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ANIONIC AND NEUTRAL RHODIUM(I) COMPLEXES CONTAINING TRICHLOROSTANNATO LIGANDS

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Summary

The complexes $Et_4N[Rh(SnCl_3)_2(diolefin)(PR_3)]$ (diolefin = COD or NBD) have been isolated and their reactions studied. Reaction with arylic tertiary phosphines led to $SnCl_3^-$ displacement and isolation of neutral pentacoordinated $Rh(SnCl_3)(diolefin)(PR_3)_2$ complexes. Reaction with carbon monoxide involved diolefin displacement when the diolefin was COD, thus giving $Et_4N[Rh(SnCl_3)_2(CO)_2(PR_3)]$ compounds, but $SnCl_3^-$ displacement when it was NBD, thus yielding $Rh(SnCl_3)(CO)(NBD)(PR_3)$ complexes. The complexes $[Rh(diolefin)Cl]_2$ were found to react with triarylphosphines in the presence of $SnCl_2$ and with CO bubbling through the solution to give $Rh(SnCl_3)(CO)(NBD)(PR_3)$ when the diolefin was NBD but $Rh(Cl)(CO)(PR_3)_2$ when the diolefin was COD.

Introduction

The reactions between Group VIII transition metals complexes and tin(II) halides, have given many stable compounds containing trihalostannato groups [1]. Although most of the diolefinic rhodium(I) complexes are tetracoordinated, the tendency to pentacoordination increases markedly when SnX_3^- ligands are present, and these pentacoordinated complexes may undergo dissociation of SnX_3^- or SnX_2 groups in solution [2–5]. Usually, trichlorostannato diolefinic rhodium(I) complexes react with carbon monoxide with displacement of the diolefin to give dicarbonylated species [2,6,7]. It has been reported that carbon monoxide displaces one $SnCl_3^-$ group in $[Ir(SnCl_3)_2(COD)(PR_3)]^-$ species to give $Ir(SnCl_3)(CO)(COD)(PR_3)$ complexes [8]. In view of the close similarity in chemical behaviour between analogous rhodium(I) and iridium(I) complexes [8–10], we decided to undertake a study of the reactions of $[Rh(SnCl_3)_2(diolefin)(PR_3)]^-$ species with carbon monoxide and with triarylphosphines, and the results are presented below.

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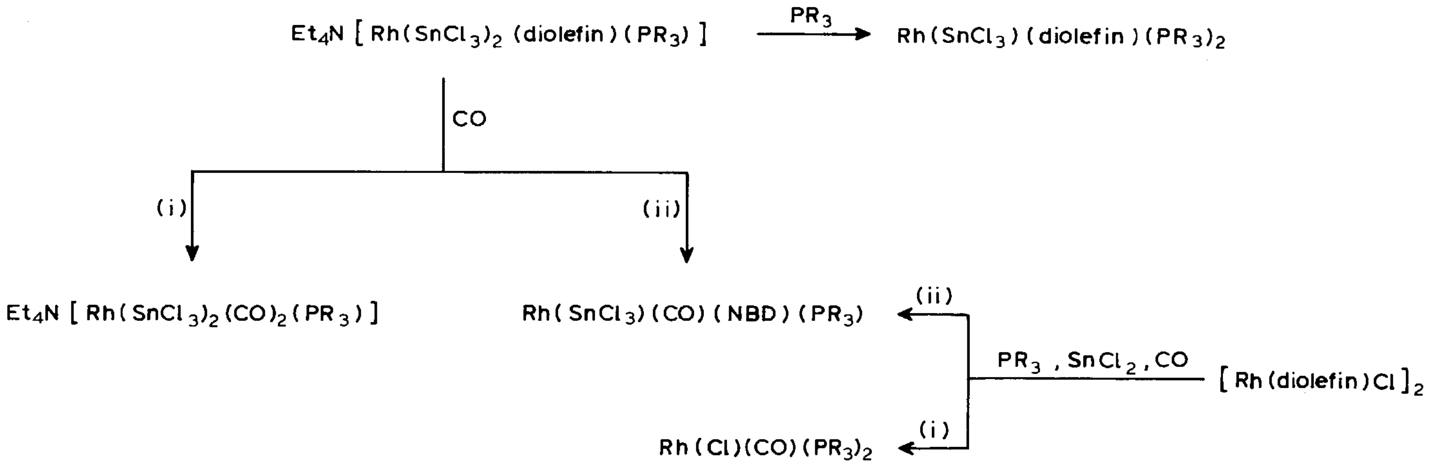

SCHEME 1. (i): diolefin = COD; (ii) diolefin = NBD.

Results and discussion

The $[Rh(diolefin)Cl]_2$ dimers react with triarylphosphines, PR_3, ($Rh/P = 1/1$) and tin(II) chloride ($Rh/SnCl_2 = 1/2$) to give red solutions. The addition of chloride bulky cations allows the isolation of anionic complexes containing two $SnCl_3^-$ groups bonded to the rhodium atom [8]. In order to study the reactions of these compounds we isolated the tetraethylammonium salts, $Et_4N[Rh(SnCl_3)_2(diolefin)(PR_3)]$ ($R = C_6H_5$, p-FC_6H_4, p-ClC_6H_4, p-$CH_3OC_6H_4$ and m-$CH_3C_6H_4$); analytical and conductivity data of some representative compounds are shown in Table 1 (I–IV). The reactions of these anionic compounds with triarylphosphines and with carbon monoxide are depicted in Scheme 1.

Triarylphosphines displace one $SnCl_3^-$ group from anionic $[Rh(SnCl_3)_2(NBD)(PR_3)]^-$ species to give the neutral pentacoordinated $Rh(SnCl_3)(NBD)(PR_3)_2$ compounds. All the complexes studied gave similar results, and Table 1 lists some

TABLE 1

ANALYSES AND CONDUCTIVITY DATA FOR TRICHLOROSTANNATO COMPLEXES

Complex	Analyses (Found (calc) (%))			Λ_M (ohm^{-1} cm^2 mol^{-1})
	C	H	N	
$Et_4N[Rh(SnCl_3)_2(COD)(m\text{-}CH_3C_6H_4)_3P]$ (I)	40.93	5.02	1.35	120
	(40.63)	(5.15)	(1.28)	
$Et_4N[Rh(SnCl_3)_2(COD)(p\text{-}FC_6H_4)_3P]$ (II)	36.92	4.05	1.27	110
	(36.99)	(3.53)	(1.26)	
$Et_4N[Rh(SnCl_3)_2(NBD)(m\text{-}CH_3C_6H_4)_3P]$ (III)	40.15	4.57	1.39	135
	(40.07)	(4.54)	(1.29)	
$Et_4N[Rh(SnCl_3)_2(NBD)(p\text{-}FC_6H_4)_3P]$ (IV)	36.24	3.75	1.28	139
	(36.33)	(3.66)	(1.28)	
$Et_4N[Rh(SnCl_3)_2(CO)_2(p\text{-}CH_3OC_6H_4)_3P]$ (V)	34.01	3.76	1.23	102
	(34.14)	(3.49)	(1.28)	
$Et_4N[Rh(SnCl_3)_2(CO)_2(m\text{-}CH_3C_6H_4)_3P]$ (VI)	35.71	3.99	1.31	100
	(35.60)	(3.91)	(1.33)	
$Et_4N[Rh(SnCl_3)_2(CO)_2(C_6H_5)_3P]$ (VII)	35.30	3.41	1.35	100
	(33.57)	(3.49)	(1.39)	
$Et_4N[Rh(SnCl_3)_2(CO)_2(p\text{-}FC_6H_4)_3P]$ (VIII)	31.74	3.54	1.67	95
	(31.87)	(3.03)	(1.33)	
$Et_4N[Rh(SnCl_3)_2(CO)_2(p\text{-}ClC_6H_4)_3P]$ (IX)	29.17	4.30	1.66	102
	(30.54)	(2.90)	(1.32)	
$Rh(SnCl_3)(CO)(NBD)(p\text{-}CH_3OC_6H_4)_3P$ (X)	42.42	3.71	-	-
	(43.58)	(3.66)		
$Rh(SnCl_3)(CO)(NBD)(m\text{-}CH_3C_6H_4)_3P$ (XI)	45.61	3.98	-	-
	(46.29)	(3.89)		
$Rh(SnCl_3)(CO)(NBD)(C_6H_5)_3P$ (XII)	42.87	3.03	-	-
	(43.97)	(3.27)		
$Rh(SnCl_3)(CO)(NBD)(p\text{-}FC_6H_4)_3P$ (XIII)	40.82	2.50	-	-
	(40.85)	(2.64)		
$Rh(SnCl_3)(CO)(NBD)(p\text{-}ClC_6H_4)_3P$ (XIV)	37.80	2.17	-	-
	(38.27)	(2.48)		
$Rh(SnCl_3)(NBD)[(m\text{-}CH_3C_6H_4)_3P]_2$ (XV)	56.41	4.97	-	-
	(57.22)	(4.86)		
$Rh(SnCl_3)(NBD)[(p\text{-}FC_6H_4)_3P]_2$ (XVI)	49.22	3.14	-	-
	(49.07)	(3.04)		

TABLE 2

IR DATA FOR TRICHLOROSTANNATO COMPLEXES (cm^{-1})

R	$Rh(SnCl_3)(NBD)(PR_3)_2$		$Et_4N[Rh(SnCl_3)_2(L_2)(PR_3)]$							$Rh(SnCl_3)(CO)(NBD)(PR_3)$		
			L_2 = COD		L_2 = NBD		L = CO					
	ν(Sn–Cl)		ν(Sn–Cl)		ν(Sn–Cl)		ν(Sn–Cl)		ν(C≡O)	ν(Sn–Cl)		ν(C≡O)
	sym	*asym*	*sym*	*asym*	*sym*	*asym*	*sym*	*asym*		*sym*	*asym*	
p-$CH_3OC_6H_4$	305	275	312	298, 285	318	298	315	300	1998, 1955	315	295	2010
m-$CH_3C_6H_4$	310	290	318	300, 290	320	285	315	298	1995, 1975	315	295	2020
C_6H_5	305 [a]	280	322	298, 288	322	305, 280	322	300, 285	1995, 1975, 1965	318	303	2010
p-FC_6H_4	315	290	322	300, 288	325	305, 285	320 (br)		1995, 1965	320	301	2020
p-ClC_6H_4	300	280	318	300, 285	320	298	315(br)		2000, 1975, 1965	310	295	2030

[a] In ref. 11.

representative analytical and conductivity data (XV–XVI). These neutral complexes can also be obtained by a more direct route, starting from $[Rh(NBD)Cl]_2$ [11].

The anionic complexes react with carbon monoxide, and different products are obtained depending on which diolefin is present in the starting complex. Thus, when the diolefin is COD, displacement of diolefin occurs, and dicarbonylated anionic $Et_4N[Rh(SnCl_3)_2(CO)_2(PR_3)]$ complexes (V–IX) are formed (Table 1). When the diolefin is NBD, displacement of one $SnCl_3^-$ group occurs and monocarbonylated diolefinic neutral $Rh(SnCl_3)(CO)(NBD)(PR_3)$ compounds (X–XIV) are isolated. This difference in behaviour between complexes containing COD, which is easily displaced by CO, or NBD, which is retained in the products, indicates that Rh-NBD is stronger than Rh-COD bonding, and this may be due to the higher π-acceptor ability of NBD [12].

The monocarbonylated diolefinic neutral $Rh(SnCl_3)(CO)(NBD)(PR_3)$ complexes are similar to the $Ir(SnCl_3)(CO)(COD)(PR_3)$ compounds formed in the reaction between $[Ir(SnCl_3)_2(COD)(PR_3)]^-$ species and carbon monoxide [8]. As previously indicated, carbon monoxide displaces COD from $[Rh(SnCl_3)_2(COD)(PR_3)]^-$ species, and this difference may be due to stronger Ir-COD than Rh-COD interaction, as previously suggested [13].

In the light of the above results, we studied the reaction between $[Rh(diolefin)Cl]_2$, arylic tertiary phosphines and tin(II) chloride in the presence of carbon monoxide, since this might have provided a more direct route to isolated $Rh(SnCl_3)(CO)(diolefin)(PR_3)$ complexes. Once again, the results obtained differed depending on the diolefin in the initial dimer (see Scheme 1). Thus, when the diolefin was NBD, the desired $Rh(SnCl_3)(CO)(NBD)(PR_3)$ complexes were obtained, whereas when it was COD the only isolated species were $Rh(Cl)(CO)(PR_3)_2$ complexes, showing that displacement of COD by carbon monoxide had occurred.

All the compounds containing $SnCl_3^-$ groups show two or three strong bands in the far IR due to ν(Sn–Cl) of the coordinated $SnCl_3^-$ groups [14], and the relevant values are listed in Table 2. For any particular triarylphosphine, complexes containing only one phosphine group bonded to rhodium, i.e. $Et_4N[Rh(SnCl_3)_2(L_2)(PR_3)]$ and $Rh(SnCl_3)(CO)(NBD)(PR_3)$, show higher ν_{sym}(Sn–Cl) values than those containing two phosphine groups so bonded to the metal, i.e. $Rh(SnCl_3)(NBD)(PR_3)_2$. Since the electron density around the rhodium atom is lower, it becomes a better acceptor, so that the $SnCl_3^-$ group donates more charge and the Sn–Cl bonds are strenghtened [15].

The anionic dicarbonylated compounds show two strong absorption bands at frequencies below 2000 cm^{-1}, while the monocarbonylated neutral complexes show a single band above 2000 cm^{-1}. Back-donation is thus stronger in the anionic complexes. The compounds containing the least basic ligand, $(p\text{-}ClC_6H_4)_3P$, show the highest $\nu(C{\equiv}O)$ frequency.

The $^{31}P\ \{^1H\}$NMR, spectra for $Rh(SnCl_3)(CO)(NBD)(PR_3)$ complexes (Table 3) show a doublet due to ^{103}Rh splitting, flanked by satellite signals due to spin $I = 1/2$ isotopes ^{119}Sn, 8.6% and ^{117}Sn, 7.6%, although, as in other rhodium(I) compounds [2,4,8], these satellites are only observable below 0°C.

The ^{31}P shifts and the $^1J(^{103}Rh, ^{31}P)$ and $^2J(^{119}Sn, ^{31}P)$ coupling constants are very similar for all the compounds, and show no dependence on the ligand basicity. The coupling constants $^1J(^{103}Rh, ^{31}P)$ are in the range 115–118 Hz, consistent with data reported for analogous complexes [2,8].

TABLE 3

$^{31}P\{H\}$NMR DATA FOR $Rh(SnCl_3)(CO)(NBD)(PR_3)$ COMPLEXES [a]

R	$\delta(^{31}P)$	$^1J(^{103}Rh, ^{31}P)$	$^2J(^{119}Sn, ^{31}P)$
p-$CH_3OC_6H_4$	42.0	115	294
m-$CH_3C_6H_4$	46.4	116	284
C_6H_5	46.7	117	294
p-FC_6H_4	44.5	118	289
p-ClC_6H_4	45.2	118	283

[a] Chemical shifts in ppm relative to H_3PO_4 (external standard), coupling constants in Hz. Measured in acetone at 213 K.

The $^2J(^{119}Sn, ^{31}P)$ coupling constants are in the range 283–294 Hz, lower than those in $[Rh(SnCl_3)_2(NBD)(PR_3)]^-$ species (344–349 Hz) [8] and higher than those reported for $Rh(SnCl_3)(NBD)(PR_3)_2$ complexes (152–190 Hz) [2]. The difference between $Rh(SnCl_3)(CO)(NBD)(PR_3)$ and $[Rh(SnCl_3)_2(NBD)(PR_3)]^-$ species is similar to that between analogous Ir^I compounds [8].

The ^{31}P NMR spectra, though measured on samples having satisfactory elemental analysis (Table 1), show, in addition to the main signal, an small signal that we identified as coming from the corresponding $Rh(Cl)(CO)(PR_3)_2$ complex, which may be formed in solution as a consequence of partial dissociation of $SnCl_2$ [4] or $SnCl_3^-$ [3,5,10], especially in acetone [16]. In keeping with this, when the samples studied contained small amounts of $SnCl_2$, no signal due to $Rh(Cl)(CO)(PR_3)_2$ appeared.

Experimental

The complexes $[Rh(COD)Cl]_2$ [17] and $[Rh(NBD)Cl]_2$ [18] were prepared by published methods. The C, H and N microanalyses were carried out with a Perkin–Elmer 240C microanalyzer. Conductivities were measured in ca. 2.5×10^{-4} M solutions with a Metrohm 518 conductimeter. The IR spectra were recorded on a Perkin–Elmer 598 spectrophotometer in the range 4000–200 cm^{-1} using Nujol mulls between polyethylene sheets. The ^{31}P $\{^1H\}$ NMR spectra were recorded for samples in acetone in 10 mm tubes, on a Bruker WP-80 SY; the chemical shifts are quoted relative to external 85% H_3PO_4 at 213 K.

Preparation of complexes of the type $Et_4N[Rh(SnCl_3)_2(diolefin)(PR_3)]$

To a CH_2Cl_2 yellow solution of $[Rh(diolefin)Cl]_2$ (0.04 mmol) was added the stoichiometric amount of the phosphine PR_3 (0.08 mmol). Addition of tin(II) chloride (0.16 mmol) in MeOH produced a red solution, to which was added a stoichiometric amount of Et_4NCl (0.08 mmol). After a few minutes shaking, an orange solid separated, and this was filtered off, washed with methanol, and air-dried. Yields: 54–70%.

Some of the products were more soluble, and in those cases it was necessary to evaporate off the CH_2Cl_2 to bring out separation of the solid.

Reaction of $Et_4N[Rh(SnCl_3)_2(NBD)(PR_3)]$ with PR_3

To a CH_2Cl_2 solution of $Et_4N[Rh(SnCl_3)_2(NBD)$ $(PR_3)]$ (0.04 mmol) was added an stoichiometric amount of the phosphine, PR_3 (0.04 mmol). The opalescent solution obtained was filtered and MeOH was added. Evaporation of CH_2Cl_2 produced an orange precipitate of the $Rh(SnCl_3)(NBD)(PR_3)_2$ complex, which was filtered off, washed with methanol, and air-dried. Yields: 55–65%.

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

Carbon monoxide at atmosphere pressure was bubbled for 5 min through CH_2Cl_2/MeOH solutions of $Et_4N[Rh(SnCl_3)_2(NBD)(PR_3)]$ (0.06 mmol). Filtration of the opalescent solutions and evaporation of CH_2Cl_2 gave the yellow $Rh(SnCl_3)(CO)(NBD)(PR_3)$, which was filtered off, washed with methanol, and air-dried. Yields: 15–45%.

Direct preparation of $Rh(SnCl_3)(CO)(NBD)(PR_3)$ compounds

To a solution of $[Rh(NBD)Cl]_2$ (0.06 mmol) in CH_2Cl_2 was added the phosphine. (0.12 mmol) and a MeOH solution of tin(II) chloride (0.18 mmol). Evaporation of the CH_2Cl_2 was followed by bubbling of carbon monoxide at atmophere pressure for 5 min. The yellow precipitate was then filtered off, washed with methanol and air-dried. Yields: 40–70%.

Reaction of $Et_4N[Rh(SnCl_3)_2(COD)(PR_3)]$ with CO

Carbon monoxide at atmosphere pressure was bubbled for 1 h through CH_2Cl_2/MeOH solutions of $Et_4N[Rh(SnCl_3)_2(COD)(PR_3)]$ (0.04 mmol). Evaporation of CH_2Cl_2 gave yellow $Et_4N[Rh(SnCl_3)_2(CO)_2(PR_3)]$, which was filtered off, washed with methanol, and air-dried. Yields: 35–45%.

Reaction of $[Rh(COD)Cl]_2$ with PR_3 and $SnCl_2$ under CO

Carbon monoxide at atmosphere pressure was bubbled for 5 min through CH_2Cl_2/MeOH solutions containing stoichiometric amounts of $[Rh(COD)Cl]_2$ (0.06 mmol), PR_3 (0.12 mmol) and $SnCl_2$ (0.12 mmol). Evaporation of CH_2Cl_2 led to precipitation of yellow $Rh(Cl)(CO)(PR_3)_2$ in low yields (as expected because of the small amount of PR_3 used).

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