Inorganica Chimica Acta, 180 (1991) 177–181

Trichlorostannato ethylene rhodium(I) complexes

Victoria García and **María A. Garralda***
Facultad de Ciencias Químicas de San Sebastián, Universidad del País Vasco, Apdo. 1072, 20080 San Sebastián (Spain)

(Received September 4, 1990)

Abstract

$[Rh(C_2H_4)_2Cl]_2$ reacts with triarylphosphines and tin(II) chloride (Rh/P/Sn = 1/2/1) to give pentacoordinated bis(ethylene) neutral complexes $Rh(SnCl_3)(C_2H_4)_2(PR_3)_2$. When using Rh/P/Sn = 1/1/2 stoichiometric ratios, anionic compounds $[Rh(SnCl_3)_2(C_2H_4)_2(PR_3)]^-$, isolated as bulky cations salts, are obtained. At room temperature and atmospheric pressure, ethylene is not displaced by carbon monoxide from these complexes. While neutral compounds remain unchanged, anionic compounds react with carbon monoxide that displaces one $SnCl_3^-$ group, thus yielding $Rh(SnCl_3)(CO)(C_2H_4)_2(PR_3)$ complexes. These monocarbonylated complexes could also be obtained by direct reaction with Rh/P/Sn = 1/1/1 stoichiometric ratios, under bubbling CO in ambient conditions. The temperature dependence of the ^1H NMR spectra indicates rotation of the ethylene groups around the rhodium–olefin axis. ^{31}P NMR spectra show no temperature dependence suggesting intramolecular processes are still rapid at −60 °C.

Introduction

Transition metal complexes containing covalently bonded tin compounds are of considerable interest, partly due to their potential catalytic activity in organic transformations; their chemistry has recently being reviewed [1]. Several rhodium(I) complexes containing trichlorostannato groups and diolefins have been described [2–8]. Most of these compounds are pentacoordinated and they have been assumed to show distorted trigonal bipyramidal structures, with the diolefinic ligands occupying one axial and one equatorial position [2, 9, 10]. Reactivity studies on these diolefinic rhodium(I) compounds containing P-donor ligands, have shown that while 1,5-cyclooctadiene can be easily displaced by carbon monoxide, norbornadiene is not displaced under similar conditions, instead one $SnCl_3^-$ group is displaced to afford monocarbonylated complexes [8].

Monoolefins are widely used as substrates in several catalytic processes. Therefore, we thought it useful to try the isolation of trichlorostannato rhodium(I) complexes containing ethylene as the olefinic ligand and study their solution behaviour along with the possibility of displacement of ethylene by CO. We report now our results for some new ethylene trichlorostannato complexes.

Experimental

The preparation of the metal complexes was carried out at room temperature under nitrogen by standard Schlenk techniques. $[Rh(C_2H_4)_2Cl]_2$ was prepared as previously reported [11].

Microanalyses were carried out with a Perkin-Elmer 240C microanalyzer. Conductivities were measured in *c.* 2.5×10^{-4} M acetone solutions with a Metrohm E 518 conductimeter. IR spectra were recorded with a Perkin-Elmer 598 spectrophotometer in the range 4000–200 cm^{-1} using nujol mulls between polyethylene sheets. NMR spectra were recorded with an XL-300 Varian spectrometer; ^1H (TMS internal standard) and ^{31}P (H_3PO_4 external standard) spectra were measured from $CDCl_3$ at variable temperature in 5 mm tubes; ^{119}Sn (Me_4Sn external standard) spectra were measured from acetone/acetone d^6 = 3/1 solutions at room temperature in 10 mm tubes.

Preparation of $Rh(SnCl_3)(C_2H_4)_2(PR_3)_2$ compounds

To stirred CH_2Cl_2 suspensions of $[Rh(C_2H_4)_2Cl]_2$ (0.06 mmol), a stoichiometric quantity of PR_3 dissolved in CH_2Cl_2 in the Rh/PR_3 = 1/2 ratio was added, whereupon the complexes dissolved. The addition of stoichiometric amounts of $SnCl_2\cdot2H_2O$ (Rh/Sn = 1/1) in methanol, followed by evaporation of CH_2Cl_2 led to the corresponding trichlorostannato

---

*Author to whom correspondence should be addressed.

0020-1693/91/$3.50

compounds. The complexes were filtered off, washed with methanol and dried. Yields: 26–40%.

Preparation of anionic compounds

To CH_2Cl_2 suspensions fo $[Rh(C_2H_4)_2Cl]_2$ (0.06 mmol) was added the stoichiometric amount of PR_3 and a MeOH solution of $SnCl_2 \cdot 2H_2O$ (Rh/P/Sn = 1/1/2), whereupon red solutions were obtained. Addition of the stoichiometric amount of Et_4NCl or PPNCl in methanol followed by CH_2Cl_2 evaporation gave orange solids that were filtered off, washed with methanol and dried. Yields: 10–45%.

Reaction of $Et_4N[Rh(SnCl_3)_2(C_2H_4)_2(PR_3)]$ with carbon monoxide

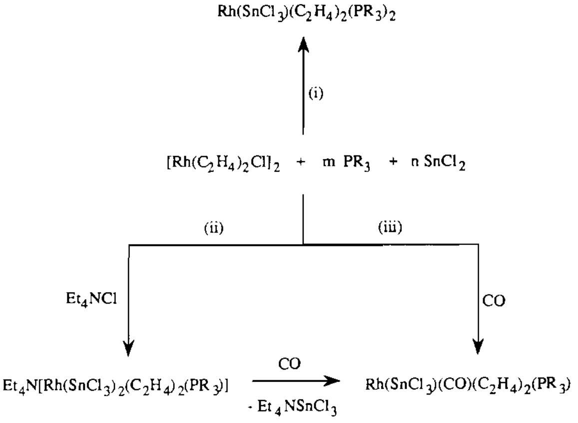
Carbon monoxide at atmospheric pressure was bubbled for 10 min through CH_2Cl_2/MeOH red solutions containing $Et_4N[Rh(SnCl_3)_2(C_2H_4)_2(PR_3)]$ prepared *in situ* by the above method. Filtration of the opalescent solutions followed by evaporation of CH_2Cl_2 gave yellow solids that were filtered off, washed with methanol and dried.

Direct preparation of $Rh(SnCl_3)(CO)(C_2H_4)_2(PR_3)$ compounds

To suspensions of $[Rh(C_2H_4)_2Cl]_2$ (0.06 mmol) in CH_2Cl_2 was added the corresponding phosphine dissolved in CH_2Cl_2 and a MeOH solution of $SnCl_2 \cdot 2H_2O$ (Rh/P/Sn = 1/1/1) whereupon orange solutions were obtained. Bubbling of carbon monoxide at atmospheric pressure for 10 min, followed by CH_2Cl_2 evaporation gave yellow solids that were filtered off, washed with methanol and dried. Yields: 20–30%.

Results and discussion

$[Rh(C_2H_4)_2Cl]_2$ reacts with triarylphosphines and tin(II) chloride (Rh/P/Sn = 1/2/1) to give neutral pentacoordinated bis(ethylene)complexes, $Rh(SnCl_3)(C_2H_4)_2(PR_3)_2$ ($R = C_6H_5, p\text{-}FC_6H_4, p\text{-}ClC_6H_4, p\text{-}CH_3OC_6H_4, p\text{-}CH_3C_6H_4, m\text{-}CH_3C_6H_4$). These complexes remain unchanged after bubbling CO through their CH_2Cl_2 solutions for 1 h at room temperature and atmospheric pressure. When the former reactions are performed under carbon monoxide only mixtures of bis(ethylene) or carbonylated compounds are obtained. When using Rh/P/Sn = 1/1/2 stoichiometric ratios, red solutions are obtained and addition of chloride bulky cations, such as tetraethylammonium or bis(triphenylphosphineimine) (PPN), allows the isolation of anionic complexes $[Rh(SnCl_3)_2(C_2H_4)_2(PR_3)]^-$ containing two $SnCl_3^-$ groups bonded to the rhodium atom, that behave as 1:1 electrolytes in acetone solution. These anionic complexes react with carbon monoxide and displacement of one $SnCl_3^-$ group occurs, while both ethylene groups remain coordinated, giving monocarbonylated bis(ethylene) neutral compounds. This behaviour is similar to that of analogous anionic norbornadiene complexes [8]. This similarity prompted us to try the more direct route of reaction between $[Rh(C_2H_4)_2Cl]_2$, PR_3 and tin(II) chloride (Rh/P/Sn = 1/1/1) in the presence of carbon monoxide, thus obtaining the same monocarbonylated bis(ethylene) complexes $Rh(SnCl_3)(CO)(C_2H_4)_2(PR_3)$. All these reactions are depicted in Scheme 1 and indicate a high reluctancy of ethylene groups to suffer displacement reactions in these trichlorostannato 18 e$^-$ complexes. Table 1 collects the analytical, conductivity and IR data for the isolated compounds.



Scheme 1. (i) $m = 4$, $n = 2$; (ii) $m = 2$, $n = 4$; (iii) $m = 2$, $n = 2$.

All the complexes show two or three strong bands in the far IR due to ν(Sn–Cl) of the coordinated $SnCl_3^-$ groups [12]. For any particular triarylphosphine, complexes containing only one phosphine group bonded to rhodium (anionic or monocarbonylated complexes) show higher ν_{sym}(Sn–Cl) values than those containing two phosphine groups bonded to the metal, i.e. $Rh(SnCl_3)(C_2H_4)_2(PR_3)_2$. In the former complexes, the $SnCl_3^-$ groups may donate more charge, with reinforcement of the Sn–Cl bonds [13]. Monocarbonylated complexes show a single band above 2000 cm^{-1} due to $\nu(C{\equiv}O)$, highest for the least basic ligand $(p\text{-}ClC_6H_4)_3P$ [14].

NMR spectra

The chemical shifts and coupling constant data for ^{31}P and the ethylene region of ^1H NMR spectra are tabulated in Table 2.

$^{31}P\{^1H\}$ NMR spectra of $Rh(SnCl_3)(C_2H_4)_2(PR_3)_2$ complexes show only one doublet due to ^{103}Rh splitting, flanked by tin satellite signals, that are observable at room temperature, unlike what happens in analogous rhodium compounds [2–4] and suggests

TABLE 1. Analytical results, IR and conductivity data for the isolated complexes

Complex	Analysis: Found (calc.) (%)			ν(Sn–Cl) (cm^{-1})	ν(C≡O) (cm^{-1})	Λ_M (ohm^{-1} cm^2 mol^{-1})
	C	H	N			
$Rh(SnCl_3)(C_2H_4)_2[(p\text{-}CH_3OC_6H_4)_3P]_2$	49.81	4.18		305(s), 280(s)		<10
	(50.73)	(4.59)				
$Rh(SnCl_3)(C_2H_4)_2[(p\text{-}CH_3C_6H_4)_3P]_2$	54.23	4.76		310(s), 290(s)		<10
	(55.64)	(5.04)				
$Rh(SnCl_3)(C_2H_4)_2[(m\text{-}CH_3C_6H_4)_3P]_2$	56.09	4.85		305(s), 285(s)		<10
	(55.64)	(5.04)				
$Rh(SnCl_3)(C_2H_4)_2[(C_6H_5)_3P]_2$	53.83	3.90		305(s), 275(s)		<10
	(52.83)	(4.18)				
$Rh(SnCl_3)(C_2H_4)_2[(p\text{-}FC_6H_4)_3P]_2$	46.68	2.74		310(s), 270(s)		<10
	(47.24)	(3.14)				
$Rh(SnCl_3)(C_2H_4)_2[(p\text{-}ClC_6H_4)_3P]_2$	43.61	2.68		305(s), 275(s)		<10
	(41.90)	(2.58)				
$Et_4N[Rh(SnCl_3)_2(C_2H_4)_2(p\text{-}CH_3OC_6H_4)_3P]$	36.76	4.05	1.11	320(s), 290(s, broad)		110
	(36.28)	(4.49)	(1.28)			
$Et_4N[Rh(SnCl_3)_2(C_2H_4)_2(p\text{-}CH_3C_6H_4)_3P]$	39.34	4.54	1.20	335(s), 305(s), 290(s)		98
	(37.95)	(4.70)	(1.34)			
$Et_4N[Rh(SnCl_3)_2(C_2H_4)_2(m\text{-}CH_3C_6H_4)_3P]$	39.60	4.58	1.27	320(s), 295(s, broad)		102
	(37.95)	(4.70)	(1.34)			
$Et_4N[Rh(SnCl_3)_2(C_2H_4)_2(p\text{-}FC_6H_4)_3P]$	34.27	3.61	1.38	330(s), 310(s), 290(s)		105
	(34.11)	(3.79)	(1.32)			
$PPN[Rh(SnCl_3)_2(C_2H_4)_2(p\text{-}FC_6H_4)_3P]$	48.32	3.42	0.78	320(s), 310(s), 290(s)		108
	(47.56)	(3.42)	(0.96)			
$Et_4N[Rh(SnCl_3)_2(C_2H_4)_2(p\text{-}ClC_6H_4)_3P]$	34.41	3.41	1.16	335(m), 300(s, broad)		115
	(32.60)	(3.62)	(1.27)			
$Rh(SnCl_3)(CO)(C_2H_4)_2[(p\text{-}CH_3OC_6H_4)_3P]$	42.38	3.45		315(s), 305(s) 290(s)	2010(s)	<10
	(40.80)	(3.80)				
$Rh(SnCl_3)(CO)(C_2H_4)_2[(p\text{-}CH_3C_6H_4)_3P]$	43.06	3.66		310(s), 290(s)	2020(s)	<10
	(43.50)	(4.05)				
$Rh(SnCl_3)(CO)(C_2H_4)_2[(C_6H_5)_3P]$	43.01	3.26		320(s), 305(s)	2000(s)	<10
	(40.93)	(3.41)				
$Rh(SnCl_3)(CO)(C_2H_4)_2[(p\text{-}FC_6H_4)_3P]$	40.90	2.68		320(s), 305(s)	2010(s)	<10
	(37.98)	(2.74)				
$Rh(SnCl_3)(CO)C_2H_4)_2[(p\text{-}ClC_6H_4)_3P]$	37.42	2.28		320(s), 300(s)	2030(s)	<10
	(35.49)	(2.57)				

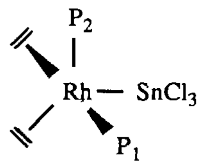
the absence of phosphine dissociation [2]. Their $^2J(^{119}Sn, ^{31}P)$ values are the lowest of all three types of compounds. The corresponding signals remain sharp and unmodified when lowering the temperature to −50 °C. At room temperature, the proton NMR spectra of these complexes dissolved in chloroform show two absorptions, due to protons of coordinated ethylenes, centered around 3.72 and 3.22 ppm, respectively. When lowering the temperature, these signals broaden and by −60 °C they are split into two broad signals each, centered at 4.02 and 3.50 and 3.35 and 3.14 ppm, respectively. This behaviour indicates ethylene rotation around the Rh–olefin axis at room temperature.

Though the low temperature data are consistent with a square pyramidal structure with $SnCl_3^-$ apical (a), a related complex, $Ir(SnCl_3)(NBD)(PMe_2Ph)_2$ presents a distorted trigonal bipyramidal geometry with the phosphine groups spanning one axial and one equatorial position [9]. On the other hand, our complexes show ^{31}P shifts (32–36 ppm) and coupling constants, $^1J(^{103}Rh, ^{31}P)$ (132–134 Hz) and $^2J(^{119}Sn, ^{31}P)$ (178–191 Hz), that are very close to those of $Rh(SnCl_3)(NBD)(PR_3)_2$ complexes [2] for which a TBP structure has been assumed with $^1J(^{103}Rh, ^{31}P)$ as an average value of $^1J(^{103}Rh, ^{31}P_{ax})$ and $^1J(^{103}Rh, ^{31}P_{eq})$. Therefore we prefer to assign our complexes structures based on a trigonal bipyramid (b), though probably distorted, with the ethylene groups in the trigonal plane with their double bonds coplanar with this plane [15, 16], the phosphine groups occupying one equatorial and one axial position and the $SnCl_3^-$ group the remaining axial position. These complexes, being stereochemically non-rigid, can undergo the Berry pseudorotation mechanism [10] that would markedly lower the barrier to ethylene rotation

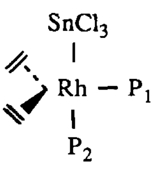
TABLE 2. ^{31}P and ethylene ^{1}H NMR data for complexes in $CDCl_3$ at 290 K

Complex	δ ^{31}P (ppm)	J^1(^{103}Rh, ^{31}P) (Hz)	J^2(^{119}Sn, ^{31}P) (Hz)	δ ^{1}H($CH_2{=}CH_2$) (ppm)
$Rh(SnCl_3)(C_2H_4)_2[(p\text{-}CH_3OC_6H_4)_3P]_2$	32.0	134	178	3.71; 3.27
$Rh(SnCl_3)(C_2H_4)_2[(p\text{-}CH_3C_6H_4)_3P]_2$	35.2	133	186	3.70; 3.22
$Rh(SnCl_3)(C_2H_4)_2[(m\text{-}CH_3C_6H_4)_3P]_2$	35.2	132	186	3.70; 3.22
$Rh(SnCl_3)(C_2H_4)_2[(C_6H_5)_3P]_2$	36.0	132	186	3.72; 3.25
$Rh(SnCl_3)(C_2H_4)_2[(p\text{-}FC_6H_4)_3P]_2$	34.6	134	190	3.78; 3.22
$Rh(SnCl_3)(C_2H_4)_2[(p\text{-}ClC_6H_4)_3P]_2$	35.4	132	191	3.74; 3.19
$Et_4N[Rh(SnCl_3)_2(C_2H_4)_2(p\text{-}CH_3C_6H_4)_3P]$	43.2	127	336	3.68
$Et_4N[Rh(SnCl_3)_2(C_2H_4)_2(m\text{-}CH_3C_6H_4)_3)P]$	44.5	128	327	3.69
$Et_4N[Rh(SnCl_3)_2(C_2H_4)_2(p\text{-}FC_6H_4)_3P]$	43.2	128	326	3.67
$PPN[Rh(SnCl_3)_2(C_2H_4)_2(p\text{-}FC_6H_4)_3P]$	44.0	130	346	3.67
$Et_4N[Rh(SnCl_3)_2(C_2H_4)_2(p\text{-}ClC_6H_4)_3P]$	44.5	126	326	3.65
$Rh(SnCl_3)(CO)(C_2H_4)_2[(p\text{-}CH_3OC_6H_4)_3P]$	42.4	115	295	3.74
$Rh(SnCl_3)(CO)(C_2H_4)_2(p\text{-}CH_3C_6H_4)_3P]$	44.6	115	287	3.88; 3.75
$Rh(SnCl_3)(CO)(C_2H_4)_2[(C_6H_5)_3P]$	46.5	116	290	3.87; 3.76
$Rh(SnCl_3)(CO)(C_2H_4)_2[(p\text{-}FC_6H_4)_3P]$	44.3	117	287	3.86; 3.81
$Rh(SnCl_3)(CO)(C_2H_4)_2[(p\text{-}ClC_6H_4)_3P]$	45.2	118	287	3.82; 3.77

[17–20] and be responsible for the equilibration of the two phosphine groups at −60 °C. Furthermore it has been suggested recently that the presence of π-acceptors on an axial position favours this Berry pseudorotation mechanism [19].



(a)



(b)

Monocarbonylated, neutral complexes, $Rh(SnCl_3)(CO)(C_2H_4)_2(PR_3)$ show in their $^{31}P\{^1H\}$ NMR spectra doublets due to ^{103}Rh splitting, flanked by tin satellite signals, also observable at room temperature. ^{31}P shifts (42–47 ppm) and the ^1J(^{103}Rh, ^{31}P) (115–118 Hz) and ^2J(^{119}Sn, ^{31}P) (287–295 Hz) coupling constants are nearly identical to those of pentacoordinated $Rh(SnCl_3)(CO)(NBD)(PR_3)$ complexes [8]. The corresponding signals remain sharp and unmodified when lowering the temperature to −50 °C. Their proton NMR spectra show two close signals due to ethylenic protons centered around 3.86 and 3.77 ppm, respectively. When cooling the samples, these signals broaden and collapse and at −60 °C they remain still unresolved, suggesting a similar equilibrating process as in $Rh(SnCl_3)(C_2H_4)_2(PR_3)_2$ but with a lower energy barrier, that can be related to the substitution of a phosphine group by a π-acceptor such as CO [19].

$^{31}P\{^1H\}$ NMR spectra of anionic species, $[Rh(SnCl_3)_2(C_2H_4)_2(PR_3)]^-$, consist of a doublet due to ^{103}Rh splitting, flanked by tin satellite signals, observable at room temperature. The corresponding signals remain sharp and unmodified when lowering the temperature to −50 °C. ^{119}Sn spectra of the rather insoluble complexes show poorly resolved quatriplets due to ^{103}Rh and ^{31}P splitting. ^{31}P shifts (43–45 ppm) and the ^1J(^{103}Rh, ^{31}P) (126–130 Hz) and ^2J(^{119}Sn, ^{31}P) (326–346 Hz) coupling constants values as well as ^{119}Sn chemicals shifts (56–65 ppm) and ^1J(^{103}Rh, ^{119}Sn) (730–757 Hz) values, are very similar to data reported for norbornadiene complexes $[Rh(SnCl_3)_2(NBD)(PR_3)]^-$ [4]. The ^2J(^{119}Sn, ^{31}P) values are the highest of all three types of compounds. All these data confirm the similar characteristics of ethylene and norbornadiene trichlorostannato complexes. The corresponding ^{1}H NMR spectra show only one signal, centered around 3.67 ppm, due to equivalent ethylenic protons that remains unaltered when cooling the samples down to −60 °C. This simplicity may indicate the occurrence of other processes with very low energy barriers, that could include ligand dissociation.

Acknowledgements

We thank the DGICYT (0083/87) and the UPV for financial support.

References

1 M. S. Holt, W. L. Wilson and J. H. Nelson, *Chem. Rev., 89* (1989) 11.

2 R. Usón, L. A. Oro, M. T. Pinillos, K. A. Ostoja-Starzewski and P. S. Pregosin, *J. Organomet. Chem., 192* (1980) 227.

3 M. Garralda, V. García, M. Kretschmer, P. S. Pregosin and H. Ruegger, *Helv. Chim. Acta, 64* (1981) 1150.

4 M. Kretschmer, P. S. Pregosin and M. A. Garralda, *J. Organomet. Chem., 244* (1983) 175.

5 M. Kretschmer, P. S. Pregosin and H. Ruegger, *J. Organomet. Chem., 241* (1983) 87.

6 R. Usón, L. A. Oro, J. Reyes, D. Carmona and P. Lahuerta, *Transition Met. Chem., 8* (1983) 46.

7 V. García, M. A. Garralda and L. Ibarlucea, *Transition Met. Chem., 10* (1985) 288.

8 V. García, M. A. Garralda and E. Zugasti, *J. Organomet. Chem., 332* (1987) 249.

9 M. R. Churchill and K. G. Lin, *J. Am. Chem. Soc., 96* (1974) 76.

10 J. R. Shapley and J. A. Osborn, *Acc. Chem. Res., 6* (1973) 305.

11 R. Cramer, *Inorg. Synth., XV* (1974) 14.

12 D. F. Shriver and M. P. Johnson, *Inorg. Chem., 6* (1967) 1265.

13 R. V. Parish and P. J. Rowbotham, *J. Chem. Soc., Dalton Trans.,* (1973) 37.

14 T. Allman and R. F. Goel, *Can. J. Chem., 60* (1982) 716.

15 A. R. Rossi and R. Hoffmann, *Inorg. Chem., 14* (1975) 365.

16 F. R. Hartley, *J. Organomet. Chem., 216* (1981) 277.

17 R. Albright, R. Hoffmann, J. C. Thibeault and D. L. Thorn, *J. Am. Chem. Soc., 101* (1979) 3801.

18 F. U. Axe and D. S. Marynick, *J. Am. Chem. Soc., 106* (1984) 6230.

19 E. G. Lundquist, K. Folting, W. E. Streib, J. C. Huffman, O. Eisenstein and K. G. Caulton, *J. Am. Chem. Soc., 112* (1990) 855.

20 S. T. Wilson, N. J. Coville, J. R. Shapley and J. A. Osborn, *J. Am. Chem. Soc., 96* (1974) 4038.