

## Synthesis and Catalytic Activity of Trihalotin–Iridium Complexes

R. USON, L. A. ORO, M. J. FERNANDEZ and M. T. PINILLOS  
 Department of Inorganic Chemistry, University of Saragossa, Spain  
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The addition of phosphine derivatives and  $\text{SnX}_2$  ( $X = \text{Cl}$  or  $\text{Br}$ ) to solutions of  $[\text{IrCl}(\text{COD})]_2$  ( $\text{COD} = 1,5\text{-cyclooctadiene}$ ) leads to the preparation of the pentacoordinated complexes  $[\text{Ir}(\text{SnX}_3)(\text{COD})\text{L}_2]$ , which carbonylated or hydrogenated at ordinary pressure and at room temperature yield  $[\text{Ir}(\text{SnCl}_3)(\text{CO})_2\text{L}_2]$  or, respectively,  $[\text{Ir}(\text{SnCl}_3)\text{H}_2\text{L}_2]$ . The latter catalyze both the hydrogenation and the isomerization of *n*-heptene; the rates of these reactions decrease with decreasing basicity of the phosphine.

### Introduction

As reported [1, 2] some pentacoordinated complexes of the general formula  $[\text{Ir}(\text{SnCl}_3)(\text{diolefin})_2]$  (diolefin = 1,5-cyclooctadiene(COD) or 2,5-norbornadiene (NBD)) can be prepared by addition of solutions of  $\text{SnCl}_2$  in dilute hydrochloric acid to sodium hexachloroiridate(IV) in the presence of the respective diolefin and one of the diolefin molecules can be substituted by phosphines or arsines to give complexes of the type  $[\text{Ir}(\text{SnCl}_3)(\text{diolefin})\text{L}_2]$  [1–3].

TABLE I. Analytical and Ir Data for  $[\text{Ir}(\text{SnClX}_2)(\text{COD})\text{L}_2]$  Complexes.

Complex		Found (calcd.) (%)		$\Lambda_M$ ( $\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ )	Yield (%)	$\nu(\text{Sn-X})^a$ ( $\text{cm}^{-1}$ )
		C	H			
$[\text{Ir}(\text{SnCl}_3)(\text{COD})(\text{P}(p\text{-MeOC}_6\text{H}_4)_3)_2]$	(I)	49.30 (48.81)	4.18 (4.39)	15	80	310, 290sh
$[\text{Ir}(\text{SnCl}_3)(\text{COD})(\text{P}(p\text{-MeC}_6\text{H}_4)_3)_2]$	(II)	52.26 (52.94)	4.85 (4.79)	13	85	310, 290, 280sh
$[\text{Ir}(\text{SnCl}_3)(\text{COD})(\text{P}(\text{C}_6\text{H}_5)_3)_2]$	(III)	50.14 (50.32)	4.05 (4.03)	13	84	310, 295, 285sh
$[\text{Ir}(\text{SnCl}_3)(\text{COD})(\text{P}(p\text{-FC}_6\text{H}_4)_3)_2]$	(IV)	45.44 (45.61)	3.24 (3.11)	14	80	315, 295, 285
$[\text{Ir}(\text{SnCl}_3)(\text{COD})(\text{P}(p\text{-ClC}_6\text{H}_4)_3)_2]$	(V)	41.09 (42.04)	2.75 (2.86)	13	60	310, 300, 290sh
$[\text{Ir}(\text{SnClBr}_2)(\text{COD})(\text{P}(\text{C}_6\text{H}_5)_3)_2]$	(VI)	45.49 (46.35)	3.84 (3.72)	12	51	295, 215, 205 <sup>b</sup>
$[\text{Ir}(\text{SnCl}_3)(\text{COD})(\text{dppe})]$	(VII)	44.04 (44.19)	3.39 (3.90)	1	86	308, 290
$[\text{Ir}(\text{SnCl}_3)(\text{COD})(\text{dppb})]$	(VIII)	45.18 (45.42)	4.08 (4.24)	2	67	310, 290, 280
$[\text{Ir}(\text{SnCl}_3)(\text{COD})(\text{dppen})]$	(IX)	45.24 (44.32)	3.91 (3.71)	1	79	305, 290, 285
$[\text{Ir}(\text{SnCl}_3)(\text{COD})(\text{diop})]$	(X)	45.77 (45.75)	4.36 (4.33)	1	73	310, 295
$[\text{Ir}(\text{SnClBr}_2)(\text{COD})(\text{dppe})]$	(XI)	40.62 (40.32)	3.79 (3.58)	0	29	290, 215, 200 <sup>b</sup>
$[\text{Ir}(\text{SnClBr}_2)(\text{COD})(\text{dppen})]$	(XII)	40.50 (40.40)	3.58 (3.39)	6	40	290, 215 <sup>b</sup>

<sup>a</sup> $\nu(\text{Sn-Cl})$  unless otherwise indicated (nujol mulls). <sup>b</sup>X = Cl or Br.

TABLE II. Analytical and Ir Data for  $[\text{Ir}(\text{SnCl}_3)\text{Y}_2\text{L}_2]$  Complexes (Y = CO or H).

Complex		Found (calcd.) (%)		$\Lambda_M$	Yield (%)	$\nu(\text{Sn-Cl})^a$ ( $\text{cm}^{-1}$ )	Other Bands ( $\text{cm}^{-1}$ )
		C	H				
$[\text{Ir}(\text{SnCl}_3)(\text{CO})_2(\text{P}(p\text{-MeOC}_6\text{H}_4)_3)_2]$	(XIII)	44.77 (44.85)	3.75 (3.56)	9	63	320, 305	2000, 1975 <sup>b</sup>
$[\text{Ir}(\text{SnCl}_3)(\text{CO})_2(\text{P}(p\text{-MeC}_6\text{H}_4)_3)_2]$	(XIV)	49.09 (48.84)	4.02 (3.91)	2	81	320, 302	2020, 1975 <sup>b</sup>
$[\text{Ir}(\text{SnCl}_3)(\text{CO})_2(\text{P}(\text{C}_6\text{H}_5)_3)_2]$	(XV)	46.63 (45.72)	3.21 (3.00)	8	71	320, 305	2005, 1980 <sup>b</sup>
$[\text{Ir}(\text{SnCl}_3)(\text{CO})_2(\text{P}(p\text{-FC}_6\text{H}_5)_3)_2]$	(XVI)	42.16 (41.24)	2.60 (2.17)	4	60	320, 310	2005, 1980 <sup>b</sup>
$[\text{Ir}(\text{SnCl}_3)(\text{CO})_2(\text{P}(p\text{-ClC}_6\text{H}_5)_3)_2]$	(XVII)	36.81 (37.91)	2.10 (1.99)	4	53	320, 310, 295	2035, 1980 <sup>b</sup>
$[\text{Ir}(\text{SnCl}_3)(\text{CO})_2(\text{dppe})]$	(XVIII)	38.24 (38.58)	2.63 (2.78)	3	30	320, 310, 300	2050, 1995 <sup>b</sup>
$[\text{Ir}(\text{SnCl}_3)\text{H}_2(\text{P}(p\text{-MeOC}_6\text{H}_4)_3)_2]$	(XIX)	44.80 (44.87)	3.95 (3.91)	6	60	320, 305, 295	2220–2100 <sup>c</sup>
$[\text{Ir}(\text{SnCl}_3)\text{H}_2(\text{P}(p\text{-MeC}_6\text{H}_4)_3)_2]$	(XX)	49.19 (49.07)	4.34 (4.31)	10	76	330, 320, 310	2220–2100 <sup>c</sup>
$[\text{Ir}(\text{SnCl}_3)\text{H}_2(\text{P}(\text{C}_6\text{H}_5)_3)_2]$	(XXI)	46.63 (45.81)	3.40 (3.41)	12	70	325, 300	2210–2090 <sup>c</sup>
$[\text{Ir}(\text{SnCl}_3)\text{H}_2(\text{P}(p\text{-FC}_6\text{H}_4)_3)_2]$	(XXII)	41.85 (41.08)	3.17 (2.47)	4	34	335, 325, 315	2200–2100 <sup>c</sup>
$[\text{Ir}(\text{SnCl}_3)\text{H}_2(\text{P}(p\text{-ClC}_6\text{H}_4)_3)_2]$	(XXIII)	35.91 (37.57)	2.53 (2.26)	6	48	335, 320	2200–2080 <sup>c</sup>

<sup>a</sup>Nujol mulls. <sup>b</sup> $\nu(\text{CO})$  ( $\text{CHCl}_3$  solution). <sup>c</sup> $\nu(\text{Ir-H})$  (nujol mulls).

These complexes present either a trigonal bipyramidal structure [2], or a distorted one, midway between trigonal bipyramidal – with  $\text{SnCl}_3$  equatorial – and square pyramidal with  $\text{SnCl}_3$  axial [4]. Their solutions show a dynamic behaviour [3].

In the present paper we describe a novel and straightforward route for the preparation of complexes of the type  $[\text{Ir}(\text{SnClX}_2)(\text{COD})\text{L}_2]$ . Their reactions with carbon monoxide and hydrogen give rise to the displacement of the diolefin and lead to the formation of  $[\text{Ir}(\text{SnCl}_3)(\text{CO})_2\text{L}_2]$  or, respectively,  $[\text{Ir}(\text{SnCl}_3)\text{H}_2\text{L}_2]$ . Their catalytic behaviour is also discussed (L = monophosphines of the type  $\text{P}(p\text{-RC}_6\text{H}_4)_3$  or diphosphines (dppe = bis(1,2-diphenylphosphino)ethane, dppb = bis(1,4-diphenylphosphino)butane, dppen = *cis*-bis(1,2-diphenylphosphino)ethylene, diop = (–)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane)).

## Experimental

The C and H analyses were made with a Perkin-Elmer 240 microanalyzer; the IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer (over the range 4000–200  $\text{cm}^{-1}$ ) using Nujol mulls between polyethylene sheets; conductivities were measured in approx.  $5 \times 10^{-4}$  M acetone solutions with a Philips 9501/01 conductimeter.

Tables I and II list the analytical results, conductivities, yields and IR data for the novel complexes. All of them decompose before melting.

The catalytic behaviour was tested in a conventional hydrogenation apparatus, provided with a septum. The introduction of the reactants into the reaction flask was done in every case in the following order: solution of the catalyst, n-heptene (3 mmol), hydrogen (initial pressure: 1 atm). A 100:1 ratio of substratum to catalyst and 15  $\text{cm}^3$  dichloromethane as solvent were generally used. The rates were determined by analyzing the products in a Perkin-Elmer 3920B chromatograph. The peak areas were measured with a Minigrator Computing Integrator.

### Preparation of Complexes of the General Formulae $[\text{Ir}(\text{SnClX}_2)(\text{COD})(\text{P}(p\text{-RC}_6\text{H}_4)_3)_2]$ (I–VI) and $[\text{Ir}(\text{SnClX}_2)(\text{COD})(\text{diphosphine})]$ (VII–XII)

$[\text{IrCl}(\text{COD})]_2$  [5] (40–50 mg, ~0.07 mmol) and the respective monodentate phosphine (1:2 molar ratio) or diphosphine (1:1 molar ratio) were suspended in methanol and the stirring was continued until complete solution of the reagents. Upon addition of equimolecular amounts of  $\text{SnCl}_2$  or  $\text{SnBr}_2$  the intense-red solution quickly turned yellow. In the case of the monophosphines it was necessary to concentrate the solvent whereupon the diphosphines precipitated spontaneously. The resulting yellow compounds were filtered, washed with cold

methanol and ether recrystallized from dichloromethane-ether (30–85% yields).

*Preparation of Complexes of the General Formulae*  
 $[\text{Ir}(\text{SnCl}_3)(\text{CO})_2(\text{P}(\text{p-RC}_6\text{H}_4)_3)_2]$  (XIII–XVII) and  
 $[\text{Ir}(\text{SnCl}_3)(\text{CO})_2(\text{dppe})]$  (XVIII)

Carbon monoxide (at ordinary pressure and room temperature) was bubbled for 30 min through solutions of 50 mg of  $[\text{Ir}(\text{SnCl}_3)(\text{COD})(\text{dppe})]$  or of the corresponding complex of the type  $[\text{Ir}(\text{SnCl}_3)(\text{COD})(\text{P}(\text{p-RC}_6\text{H}_4)_3)_2]$  in chloroform. After concentration of the solutions ether was added as a precipitating agent and the resulting pale-yellow solid was filtered off, washed with ether and vacuum-dried (30–80% yields).

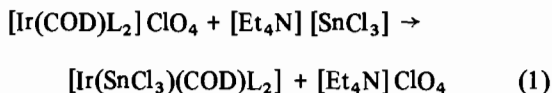
*Preparation of Complexes of the Type*  $[\text{Ir}(\text{SnCl}_3)\text{H}_2(\text{P}(\text{p-RC}_6\text{H}_4)_3)_2]$  (XIX–XXIII)

30 min bubbling of hydrogen (at ordinary pressure and room temperature) through acetone solutions of complexes of the type  $[\text{Ir}(\text{SnCl}_3)(\text{COD})(\text{P}(\text{p-RC}_6\text{H}_4)_3)_2]$  in chloroform. After concentration of the solutions ether was added as a precipitating agent and the resulting pale-yellow solid was filtered off, washed with ether and vacuum-dried (30–80% yields).

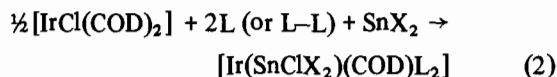
## Results and Discussion

### Complexes of the Type $[\text{Ir}(\text{SnCl}_2)(\text{COD})\text{L}_2]$

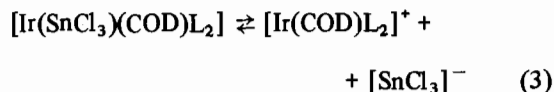
Although complexes of this type can be obtained by a process according to eqn. (1)



we generally did not start from cationic complexes since the simple addition of  $\text{SnX}_2$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) and the respective phosphine to methanol solutions of  $[\text{IrCl}(\text{COD})]_2$  leads, according to eqn. (2),



to the same products. The analytical data of the yellow complexes are listed in Table I. As may be seen, whilst the diphosphine complexes are non-conducting the monodentate phosphine complexes show a very low conductivity which, being beneath the expected value for 1:1 electrolytes, suggest the existence of an equilibrium



On the other hand, the complexes show two or three absorptions in the  $\nu(\text{Sn-Cl})$  stretching region, which coincide with those observed for analogous compounds [6]. The shift of the  $\nu(\text{Sn-X})$  frequencies towards higher energies ( $\Delta\nu = \nu(\text{Sn-X})_{\text{bonded}} - \nu(\text{Sn-X})_{\text{free}} = 15\text{--}30 \text{ cm}^{-1}$ ) confirms that the  $\text{SnClX}_2$  group is linked to the rhodium atom [7].

### Complexes of the Type $[\text{Ir}(\text{SnCl}_3)(\text{CO})_2\text{L}_2]$

The bubbling of carbon monoxide at ordinary pressure through chloroform solutions of  $[\text{Ir}(\text{SnCl}_3)(\text{COD})\text{L}_2]$  gives rise to the displacement of the diolefin and the formation of the corresponding dicarbonyls, according to eqn. (4)

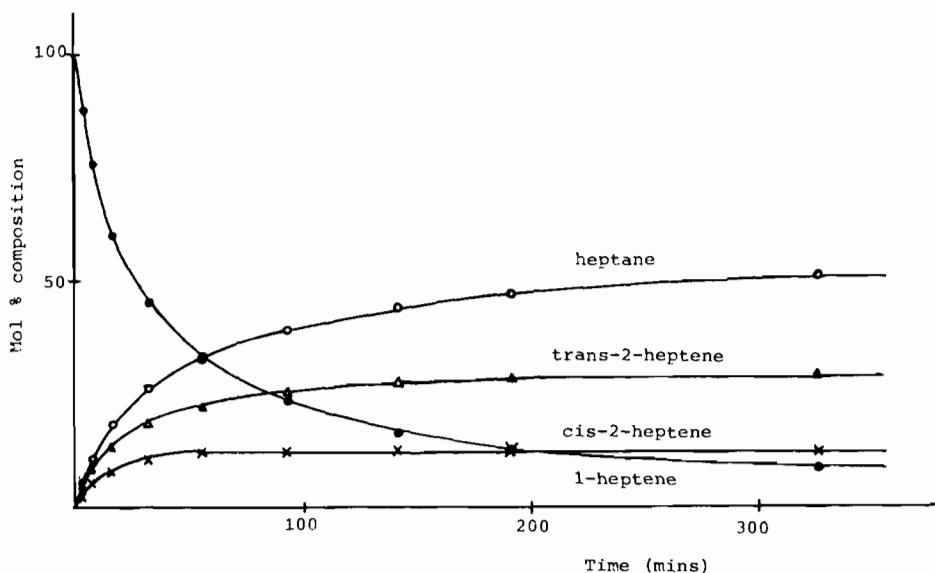
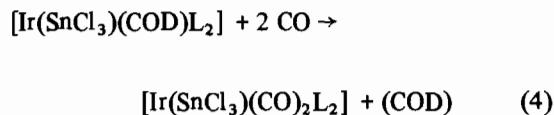


Fig. 1. The catalytic hydrogenation of n-heptene with  $[\text{Ir}(\text{SnCl}_3)(\text{COD})(\text{P}(\text{p-MeC}_6\text{H}_4)_3)_2]$  in dichloromethane.

TABLE III. The Hydrogenation of n-Heptene using  $[\text{Ir}(\text{SnCl}_3)(\text{COD})(\text{P}(p\text{-RC}_6\text{H}_4)_3)_2]$  Complexes.

R	Initial Rate <sup>a</sup> (Induction time (min))						Selectivity <sup>b</sup>
	heptane		<i>trans</i> -2-heptene		<i>cis</i> -2-heptene		
MeO	1.00	(0)	0.80	(0)	0.37	(0)	0.54
Me	1.66	(0)	1.56	(0)	0.71	(0)	0.49
H	0.21	(4)	0.23	(0)	0.11	(0)	0.44
F	0.08	(33)	0.14	(24)	0.04	(63)	0.38
Cl	0.07	(150)	0.12	(70)	0.04	(180)	0.31

<sup>a</sup>Mol (mol Rh)<sup>-1</sup> (min)<sup>-1</sup>. <sup>b</sup>(%heptane)/(% heptane + % *trans*-2-heptene + % *cis*-2-heptene) when n-heptene concentration is 60%.

This process is a general one for monophosphines, whilst the only diphosphine which reacts under these conditions is dppe.

The analytical data of the novel dicarbonyls are listed in Table II. Their IR spectra show two vibrations due to  $\nu(\text{CO})$  both in the solid state and in solution, and confirm the presence of a coordinated  $\text{SnCl}_3^-$  and the absence of diolefin. All the yellow dicarbonyls decompose before melting, and are non-conducting in acetone solution ( $\Lambda_M = 2\text{--}9 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ).

#### Complexes of the Type $[\text{Ir}(\text{SnCl}_3)\text{H}_2\text{L}_2]$

The monophosphines  $[\text{Ir}(\text{SnCl}_3)(\text{COD})\text{L}_2]$  react in acetone solution with hydrogen at ordinary pressure to give dihydrides of the type  $[\text{Ir}(\text{SnCl}_3)\text{H}_2\text{L}_2]$ , whilst the homologous diphosphines do not undergo reactions. As may be seen from Table II, the pale-yellow complexes, which are non-conducting in acetone solution ( $\Lambda_M = 4\text{--}12 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) show in every case a very broad band in the 2220–2080  $\text{cm}^{-1}$  region, assignable to  $\nu(\text{Ir-H})$ . Compared with the afore-described Ir(I) complexes the dihydrides show a stronger Ir–Sn interaction, which decreases in the sequence  $[\text{Ir}(\text{SnCl}_3)\text{H}_2\text{L}_2] > [\text{Ir}(\text{SnCl}_3)(\text{CO})_2\text{L}_2] > [\text{Ir}(\text{SnCl}_3)(\text{COD})\text{L}_2]$

#### Catalytic Activity

Since complexes of the type  $[\text{Ir}(\text{SnCl}_3)(\text{COD})(\text{P}(p\text{-RC}_6\text{H}_4)_3)_2]$  react with hydrogen we have studied the behaviour of their dichloromethane solu-

tions in the hydrogenation of n-heptene. A typical hydrogenation with the  $\text{P}(p\text{-MeC}_6\text{H}_4)_3$  complex is shown in Fig. 1, and the corresponding results are listed in Table III. As may be seen, both the hydrogenation and the isomerization rates decrease with decreasing basicity of the phosphine, so that the less active complexes require a certain induction time. On the other hand – referring to the formation of heptane – the decrease of selectivity follows the same sequence (see Table III). The position of  $\text{P}(p\text{-MeC}_6\text{H}_4)_3$  and  $\text{P}(p\text{-MeOC}_6\text{H}_4)_3$  in the aforementioned sequence, however, is reversed, as has already been observed by Augustine and Pellet [8] in catalytic hydrogenation reactions with rhodium complexes of the type chlorobis(trisubstituted-arylphosphine).

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