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Short Communication

Rhodium(I) complexes with diimines. ^1H and ^{119}Sn NMR study of the trichlorostannato compounds

Luz Fidalgo, María A. Garralda*,
Ricardo Hernández and Lourdes Ibarlucea
Facultad de Ciencias Químicas de San Sebastián, Universidad del País Vasco, Apdo. 1072, 20080 San Sebastián (Spain)

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Abstract

Reactions of $[RhL_2Cl]_2$ (L_2 = COD or NBD, L = CO) with α-diimines, $RN{:}C(CH_3)C(CH_3){:}NR'$(LL); R = R' = NH_2 (bdh); R = NH_2, R' = OH (boh); R = R' = $N(CH_3)_2$ (bdnh) or R = R' = C_6H_5 (bda) or with 2,2'-biquinoline (biqui) and $SnCl_2$ afford trichlorostannato complexes. $Rh(SnCl_3)$(NBD)(LL) compounds are neutral and according to their ^1H and ^{119}Sn NMR spectra undergo tin halide dissociation and intramolecular rearrangements. $Rh(SnCl_3)$(COD)(LL) are ionic or neutral and also undergo $SnCl_3^-$ or $SnCl_2$ dissociation. In the absence of $SnCl_2$, $[RhL_2Cl]_2$ dimers react with α-diimines to give fluxional pentacoordinated $[Rh(Cl)L_2(LL)]$ complexes (L_2 = COD or NBD) irrespective of the stoichiometric ratios employed, or ion-pair $[RhL_2(LL)]^+[RhL_2Cl_2]^-$ compounds (L = CO).

Introduction

Reaction of binuclear complexes $[RhL_2Cl]_2$ (L_2 = COD or NBD, L = CO) with potentially bidentate N-donor ligands may give different products depending on the ligands and/or the stoichiometric ratios employed [1]. α-Diimines, $RN{:}C(R')C(R'){:}NR$(LL), have shown a versatile coordination chemistry [2] and may yield pentacoordinated [3] or cationic [4, 5] compounds when using Rh/LL = 1/1 stoichiometric ratios and ion-pair [5–7] complexes or dinuclear [5, 6] compounds with bridging LL when Rh/LL = 2/1, though in solution several equilibria between the different species have been suggested [4–6, 8]. Transition metal complexes containing convalently bonded tin compounds are of considerable interest, partly due to their potential catalytic activity in organic transformations [9]. Several rhodium(I) complexes containing trichlorostannato groups and diolefins have been described but most of them contain phosphine ligands and less effort has been devoted to compounds containing N-donor ligands [10]. We report now on the reactions of $[RhL_2Cl]_2$ with diimines (LL), in the presence or absence of $SnCl_2$, that give different products depending mainly on the nature of L_2 or (LL). α-Diimines, $RN{:}C(CH_3)C(CH_3){:}NR'$, abbreviated as bdh (R = R' = NH_2), boh (R = NH_2, R' = OH), bdnh (R = R' = $N(CH_3)_2$) or bda (R = R' = Ph), derived from biacetyl with different N-substitution and 2,2'-biquinoline (biqui) have been selected. The solution behaviour of the different isolated compounds is also discussed.

Experimental

The preparation of the metal complexes was carried out at room temperature under nitrogen by standard Schlenk techniques. $[Rh(diolefin)Cl]_2$ [11, 12], $[Rh(CO)_2Cl]_2$ [13] and $[Rh(COD)_2]ClO_4$ [14] were prepared as previously reported. α-Diimines [15], $[Rh(COD)(LL)]ClO_4$ and $[Rh(CO)_2(LL)]ClO_4$ [16] and $[Rh(CO)_2(LL)][Rh(CO)_2Cl_2]$ [6, 7] were synthesized according to known procedures.

Microanalysis was carried out with a Perkin-Elmer 240C microanalyzer. Conductivities were measured in acetone solution 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) spectra were measured from $CDCl_3$, CD_2Cl_2 or acetone-d^6 solutions at variable temperature in 5 mm tubes, ^{119}Sn ($SnMe_4$ external standard) spectra were measured from acetone/acetone-d^6 = 1/1 solutions in 10 mm tubes.

Preparation of trichlorostannato complexes

To a CH_2Cl_2 solution of $[RhL_2Cl]_2$ (L_2 = diolefin, L = CO) (0.06 mmol), was added the stoichiometric amount (0.12 mmol) of the corresponding ligand. The addition of an MeOH solution of a stoichiometric amount of $SnCl_2$ (0.12 mmol) followed by evaporation of CH_2Cl_2 led to the corresponding trichlorostannato compounds. The coloured complexes (red or dark blue) were filtered off, washed with MeOH and vacuum dried. Yields 30–87%.

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*Author to whom correspondence should be addressed.

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Preparation of [Rh(Cl)(diolefin)(LL)] complexes

To a benzene solution of $[Rh(diolefin)Cl]_2$ (0.06 mmol), was added the stoichiometric amount (0.12 mmol) of the required ligand, upon which the corresponding orange (dark blue for bda) complexes were obtained, filtered off, washed with benzene and vacuum dried. Yields 58–85%.

Results and discussion

Reaction of $[Rh(diolefin)Cl]_2/LL = 1/2$ mixtures with $SnCl_2$ (LL = bdh, boh, bda, bdnh or biqui) leads to compounds containing the trichlorostannato group (Table 1). The nature of the obtained compounds depends on both the diimine ligand and the diolefin. Thus, when diolefin = NBD, neutral pentacoordinated $Rh(SnCl_3)$(NBD)(LL) compounds are obtained. Their IR spectra show bands due to LL coordinated through the imine nitrogens and the ν(Sn–Cl) vibration is indicative of the $SnCl_3^-$ group being covalently bonded to rhodium [17]. Some of the conductivity values, though well below the range expected for 1:1 electrolytes in acetone solution (100–140 Ω^{-1} cm^2 mol^{-1}) [18], are slightly high and suggest a certain degree of ionic dissociation in solution.

In order to study the solution behaviour of these complexes, a variable temperature NMR study was undertaken. Table 2 collects ^{1}H and ^{119}Sn NMR data. At room temperature the ^{119}Sn NMR spectrum of $Rh(SnCl_3)$(NBD)(bda) in acetone solution shows only a broad singlet, at lower fields relative to $SnMe_4$, indicating tin dissociation that can occur either through $SnCl_2$ or $SnCl_3^-$ groups. The low conductivity of this compound in acetone solution along with the evidence of SnX_2 scrambling processes in trihalostannato (bis)phosphine compounds [19] suggest equilibrium (1) as most likely:

$$Rh(SnCl_3)(NBD)(bda) \rightleftharpoons Rh(Cl)(NBD)(bda) + SnCl_2 \quad (1)$$

On lowering the temperature this equilibrium is shifted to the left and by −40 °C the tin signal is a doublet due to coordination to rhodium and the values of chemical shift and coupling constant are in agreement with analogous compounds containing phosphines [19]. The ^{1}H NMR spectrum in CD_2Cl_2 solution shows, at room temperature, only one resonance for all olefinic protons, one resonance for both methinic protons of norbornadiene and one signal for the two diimine CH_3 groups. At −40 °C, when the $SnCl_3^-$ group is covalently bonded also in solution, the same pattern is observed and suggests an intramolecular exchange taking place in the pentacoordinated compounds. On further lowering the temperature collapse and splitting of the norbornadiene signals occur. At −80 °C, two signals for the olefinic protons and two signals for the methinic protons of norbornadiene are observed, while the signal due to the diimino CH_3 groups remains sharp. On account of the π-acceptor character of the $SnCl_3^-$ group, this low temperature spectrum agrees with a trigonal bipyramidal structure undergoing Berry pseudorotation [20] or with a limiting structure corresponding to a square pyramid with the $SnCl_3^-$ group occupying the axial position. Recently, some pentacoordinated norbornadiene rhodium(I) complexes have been reported to show square-pyramidal crystal structures [21, 22].

Other NBD complexes show a similar behaviour (see Table 2), though slowing down of the different processes requires lower temperatures. When LL = boh, tin dissociation is also slow at −40 °C but collapse of the olefinic and methinic signals due to norbornadiene occurs around −80 °C. At this temperature two sharp signals at 2.13 and 2.10 ppm, respectively, are observed for the two CH_3 groups bonded to differently substituted imino nitrogens. At higher temperatures these very close resonances appear at 2.16 ppm. When LL = bdh, rhodium coupling in the ^{119}Sn spectrum is observed around −70 °C and at this temperature norbornadiene proton resonances begin broadening.

When diolefin = COD and according to ν(Sn–Cl) values [17] neutral pentacoordinated $Rh(SnCl_3)$(COD)(LL) compounds are obtained if LL = bda, biqui or boh, while an ionic [Rh(COD)(bdh)]($SnCl_3$) compound is obtained if LL = bdh. These complexes also undergo different equilibria in solution and their conductivity values are higher than those of the corresponding NBD complexes. $Rh(SnCl_3)$(COD)(bda) shows a temperature dependent ^{1}H NMR spectrum (Table 2). Its behaviour is similar to that observed for the NBD complex. Unfortunately measurement of the corresponding ^{119}Sn NMR spectra proved impossible due to low solubility. The bdh complex [Rh(COD)(bdh)]($SnCl_3$) behaves as a 1:1 electrolyte in acetone solution but its ^{1}H NMR spectrum, invariable in the range −40 to 16 °C, shows the presence of two groups of signals (Table 2). The intensity ratios of the resonances indicate one major species in solution corresponding to the $[Rh(COD)(bdh)]^+$ (**a**) cation, identified by comparison with the spectrum of a pure sample isolated independently [4], and one minor species corresponding to the neutral [Rh(Cl)(COD)(bdh)] (**b**) compound (*vide infra*) whose presence would account for the slightly low conductivity value. ^{119}Sn NMR suggests a tin association–dissociation equilibrium in solution. Only a sharp singlet is observed in the studied temperature range −80 to +20 °C but its chemical

TABLE 1. Analyses, conductivity and selected IR data

Compound	Anal.: found (calc.) (%)			Molar conductivity (Ω^{-1} cm^2 mol^{-1})	Infrared bands (cm^{-1})[b]			
	C	H	N		ν(M–Cl)	ν(C≡O)	ν(N–H)	ν(C=N)
[Rh(SnCl$_3$)(NBD)(bda)]	41.9 (42.1)	3.5 (3.7)	4.1 (4.3)	< 10	305s, 290s			1585m
[Rh(SnCl$_3$)(NBD)(boh)]	25.0 (24.7)	3.3 (3.2)	7.5 (7.5)	20	310s, 270s		3360w, 3340w 3280w	1585w
[Rh(SnCl$_3$)(NBD)(bdh)]	24.7 (24.8)	3.2 (3.0)	10.4 (10.5)	22; 53[a]	305s, 260s		3360s, 3290s 3220w	1570s
[Rh(SnCl$_3$)(NBD)(bdnh)]	30.2 (30.5)	4.2 (4.4)	8.2 (9.5)	34	300br			
[Rh(SnCl$_3$)(NBD)(biqui)]	44.5 (44.4)	3.0 (3.0)	4.1 (4.1)	13	300s, 278s			1590m
[Rh(SnCl$_3$)(COD)(bda)]	42.3 (42.9)	4.2 (4.2)	4.1 (4.2)	15	305s, 285s			1585m
[Rh(SnCl$_3$)(COD)(biqui)]	44.9 (45.1)	3.4 (3.5)	3.9 (4.0)	35	328s, 312s 302s			1595s
[Rh(SnCl$_3$)(COD)(boh)]	25.6 (26.1)	3.9 (3.8)	6.9 (7.6)	67	300s, br		3360w, 3290w 3210w	1590w
[Rh(COD)(bdh)](SnCl$_3$)	26.5 (26.2)	4.0 (4.0)	9.9 (10.2)	90	240s, 215s		3380s, 3280s 3220w	1570s
[Rh(SnCl$_3$)(CO)$_2$(biqui)]	36.8 (37.5)	2.1 (1.9)	4.2 (4.4)	37	325sh, 310s	2085m, 2045s, 2020m, 1955s, 1920s [2060s, 1975s][c]		1595m
[RhCl(NBD)(bda)]	59.6 (59.2)	5.2 (5.1)	5.9 (6.0)	< 10				1585s, br
[RhCl(NBD)(bdh)]	37.8 (38.3)	4.9 (5.3)	14.9 (16.3)	52[a]			3300s, 3140s	1580m
[RhCl(COD)(bda)]	59.5 (59.7)	5.9 (5.8)	5.5 (5.8)	15				1634s, 1595s 1522s
[RhCl(COD)(bdh)]	41.5 (40.0)	5.8 (6.1)	13.1 (15.5)	< 10; 70[a]			3300s, 3140s	1580m
[RhCl(COD)(boh)]	38.1 (39.8)	5.3 (5.8)	10.5 (11.6)	< 10			3320m, 3280m 3150s	1595m, 1520s
[Rh(COD)(boh)]ClO$_4$	33.0 (33.9)	5.0 (5.0)	10.0 (9.9)	140			3400s, 3220s	1550m
[Rh(CO)$_2$(bdh)][Rh(CO)$_2$Cl$_2$]	18.8 (19.0)	2.1 (2.4)	10.6 (11.1)	81	315m, 280m	2100s, 2060s 2040s, 1985s	3360w, 3270m 3210m	1590w
[Rh(CO)$_2$(boh)][Rh(CO)$_2$Cl$_2$]	19.1 (19.1)	1.9 (1.8)	8.5 (8.3)	38	300m, 250m	2100s, 2060s 2040s, 1995s	3220sh, 3140m	1550m
[Rh(CO)$_2$(bdnh)][Rh(CO)$_2$Cl$_2$]	26.5 (25.8)	3.6 (3.2)	11.2 (10.0)	70	330w	2080s, 2060s 2020s, 1980s, br		
[Rh(CO)$_2$(bdh)]ClO$_4$	20.1 (19.3)	3.0 (2.7)	13.7 (15.0)	144		2070s, 2120s	3390s, 3310s 3240s	1590s
[Rh(CO)$_2$(boh)]ClO$_4$	20.8 (19.3)	2.8 (2.4)	10.6 (11.2)	129		2130s, 2110s 2070s	3400m, 3310s 3220s	1625m, 1550m

Λ_M in acetone or methanol[a] c. 2.5×10^{-4} M solutions. [b]Nujol suspension. [c]CH$_2$Cl$_2$ solution.

shift (Table 2) values lie at a much lower field than those reported for SnCl$_2$ [23] or SnCl$_3^-$ [24] which appear at $\delta=-236$ and $\delta=-388$ ppm, respectively. It varies markedly when lowering the temperature. These data indicate an equilibrium between species **a** and **b**, probably through a covalent trichlorostannato ‘Rh(SnCl$_3$)(COD)(bdh)’ intermediate (equilibrium (2)).

$$\underset{\mathbf{a}}{[Rh(COD)(bdh)]^+(SnCl_3)^-} \rightleftharpoons \text{‘}[Rh(SnCl_3)(COD)(bdh)]\text{’} \rightleftharpoons \underset{\mathbf{b}}{[Rh(Cl)(COD)(bdh)]} + SnCl_2 \quad (2)$$

Reaction of [Rh(CO)$_2$Cl]$_2$/LL = 1/2 mixtures with SnCl$_2$, yields Rh(SnCl$_3$)(CO)$_2$(LL) pentacoordinated compounds when LL = biqui or bda. The biqui complex can be isolated. Its IR spectrum shows a covalently bonded trichlorostannato group and is rather complex in the ν(C≡O) region in the solid state, probably due

TABLE 2. Selected ^{1}H and ^{119}Sn NMR data

Compound	Temp (°C)	NH_2	CH_3	HC=	HC$\leqslant$	δ^{119}Sn^{f}	$^{1}J(^{103}$Rh, ^{119}Sn)
[Rh($SnCl_3$)(NBD)(bda)]	20^{c}		2.02	3.21	3.46	250br	
	−40^{c}		2.00	3.16	3.63; 3.19	251d	615
	−80^{c}		2.04	3.15; 3.09	3.64; 3.26		
[Rh($SnCl_3$)(NBD)(boh)]	16^{d}	6.34	2.17	3.91	3.67	185br	
	−40^{d}	6.65	2.16	3.88	3.34	183d	535
[Rh($SnCl_3$)(NBD)(bdh)]	−40^{d}	6.36	2.09	3.81	3.63	175br	
	−80					175d	535
[Rh($SnCl_3$)(COD)(bda)]	20^{c}		1.96	3.72			
	−40^{c}		1.94	3.63			
	−80^{c}		1.95	3.94; 3.24			
[Rh(COD)(bdh)]($SnCl_3$)	16^{e}	5.29^{a}	2.14^{a}	4.42^{a}		125s	
		5.6^{b}	2.40^{b}	4.26^{b}			
	−40^{e}	5.37^{a}	2.14^{a}	4.41^{a}		147s	
		5.6^{b}	2.4^{b}	4.2^{b}			
	−80					152s	
[RhCl(NBD)(bda)]	16^{e}		1.89	3.14	3.43		
[RhCl(COD)(bda)]	16^{e}		1.84	3.68			
[RhCl(COD)(boh)]	16^{e}	5.59	2.37	4.22			
[RhCl(COD)(bdh)]	16^{e}	5.70	2.37	4.23			
[Rh(COD)(bdh)]ClO_4	16^{c}	5.46	2.13	4.66			
[Rh(COD)(boh)]ClO_4	16^{d}	6.8	2.30; 2.22	4.84			
[Rh$(CO)_2$(bdh)][Rh$(CO)_2Cl_2$]	16^{d}	7.32	2.32				
[Rh$(CO)_2$(boh)]ClO_4	16^{d}		2.45; 2.32				

[a]Major species in solution corresponding to cationic [Rh(COD)(bdh)]$^{+}$ species. [b]Minor species in solution corresponding to the pentacoordinated complex Rh(Cl)(COD)(bdh). [c]In acetone-d_6. [e]In $CDCl_3$. [f]Chemical shifts relative to $SnMe_4$ from acetone solutions.

to interactions in the solid state, as in CH_2Cl_2 solution only two bands are observed, very similar to those reported for neutral Rh(Cl)$(CO)_2$(biqui) [25]. The conductivity in acetone solution is relatively high, showing some extent of ionic dissociation but its low solubility precludes any ^{119}Sn NMR study. The bda compound cannot be isolated pure, however it can be characterized by ^{119}Sn NMR of the '*in situ*' obtained product (δ^{119}Sn = 197(br) at −40 °C in acetone solution).

In the absence of $SnCl_2$, [Rh(diolefin)Cl]$_2$ (diolefin = COD or NBD) dimers react with bdh, boh or bda to give neutral pentacoordinated complexes Rh(Cl)(diolefin)(LL) (Table 1), analogous to those reported for biqui [25], irrespective of the stoichiometric ratios employed (Rh/LL = 2/1 or 1/1). They behave as non-electrolytes in acetone solution, though in stronger ionizing solvents such as methanol (conductivity range: 80–115 Ω^{-1} cm^{2} mol^{-1} [18]) they behave as 1:1 electrolytes, due to chlorine dissociation. ν(C=N) vibrations are slightly modified upon coordination and indicate bonding through both imino nitrogens. ν(N–H) in bdh or boh compounds are displaced towards lower frequencies by *c*. 80 cm^{-1} with respect to the free ligands and this can be attributed to intramolecular NH_2---Cl interaction [26], indicating chlorine coordination to the rhodium atom. These data indicate pentacoordination in the solid state as ionic [Rh(COD)(LL)]ClO_4 compounds, containing an anion with lower coordinating ability, show no displacement of these ν(N–H) vibrations with respect to the free ligands.

^{1}H NMR spectra of the slightly soluble complexes were measured in $CDCl_3$ at room temperature and −40 °C. The spectra obtained at both temperatures are analogous and show only one resonance for all the olefinic protons and one singlet for the CH_3 groups of the diimine ligand (Table 2). Comparison of these spectra with those of cationic [Rh(COD)(LL)]$^{+}$ species suggests that pentacoordination may remain in solution. Nevertheless, the pattern observed indicates fluxionality probably due to Berry pseudorotation [20], though rapid ligand dissociation cannot be excluded.

When the reaction between [Rh(COD)Cl]$_2$ dimers and LL (Rh/LL = 2/1) is performed under carbon monoxide, ionic carbonylated [Rh$(CO)_2$(LL)][Rh$(CO)_2Cl_2$] complexes are formed. These complexes can also be obtained by direct [Rh$(CO)_2$Cl]$_2$/LL = 1/1 reaction [6, 7]. The new compounds (Table 1) show the expected four bands in the ν(C≡O) region and behave as 1:1 electrolytes in acetone solution, though the boh compound, containing an OH group, shows a rather low value that indicates stronger cation–anion association. The dicarbonylated cations are also readily formed by displacement of COD from [Rh(COD)(LL)]ClO_4 complexes, on reaction with CO [16].

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