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ISOLATION OF $[Rh(DIOLEFIN)X_2]^-$ SPECIES AND THEIR REACTIONS WITH P- OR N-DONOR LIGANDS, TIN(II) HALIDES AND CARBON MONOXIDE

M. A. GARCIA, M. A. GARRALDA* and L. IBARLUCEA

Catedra de Quimica Inorganica, Facultad de Quimica, Universidad del Pais Vasco,
San Sebastian, Spain

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Abstract—Anionic $[Rh(diolefin)X_2]^-$ species (X = Cl, Br) have been prepared and their reactions studied. The reactions with monodentate ligands led to neutral tetracoordinated complexes, and with N-donor bidentate ligands (Rh : LL = 2 : 1) gave Rh(X)(diolefin)(LL), $[Rh(diolefin)(LL)]^+[Rh(diolefin)X_2]^-$, or [Rh(diolefin)(LL)]X compounds, depending on the nature of LL or X. Reactions with carbon monoxide involved diolefin displacement. A trichlorostannato complex was obtained from the $[Rh(COD)Cl_2]^-$ species. Reactions of $[Rh(COD)Br]_2$ with bidentate N-donor ligands were also studied.

The reaction between $[Rh(diolefin)Cl]_2$ and some bidentate N-donor ligands (Rh : LL = 2 : 1) may give, depending on the nature of LL, ion-pair $[Rh(diolefin)(LL)]^+[Rh(diolefin)Cl_2]^-$ complexes, that contain diolefinic rhodium(I) anions.[1–4] While anionic carbonylated rhodium(I) species $[Rh(CO)_2X_2]^-$ have been extensively studied[5–12] and the crystal structure of $[Rh(CO)_2Cl_2]^-$ has been determined,[6–8] similar diolefinic $[Rh(diolefin)X_2]^-$ species have received less attention. $AsPh_4[Rh(COD)Cl_2]$ has been isolated[13] and the molecular structure of an ionic complex containing the $[Rh(COD)Cl_2]^-$ anion has been reported.[14]

In the present paper, we describe the synthesis of different $[Rh(diolefin)X_2]^-$ species and their reactivity with mono- and bidentate ligands containing N- or P-donor atoms, with carbon monoxide and with tin(II) halides.

RESULTS AND DISCUSSION

$[Rh(diolefin)X_2]^-$ species may be easily prepared by the reaction of $[Rh(diolefin)X]_2$ dimers with a stoichiometric amount of the corresponding halide as the salt of bulky cations that favour precipitation [eq. (1)]

$$[Rh(diolefin)X]_2 + 2RX \rightarrow 2R[Rh(diolefin)X_2]. \qquad (1)$$

The complexes (I–III) thus obtained (see Table 1) are yellow and air stable, behave as 1 : 1 electrolytes in acetone solution and their IR spectra show, along with the bands due to the corresponding cations and diolefins, one or two bands in the far-IR due to ν (Rh—X). The ^{1}H-NMR spectra of the two anions containing 1,5-cyclooctadiene (X = Cl, Br) show three groups of resonances, around 4.3, 2.4 and 1.7 ppm. These values agree with those found in the literature for the anion $[Rh(COD)Cl_2]^-$ isolated as the tetraphenylarsonium salt by a more complicated method.[13] The anion $[Rh(NBD)Cl_2]^-$ shows the corresponding signals around 3.8, 3.6 and 1.1 ppm. All these signals are very similar to those corresponding to the starting dimers $[Rh(diolefin)X]_2$.[15]

The reactivity of $[Rh(COD)X_2]^-$ with aliphatic diamines (LL) depends on the degree of N-substitution in the diamine. Thus, when LL = ethylenediamine (en), pentacoordinated neutral Rh(X)(COD)(en) compounds are obtained, irrespective of the stoichiometric ratios employed (Rh : LL = 2 : 1 or 1 : 1) [eq. (2)]

$$Et_4N[Rh(COD)X_2] + en \rightarrow Rh(X)(COD)(en) + Et_4NX, \qquad (2)$$

but when the more crowded LL = N,N,N′,N′-tetramethylethylenediamine (tmen) is used, no reaction occurs and the starting products are recovered unchanged.

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*Author to whom correspondence should be addressed.

The anions $[Rh(COD)X_2]^-$ react with bidentate heterocyclic N-donor ligands to give products that depend on the type of halogen, X. Thus, $Et_4N[Rh(COD)Cl_2]$ reacts with 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen), 5,6-dimethyl-1,10-phenanthroline (5,6-Me_2phen) or 4,7-diphenyl-1,10-phenanthroline (4,7-Ph_2phen) to yield ion-pair compounds $[Rh(COD)(LL)]^+[Rh(COD)Cl_2]^-$ when Rh : LL = 2 : 1 or ionic tetracoordinated [Rh(COD)(LL)]Cl when Rh : LL = 1 : 1. These products may also be obtained by the reaction of $[Rh(COD)Cl]_2$ with these ligands.[3,16] On the other hand, the reaction of $Et_4N[Rh(COD)Br_2]$ with these ligands gave only tetracoordinated ionic [Rh(COD)(LL)]Br complexes, irrespective of the stoichiometric ratios employed (Rh : LL = 2 : 1 or 1 : 1). The elemental analyses, molar conductivities and yields for the complexes obtained (**IV–VII**) are collected in Table 1.

$$[Rh(COD)X_2]^- \begin{cases} \xrightarrow{(i)} 1/2[Rh(COD)(LL)]^+[Rh(COD)X_2]^- + X^- \\ \xrightarrow[(ii)]{} [Rh(COD)(LL)]X + X^- \end{cases} \tag{3}$$

(i) = 1/2LL (X = Cl); (ii) = LL (X = Cl, Br).

These results indicate a lower tendency to form the ion-pair compounds, when the anionic species contain bromine.

Monodentate P- or N-donor ligands, such as quinoline (quin) or triphenylphosphine, react easily with $[Rh(diolefin)X_2]^-$ species (Rh : L = 1 : 1), and displace one halide atom, yielding neutral tetracoordinated compounds [eq. (4)]

$$Et_4N[Rh(COD)X_2] + L \rightarrow Rh(X)(COD)L + Et_4NX \tag{4}$$

$$L = \text{quin}, Ph_3P.$$

Carbon monoxide displaces the coordinated diolefin, leading to the well-known dicarbonylated anions $[Rh(CO)_2Cl_2]^-$[5] identified through the IR spectra of the solutions obtained.

$Et_4N[Rh(COD)Cl_2]$ reacts with $SnCl_2$ but needs Rh : Sn = 1 : 3 molar ratios to react completely and give $(Et_4N)_2[Rh(SnCl_3)_3(COD)]$,[17] while $Et_4N[Rh(COD)Br_2]$ does not react with $SnBr_2$ under the same conditions and the starting product is recovered unchanged.

In the light of the above results, we have studied the reaction between $[Rh(COD)Br]_2$, prepared *in situ* from $[Rh(COD)Cl]_2$,[1] and bidentate N-donor ligands (Rh : LL = 2 : 1). The reaction with LL = bipy, phen, 5,6-Me_2phen, 4,7-Ph_2phen or tmen, gave ion-pair compounds [eq. (5)]

$$[Rh(COD)Br]_2 + LL \rightarrow [Rh(COD)(LL)]^+[Rh(COD)Br_2]^-. \tag{5}$$

The complexes obtained are collected in Table 1 (**X–XVI**), they behave as 1 : 1 electrolytes in acetone solution and their IR spectra show bands due to ν (Rh—Br) of the anion $[Rh(COD)Br_2]^-$. In keeping with previous suggestions[18] we could attribute the behaviour of $[Rh(COD)Br]_2$, to a bridge cleavage mechanism via five-coordinate intermediates that could avoid free bromine appearing in solution.

The reaction of $[Rh(COD)Br]_2$ with ethylenediamine, 2,9-dimethyl-1,10-phenanthroline (2,9-Me_2phen) or 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (2,9-Me_2-4,7-Ph_2phen) (Rh : LL = 1 : 1 or 2 : 1) gave only pentacoordinated neutral compounds Rh(Br)(COD)(LL) (**XV–XVII**), analogous to those obtained from $[Rh(COD)Cl]_2$[3,4] [eq. (6)]

$$[Rh(COD)Br]_2 + 2LL \rightarrow 2Rh(Br)(COD)(LL). \tag{6}$$

These compounds behave as non-electrolytes in acetone solution and their IR spectra show one band around 200 cm^{-1} that may be due to ν (Rh—Br), thus confirming the bromine being bonded to the rhodium atom. Rh(Br)(COD)(en) shows bands due to the coordinated diamine at ν (N—H) = 3190 ($\Delta\nu$ = 180), 3170 ($\Delta\nu$ = 200) and 3080 ($\Delta\nu$ = 205) cm^{-1}. The band at the higher frequency is split, probably due to crystal lattice effects. The ν (N—H) decreases upon coordination are smaller than in the analogous Rh(Cl)(COD)(en).[4]

EXPERIMENTAL

$[Rh(COD)Cl]_2$, *in situ* $[Rh(COD)Br]_2$[1] and $[Rh(NBD)Cl]_2$[19] compounds were prepared by published methods. The C, H and N microanalysis were carried out with a Perkin–Elmer 240C microanalyser. Conductivities were measured in *ca* 2.5×10^{-4} M acetone solutions with a Metrhom E518 conductimeter. Proton NMR spectra were recorded at room temperature with an XL-200 Varian spectrometer with tetramethylsilane as the internal standard and deuterochloroform as the solvent. IR spectra were recorded on a Perkin–Elmer 598 spectrophotometer in the range 4000–200 cm^{-1} using Nujol mulls between polyethylene sheets and

Table 1. Analytical, conductivity and IR data and yields for the isolated compounds

Compound	Found (calc.)			Λ_M (Ω^{-1} cm^2 mol^{-1})	ν (Rh—X) (cm^{-1})	Yield (%)
	%C	%H	%N			
$Et_4N[Rh(COD)Cl_2]$ (I)	45.3	7.4	3.2	106	270(sh)	61
	(46.4)	(7.8)	(3.4)		258(s)	
$AsPh_4[Rh(NBD)Cl_2]$ (II)	56.2	4.3	—	112	275(m)	76
	(57.3)	(4.3)			260(m)	
$Et_4N[Rh(COD)Br_2]$ (III)	38.4	7.1	2.8	136	188(s)	74
	(38.3)	(6.4)	(2.8)			
[Rh(COD)(phen)]Br (IV)	49.9	4.3	5.9	[a]	—	52
	(51.0)	(4.3)	(5.9)			
[Rh(COD)(bipy)]Br (V)	46.9	4.7	6.1	109	—	70
	(48.4)	(4.5)	(6.3)			
[Rh(COD)(5,6-Me_2phen)]Br (VI)	50.4	4.5	5.6	121	—	75
	(52.9)	(4.8)	(5.6)			
[Rh(COD)(4,7-Ph_2phen)]Br (VII)	60.1	4.8	4.3	114	—	66
	(61.6)	(4.5)	(4.5)			
Rh(Br)(COD)(quin) (VIII)	47.5	4.8	3.5	10	193(s)	53
	(48.6)	(4.6)	(3.3)			
Rh(Cl)(COD)(quin) (IX)	54.0	5.0	4.4	10	285(sh)	31
	(54.3)	(4.5)	(3.7)		265(m)	
[Rh(COD)(4,7-Ph_2phen)] [Rh(COD) Br_2] (X)	51.8	4.4	3.3	96	178(m)	72
	(52.5)	(4.4)	(3.1)			
[Rh(COD)(phen)] [Rh(COD)Br_2] (XI)	43.8	4.3	3.7	[a]	191(s)	69
	(44.1)	(4.2)	(3.7)			
[Rh(COD)(5,6-Me_2phen)] [Rh(COD)Br_2] (XII)	45.4	4.6	3.4	[a]	179(s)	65
	(45.6)	(4.6)	(3.5)			
[Rh(COD)(bipy)] [Rh(COD)Br_2] (XIII)	42.7	4.3	4.1	104	190(m)	47
	(42.3)	(4.4)	(3.8)			
[Rh(COD)(tmen)] [Rh(COD)Br_2] (XIV)	36.0	5.8	4.1	116	195(s)	79
	(37.8)	(5.8)	(4.0)			
Rh(Br)(COD)(2,9-Me_2phen) (XV)	51.6	4.8	5.4	2	202(s)	48
	(52.9)	(4.8)	(5.6)			
Rh(Br)(COD)(2,9-Me_2-4,7-Ph_2phen) (XVI)	61.6	5.0	4.5	2	202(s)	85
	(62.6)	(4.9)	(4.3)			
Rh(Br)(COD)(en) (XVII)	33.6	5.7	7.2	[a]	202(s)	65
	(34.2)	(5.7)	(8.0)			

[a] Insoluble in acetone.

with a Nicolet 60SX spectrophotometer in the range 500–140 cm^{-1}, using polyethylene pellets.

Preparation of $Et_4N[Rh(COD)X_2]$ *complexes*

To 5 cm^3 of dichloromethane solutions of $[Rh(COD)X]_2$ (0.12 mmol), the appropriate Et_4NX (0.24 mmol) was added. Upon addition of diethyl ether yellow precipitates were formed, filtered off, washed with diethyl ether and air-dried.

Preparation of $Ph_4As[Rh(NBD)Cl_2]$

Addition of Ph_4AsCl (0.24 mmol) to 5 cm^3 of a dichloromethane solution of $[Rh(NBD)Cl]_2$ (0.12 mmol), followed by addition of n-hexane gave a yellow solid that was filtered off, washed with n-hexane and air-dried.

Reactions of $Et_4N[Rh(COD)X_2]$

(i) *Reaction with ethylenediamine.* Addition of ethylenediamine (0.12 mmol) to solutions of $Et_4N[Rh(COD)X_2]$ (0.12 mmol) in 5 cm^3 of dichloromethane yield yellow solids that were filtered off, washed with dichloromethane and air dried. The solids obtained were identified as Rh(X)(COD)(en).

(ii) *Reaction with phenanthroline type ligands.* To $Et_4N[Rh(COD)X_2]$ (0.12 mmol) solutions in 5 cm^3 of dichloromethane, the corresponding stoichiometric amounts (0.12 mmol) of 1,10-phenanthroline, 2,2′-bipyridine, 5,6-dimethyl-1,10-phenanthroline or 4,7-diphenyl-1,10-phenanthroline were added, whereupon the solution turned red or violet. The formed [Rh(COD)(LL)]Br complexes precipitated immediately as red crystals when LL = 1,10-phenanthroline or 5,6-dimethyl-1,10-phenanthroline were added and required elimination of CH_2Cl_2 and addition of acetone when LL = 2,2′-bipyridine (red crystals) or 4,7-diphenyl-1,10-phenanthroline (violet crystals) was used. The complexes obtained were filtered off, washed with acetone and air-dried.

(iii) *Reaction with triphenylphosphine*. Ph_3P (0.08 mmol) was added to yellow solutions of $Et_4N[Rh(COD)X_2]$ (0.08 mmol) in 5 cm^3 of CH_2Cl_2/MeOH (1 : 1) whereupon the solutions became orange. The elimination of dichloromethane yielded orange Rh(X)(COD)(Ph_3P) compounds that were filtered off, washed with methanol and air-dried.

(iv) *Reaction with quinoline*. Quinoline (0.12 mmol) was added to 5 cm^3 of yellow dichloromethane solutions of $Et_4N[Rh(COD)X_2]$ (0.12 mmol). Addition of methanol (3 cm^3) and elimination of dichloromethane led to yellow precipitates of Rh(X)(COD)(quin) complexes that were filtered off, washed with methanol and air-dried.

(v) *Reaction with carbon monoxide*. Carbon monoxide (P = 1 atm) was bubbled through dichloromethane solutions of $Et_4N[Rh(COD)X_2]$ (0.12 mmol) for 30 min. IR spectra of the yellow solutions obtained confirmed the formation of $Et_4N[Rh(CO)_2X_2]$ complexes.

(vi) *Reaction with tin*(II) *halides*. $SnCl_2 \cdot 2H_2O$ (0.30 mmol) in 5 cm^3 of methanol was added to 5 cm^3 of $Et_4N[Rh(COD)Cl_2]$ (0.10 mmol) in dichloromethane. The addition of Et_4NCl (0.10 mmol) followed by elimination of dichloromethane gave $(Et_4N)_2[Rh(SnCl_3)_3(COD)]$ that was filtered off, washed with methanol and air-dried.

$Et_4N[Rh(COD)Br_2]$ did not react with $SnBr_2$ under the same conditions.

Preparation of $[Rh(COD)(LL)]^+[Rh(COD)Br_2]^-$ *complexes*

Addition of the corresponding ligand (0.06 mmol) to 5 cm^3 of dichloromethane solutions of *in situ* prepared $[Rh(COD)Br]_2$ (0.06 mmol) gave red solids when LL = 1,10-phenanthroline, 2,2′ bipyridine or 5,6-dimethyl-1,10-phenanthroline. When LL = 4,7-diphenyl-1,10-phenanthroline or N,N,N′,N′-tetramethylethylenediamine, addition of diethyl ether was necessary to afford precipitation of the corresponding compounds. The complexes obtained were filtered off, washed with diethyl ether and air-dried.

Preparation of Rh(Br)(COD)(LL) *complexes*

0.12 mmol of the corresponding ligand were added to 5 cm^3 of dichloromethane solutions of *in situ* prepared $[Rh(COD)Br]_2$ (0.06 mmol). When LL = ethylenediamine, a yellow solid appeared immediately. When LL = 2,9-dimethyl-1,10-phenanthroline or 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, addition of diethyl ether gave yellow solids. The complexes thus obtained, were filtered off, washed with diethyl ether and air-dried.

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