl_3)P_3$ (**2**), as shown in Scheme 2.

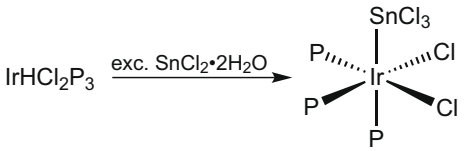
No loss of phosphite was observed, and the reaction seemed to proceed only with substitution of the hydride by the $SnCl_3^-$ group, giving final dichloro complex **2**. Its formation was somewhat unexpected, in view of the results obtained with $IrHCl_2(PPh_3)_3$ (Scheme 1), but was explained on the basis of the initial insertion of $SnCl_2$ into one Ir–Cl bond to give the intermediate $IrHCl(SnCl_3)P_3$, in which the $SnCl_3$ group may be *trans* to the hydride. The well-known *trans* labilising effect [14] of $SnCl_3$, in the presence of excess $SnCl_2$, should favour the substitution of hydride by one Cl^- to yield the final complex $IrCl_2(SnCl_3)P_3$ (**2**). However, the insertion of $SnCl_2$ into the Ir–H bond, giving $IrCl_2(SnHCl_2)P_3$, followed by chloride exchange of the tin–hydride group $SnHCl_2$ yielding **2**, cannot be excluded.

In every case, the nature of the phosphine ligand (P) is important in determining the nature of the reaction product of hydrides $IrHCl_2P_3$ with $SnCl_2{\cdot}2H_2O$. Although triphenylphosphine yielded pentacoordinate hydridebis(trichlorostannyl) complex **1**, octahedral complex **2** was exclusively formed with phosphites $P(OEt)_3$ and $PPh(OEt)_2$. In the first case, the dissociation of the bulky triphenylphosphine probably favours the insertion of two $SnCl_2$ into two Ir–Cl bonds, yielding pentacoordinate bis(stannyl) complex **1**. Instead, with the less bulky phosphites, no dissociation of ligand was observed and octahedral monostannyl complex **2** resulted. However, the reaction with $SnCl_2$ probably involves several steps which lead to substitution of the hydride ligand.



1 (I)

Scheme 1.



2 (II)

P = $P(OEt)_3$ (**a**), $PPh(OEt)_2$ (**b**)

Scheme 2.

Hydride complexes $IrHCl_2(HRpz)P_2$ [11] (R = H, 3-Me; P = PPh_3, P^iPr_3), containing pyrazole as a ligand, also react with $SnCl_2{\cdot}2H_2O$ to give the trichlorostannyl derivatives $IrHCl(SnCl_3)(HRpz)P_2$ (**3**, **4**), as shown in Scheme 3.

The reaction proceeds with the insertion of $SnCl_2$ into only one Ir–Cl bond to give hydride–chlorostannyl complexes **3**, **4**, which were isolated in good yield and characterised.

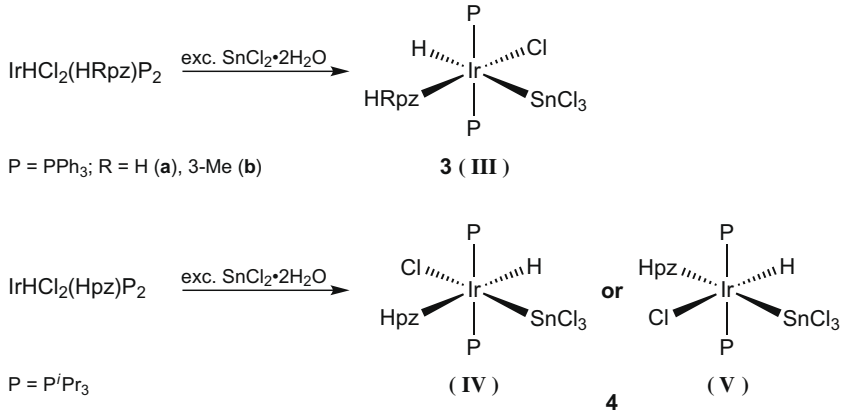
The easy formation of stannyl complexes stabilised by pyrazole ligands prompted us to extend reactions with $SnCl_2$ to other iridium complexes containing N-donor ligands. Our attention focused on both 1,2-bipyridine (bpy) complexes $IrHCl_2(bpy)P$ and 1,3-diaryltriazenide derivatives $IrHCl(1,3\text{-}PhNNNPh)P_2$ (P = PPh_3, P^iPr_3), and results showed that, whereas the 1,2-bipyridine complexes react quickly with $SnCl_2{\cdot}2H_2O$ to give trichlorostannyl derivatives $IrHCl(SnCl_3)(bpy)P$ (**5**) (Scheme 4), triazenide compounds do not react with $SnCl_2{\cdot}2H_2O$ and the starting complexes were recovered unchanged, even after long reaction times in refluxing ethanol (Scheme 5).

The lack of reactivity of the 1,3-triaryldiazenide complexes towards $SnCl_2$ was quite unexpected, and was attributed to the stoichiometry of the complexes, which contain only one chloride ligand. The precursors giving trichlorostannyl complexes do contain the dichloro-hydride moiety [$IrHCl_2$], which undergoes insertion by $SnCl_2$ to afford [Ir]–$SnCl_3$ species. The anionic nature

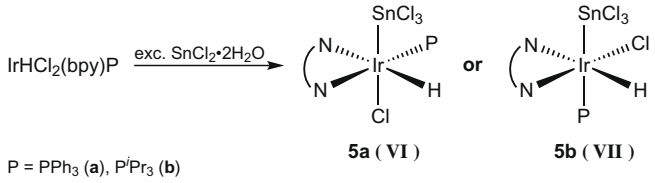
Table 2
Hydrogenation of cinnamaldehyde catalysed by iridium complexes

Run	Cat.	T (°C)	Conv. (%)	**F** yield (%)	**G** yield (%)	**H** yield (%)
1	$IrHCl_2(Hpz)(PPh_3)_2$	80	33.7	33.7	–	–
2	$IrHCl(SnCl_3)(Hpz)(PPh_3)_2$ (**3a**)	80	17.7	17.7	–	–
3	$IrHCl_2(Hpz)(PPh_3)_2$	100	91.4	75.4	16.0	–
4	$IrHCl(SnCl_3)(Hpz)(PPh_3)_2$ (**3a**)	100	60.9	48.3	3.8	8.8
5	$IrHCl_2(Hpz)(P^iPr_3)_2$	100	52.1	43.4	6.4	2.3
6	$IrHCl(SnCl_3)(Hpz)(P^iPr_3)_2$ (**4a**)	100	13.1	12.1	1.0	–
7	$IrHCl_2$(H-3-Mepz)$(PPh_3)_2$	100	6.9	4.0	2.9	–
8	$IrHCl(SnCl_3)$(H-3-Mepz)$(PPh_3)_2$ (**3b**)	100	2.0	2.0	–	–
9	$IrCl_2(SnCl_3)[P(OEt_3)]_3$ (**2a**)	100	43.1	20.9	19.3	2.9
10	$IrH(SnCl_3)_2(PPh_3)_2$ (**1**)	100	71.2	36.7	7.5	26.9

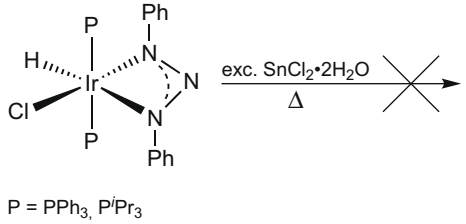
Cinnamaldehyde = 5.2 mmol; catalyst = 0.0104 mmol; substrate/catalyst (molar ratio) = 500/1; toluene = 5 mL; $p(H_2)$ = 50 atm; reaction time = 17 h.



Scheme 3.



Scheme 4.



Scheme 5.

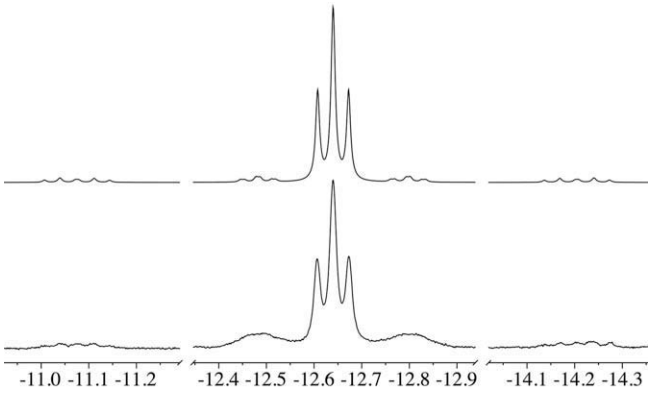


Fig. 1. Observed (bottom) and calculated (top) ^{1}H NMR spectra, in the hydride region, of complex **1** in CD_2Cl_2 at −70 °C. The simulated spectrum was obtained using the parameters reported in Section 2.

of 1,3-triazenide yields monochloro complexes IrHCl(1,3-PhNNNPh)P_2, which turn out to be unreactive towards $SnCl_2$ insertion. This lack of reactivity may be due to the *trans* influence of 1,3-triazenide itself, which makes both H^- and Cl^- ligands *trans* to the PhNNNPh unreactive towards insertion of the $SnCl_2$ group.

The new trichlorostannyl complexes **1–5** were isolated as yellow or orange solids, stable in air and in solution of common organic solvents, in which they behave as non-electrolytes. Analytical and spectroscopic data (IR and ^{1}H, ^{31}P, ^{119}Sn NMR) support the proposed formulations.

Variable-temperature NMR spectra indicate that pentacoordinate complex $IrH(SnCl_3)_2(PPh_3)_2$ (**1**) is fluxional. The singlet appearing at 20 °C in the ^{31}P spectra changes as the temperature is lowered and, at −80 °C, results in a sharp quartet with the characteristic ^{119}Sn and ^{117}Sn satellites, due to coupling with the two tin nuclei. The spectra can be simulated with an AB model with the parameters reported in Section 2, and indicate the magnetic non-equivalence of the two phosphine ligands. The two stannyl groups are also magnetically non-equivalent, matching the presence at −80 °C of two well-separated multiplets at −421.7 and at −395.8 ppm in the ^{119}Sn NMR spectrum. The multiplicity of the signals is due to coupling with the phosphorus nuclei of the two PPh_3 and the spectra can be simulated with two ABM models (M = ^{119}Sn) with the parameters reported in the Section 2. The ^{1}H NMR spectra also support the proposed formulation for **1**, showing the signals of the phenyl protons of the triphenylphosphine and those of the hydride ligand which, at −80 °C, appears as an ABX multiplet (X = ^{1}H) at −12.64 ppm (Fig. 1).

For a pentacoordinate complex, trigonal–bipyramidal (TBP) geometry may be reasonably proposed and, in the case of complex **1**, the NMR data fit one of type **I** (Scheme 1). Although square–pyramidal geometry cannot be completely excluded, literature data [15] lead us to propose a TBP structure of type **I** for our bis(trichlorostannyl) complex **1**.

In the far region, the IR spectrum of phosphite complex $IrCl_2(SnCl_3)[P(OEt)_3]_3$ **2a** shows two bands at 333 and 310 cm^{-1} attributed to the ν_{IrCl} of the two chloride ligands in a mutually *cis* position. In the temperature range between +20 and −80 °C, the ^{31}P NMR spectra of both compounds **2a** and **2b** appear as A_2B multiplets, with the characteristic satellites due to coupling with ^{117}Sn and ^{119}Sn nuclei. However, further support for the presence of the stannyl ligand comes from the ^{119}Sn NMR spectra of **2b**, which show one multiplet at −535 ppm due to coupling with ^{31}P nuclei. The spectra may be simulated with an A_2BM model (M = ^{119}Sn) with the parameters reported in Section 2. The values of $J_{^{119}Sn^{31}P}$ also indicate that the $SnCl_3$ group is probably in *trans* position with respect to one phosphite ligand. On the basis of these data, *fac* geometry **II** (Scheme 2) is proposed for trichlorostannyl compound **2**.

The IR spectra of pyrazole complexes $IrHCl(SnCl_3)(HRpz)(PPh_3)_2$ **3** show a weak band at 2308–2153 cm^{-1}, attributed to the ν_{IrH} of the hydride and the medium-intensity absorption at 3265–3270 cm^{-1} characteristic of ν_{NH} of the pyrazole ligand. The ^{1}H NMR spectra show not only the signals of the phenyl protons of

PPh_3, but also a relatively broad signal at 10.70–10.23 ppm, attributed to the NH proton of the pyrazole. Further support for the presence of this ligand comes from the signals observed at 7.15, 6.48, 5.92 (**3a**) and 6.97, 5.68 ppm (**3b**) which were correlated in a COSY experiment and attributed to the CH proton of Hpz and H-3-Mepz, respectively. A sharp triplet also appears in the low frequency region at −20.58 (**3a**) (Fig. 2) and −20.52 ppm (**3b**), with the characteristic satellites due to coupling with ^{117}Sn and ^{119}Sn nuclei, attributed to the hydride ligand. The high values observed for the $J_{^1H^{119}Sn}$ of 197.1 (**3a**) and 195.3 Hz (**3b**) also suggest a mutually *trans* position for the hydride and stannyl groups. At temperatures between +20 and −80 °C, the ^{31}P NMR spectra show a sharp singlet, matching the magnetic equivalence of the two phosphine ligands. The ^{119}Sn NMR spectrum also appears as a sharp triplet at −651.9 (**3a**) (Fig. 3) and −645.6 ppm (**3b**), due to coupling with the two equivalent phosphorus nuclei, indicating the presence of the $SnCl_3$ group. On the basis of these data, *trans* geometry **(III)** may reasonably be proposed for pyrazole complexes **3**.

The ^{1}H NMR spectra of the related triisopropylphosphine $IrHCl(SnCl_3)(Hpz)(P^iPr_3)_2$ (**4a**) shows the pyrazole NH proton at 10.2 ppm, whereas the hydride resonance appears as a triplet at −14.17 ppm, with the satellites of ^{117}Sn and ^{119}Sn. In contrast with **3,** the value of $J_{^1H^{119}Sn}$ of 49.0 Hz suggests a mutually *cis* position of the hydride and stannyl $SnCl_3$ ligands. In the temperature range between +20 and −80 °C, the ^{31}P NMR spectrum shows a sharp singlet, fitting the magnetic equivalence of the two phosphine ligands; the ^{119}Sn spectrum appears as a triplet at −400.6 ppm, fitting the proposed formulation for the complex. However, spectroscopic data do not unambiguously assign a geometry to compound **4a,** and only X-ray studies will allow us to decide between geometries **IV** and **V** (Scheme 3).

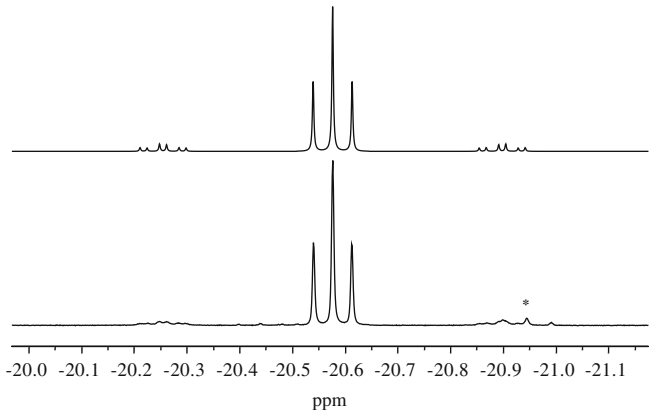


Fig. 2. Observed (bottom) and calculated (top) ^{1}H NMR spectra, in the hydride region, of complex **3a** in CD_2Cl_2 at 25 °C. The asterisk indicates an impurity. The simulated spectrum was obtained using the parameters reported in Section 2.

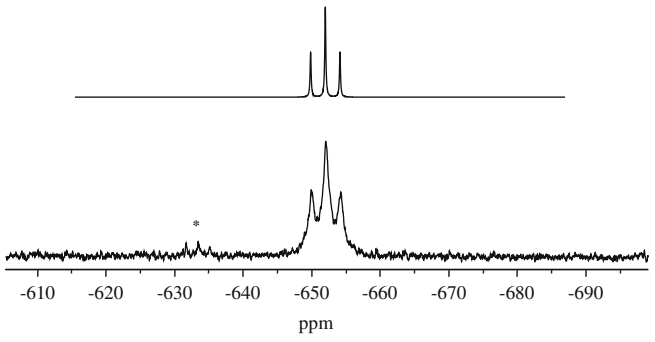


Fig. 3. Observed (bottom) and calculated (top) ^{119}Sn{^{1}H} NMR spectra of complex **3a** in CD_2Cl_2 at 25 °C. The asterisk indicates an impurity. The simulated spectrum was obtained using the parameters reported in Section 2.

The IR spectra of 2,2'-bipyridine complexes $IrHCl(SnCl_3)(bpy)P$ **5** show a medium-intensity band at 2186–2148 cm^{-1} attributed to the ν_{IrH} of the hydride ligand. The ^{1}H NMR spectra confirm its presence, showing a doublet at −19.45 (**5a**) and −18.44 ppm (**5b**), with the characteristic satellites of ^{119}Sn and ^{117}Sn nuclei, whose $J_{^1H^{119}Sn}$ values of 102.7 (**5a**) and 114.6 Hz (**5b**) suggest a mutually *cis* position between the hydride and the $SnCl_3$ ligand. The values of $J_{^1H^{31}P}$ (21 and 15.8 Hz) also suggest a mutually *cis* position between the hydride and phosphite ligands.

The ^{119}Sn NMR spectrum of $IrHCl(SnCl_3)(bpy)(PPh_3)$ **5a** appears as a doublet at −328.4 ppm, with a $J_{^{119}Sn^{31}P}$ value of 206 Hz, suggesting a mutually *cis* position between the $SnCl_3$ group and the PPh_3 ligand. On the basis of these data, *cis–cis* geometry **VI** may be proposed for triphenylphosphine complex **5a**.

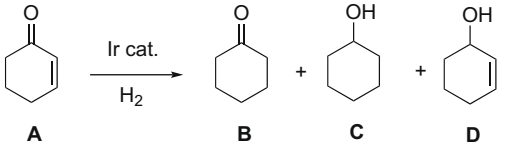
The ^{119}Sn NMR spectrum of the related $IrHCl(SnCl_3)(bpy)(P^iPr_3)$ **5b** appear as a doublet at −280.3 ppm, but with a $J_{^{119}Sn^{31}P}$ value of 3637 Hz, which suggests a mutually *trans* position of $SnCl_3$ with respect to phosphine. On the basis of these data, *cis–trans* geometry **VII** is proposed for triisopropylphosphine complex **5b**.

3.2. Catalytic activity

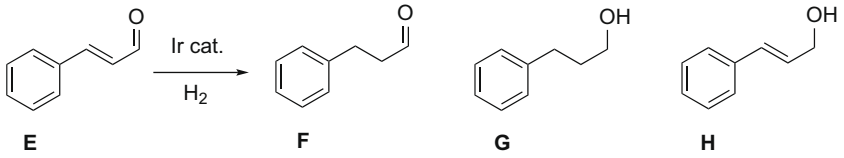
It is known that iridium(III) complexes are catalytically active in the hydrogenation of olefins [16] and, with respect to iridium(I) compounds, have higher tolerance to air oxidation; however, iridium derivatives with the metal atom in oxidation state +III are not often employed as catalyst precursors [17]. In the last few years, some iridium(III) complexes, modified with various phosphino ligands such as xyliphos or BINAP, for example, have been successfully employed in the enantioselective hydrogenation of imines [17]. To our knowledge, iridium(III) compounds containing the $SnCl_3$ moiety have never been used as catalyst precursors for the hydrogenation of unsaturated substrates. Based on the striking results obtained in processes catalysed by trichlorostannyl Pt(II) complexes [1b,18], it was interesting to evaluate the influence of the $SnCl_3$ moiety on the activity of iridium(III) catalysts. Trichlorostannyl iridium complexes were employed in the hydrogenation of the α,β-unsaturated substrates 2-cyclohexen-1-one (**A**) and cinnamaldehyde (**E**), in order to examine the selectivity of our catalytic systems towards hydrogenation of the carbon–carbon and carbon–oxygen double bonds, respectively (Schemes 6 and 7).

A set of experiments was carried out on 2-cyclohexen-1-one (**A**) at 80 °C and 50 atm of H_2 for 22 h, and the results are shown in Table 1.

We first evaluated the catalytic activity of $IrHCl_2(Hpz)(PPh_3)_2$, the precursor of trichlorostannyl derivative $IrHCl(SnCl_3)$-$(Hpz)(PPh_3)_2$ (**3a**). The catalytic system was very active and also selective, affording exclusively cyclohexanone (**B**) as a reaction product, in quantitative yield (run 1 of Table 1). Also complex **3a**, like the dichloro precursor, selectively furnished saturated ketone **B** but in about 70% yield, showing lower catalytic activity. When the reaction temperature was increased to 100 °C, cyclohexanone was selectively obtained to about 95%. Surprisingly, when $IrHCl(SnCl_3)(Hpz)(P^iPr_3)_2$ (**4a**) was used as the catalyst, the reactiv-



Scheme 6.



Scheme 7.

ity fell dramatically: at best, when the reaction was carried out at 100 °C, cyclohexanone was only obtained in traces (run 6 of Table 1). The dichloro complex not containing the $SnCl_3$ moiety also turned out to be practically inactive, affording cyclohexanone in amounts of less than 6%. Owing to the quite good results obtained with trichlorostannyl complex **3a**, containing the triphenylphosphino ligand, we tested the activity of the analogous complex $IrHCl(SnCl_3)$(H-3-Mepz)$(PPh_3)_2$ (**3b**) with a methyl group on position 3 of the pyrazole moiety. Disappointingly, this catalyst was not able to hydrogenate 2-cyclohexen-1-one and, even at 100 °C, its catalytic activity was practically negligible (runs 8 and 9 of Table 1); moreover, its direct precursor $IrHCl_2$(H-3-Mepz)$(PPh_3)_2$ did not show any catalytic activity either. Lastly, the reaction was carried out in the presence of phosphite complex $IrCl_2(SnCl_3)$-$[P(OEt_3)]_3$ (**2a**): this catalyst showed fairly good activity, affording exclusively cyclohexanone in about 58% yield (run 10 of Table 1).

Interesting results were obtained in the hydrogenation of cinnamaldehyde. The hydrogenation of α,β-unsaturated aldehydes, particularly cinnamaldehyde, is an important process in the manufacture of some useful fine chemicals as intermediates for the synthesis of pharmaceuticals, additives for food flavours, and valuable building blocks for fragrances [19]. Many rhodium-, ruthenium- and iridium-based catalytic systems have been employed in the selective hydrogenation of α,β-unsaturated aldehydes [20]: iridium complexes generally show lower activity but higher selectivity. Very recently, cinnamaldehyde was hydrogenated in the presence of iridium(I) complexes with tris(*ortho*-anisyl)phosphine and other bulky phosphine ligands: in all cases, these catalysts prevalently reduced the carbon–carbon double bond [20].

An initial experiment was carried out with $IrHCl_2$(Hpz)$(PPh_3)_2$ as the catalytic precursor: after 17 h at 80 °C and 50 atm of H_2, the conversion of substrate **E** was less than 34% and the saturated aldehyde 3-phenylpropanal (**F**) was the only reaction product (run 1 of Table 2). When the reaction temperature was increased to 100 °C, the activity of this catalyst increased greatly, reaching about 92% of substrate conversion, but at the expense of selectivity: about 75% of 3-phenylpropanal (**F**) and 16% of 3-phenylpropanol (**G**) were also found in the reaction mixture (run 3 of Table 2). Like the results observed in the hydrogenation of 2-cyclohexen-1-one, trichlorostannyl derivative $IrHCl(SnCl_3)$(Hpz)$(PPh_3)_2$ (**3a**) showed lower catalytic activity, 3-phenylpropanal only being produced in about 18% yield (run 2 of Table 2); when the reaction was carried out at 100 °C, 60.9% of substrate conversion was achieved. Also in this case, the reaction temperature also affected selectivity: besides 3-phenylpropanal (**F**), the prevailing reaction products, 3-phenylpropanol (**G**) and cinnamyl alcohol (**H**), were formed (run 4 of Table 2).

The trichlorostannyl complex containing phosphino ligand P^iPr_3 (**4a**), completely inactive towards 2-cyclohexenone hydrogenation, after 17 h at 100 °C and 50 atm of H_2 gave a quite low substrate conversion (13.1%) with more than 90% selectivity towards 3-phenylpropanal (run 6 of Table 2). The dichloro derivative precursor was more active, affording prevalently 3-phenylpropanal and small amounts of both corresponding saturated and unsaturated alcohols. Disappointing results were obtained with both complexes containing the (H-3-Mepz) moiety, being similar to the data achieved in 2-cyclohexen-1-one hydrogenation. Lastly, when phosphite complex $IrCl_2(SnCl_3)[P(OEt_3)]_3$ (**2a**) was used as catalyst, cinnamaldehyde hydrogenation afforded a mixture containing the saturated aldehyde **F** and both alcohols **G** and **H**. Unlike the case of 2-cyclohexen-1-one hydrogenation, this catalyst precursor also proved quite good at reducing the carbon–oxygen double bond, thus furnishing almost equimolecular amounts of 3-phenylpropanal (**F**) and 3-phenylpropanol (**G**) (run 9 of Table 2).

These iridium(III) complexes show interesting catalytic activity in the hydrogenation of α,β-unsaturated substrates but, contrary to our expectations, the tricholorostannyl moiety negatively affected their catalytic performance. The steric hindrance created by this bulky group certainly played a detrimental role in the catalytic cycle, lowering the yield of hydrogenation products with respect to dichloro catalyst precursors not containing the $SnCl_3$ unit. In addition, when the triphenylphosphine ligand was replaced by more hindered phosphino groups such as triisopropylphosphine, catalytic activity decreased greatly. The detrimental effect due to steric factors was also highlighted by the dramatic fall in activity when iridium triphenylphosphino complexes containing the H-3-Mepz moiety instead of the simple Hpz were used in the hydrogenation process. As expected, all these iridium complexes mainly reduce the carbon–carbon double bond of the α,β-unsaturated substrates: in particular, in the case of 2-cyclohexen-1-one hydrogenation, this peculiarity can be exploited for selective production of the corresponding saturated ketone.

Acknowledgements

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