

RHODIUM(I) COMPLEXES CONTAINING ALIPHATIC DIAMINE LIGANDS

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Summary

The reaction of $[\text{Rh}(\text{diolefin})\text{Cl}]_2$ and aliphatic diamines (LL) in 2/1 ratio, gave either the ion-pair species $[\text{Rh}(\text{diolefin})(\text{LL})]^+ [\text{Rh}(\text{diolefin})\text{Cl}_2]^-$ or neutral penta-coordinated $[\text{Rh}(\text{Cl})(\text{diolefin})(\text{LL})]$ complexes depending on the degree of *N*-substitution in the ligands. When the reactions were performed in solutions saturated with CO only ion-pair $[\text{Rh}(\text{CO})_2(\text{LL})]^+ [\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ complexes were obtained; these carbonyl derivatives show some metal-metal interaction. Reaction of $[\text{Rh}(\text{NBD})\text{Cl}]_2$ with ethylenediamine and triphenylphosphine gives pentacoordinated $[\text{Rh}(\text{NBD})(\text{en})(\text{PPh}_3)]^+$ species.

Introduction

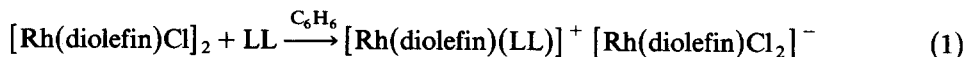
The reactions between $[\text{Rh}(\text{diolefin})\text{Cl}]_2$ complexes and neutral bidentate *N*-donor ligands, (LL), with chelating ability ($\text{Rh}/\text{LL} = 1/1$) have been extensively studied, and usually give cationic $[\text{Rh}(\text{diolefin})(\text{LL})]^+$ species [1]. Similar reactions with 2/1 Rh/LL stoichiometric ratios have received less attention, and can yield, depending on the nature of the ligands employed, dinuclear $\text{Rh}_2\text{Cl}_2(\text{diolefin})_2(\text{LL})$ compounds, containing bridging LL groups [2–4], ion-pair $[\text{Rh}(\text{diolefin})(\text{LL})]^+ [\text{Rh}(\text{diolefin})\text{Cl}_2]^-$ species [5–7], or neutral $[\text{Rh}(\text{Cl})(\text{diolefin})(\text{LL})]$ complexes; in the last case only 50% of the starting dimers react [7]. When these bridge-splitting reactions ($\text{Rh}/\text{LL} = 2/1$), are performed under carbon monoxide and with LL = 2,2'-bipyridine or a phenanthroline type ligand, they give only ion-pair $[\text{Rh}(\text{CO})_2(\text{LL})]^+ [\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ complexes [7]. Such complexes can also be obtained by direct reaction of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ with the relevant ligand [8–10]; when α -diimine ligands are used this may also give dinuclear $\text{Rh}_2\text{Cl}_2(\text{CO})_4(\text{LL})$ compounds [11].

In the present paper we describe the cleavage reactions of $[\text{Rh}(\text{diolefin})\text{Cl}]_2$ with aliphatic diamines ($\text{Rh}/\text{LL} = 2/1$) in the presence or absence of carbon monoxide, and the characterization of the isolated compounds. Reactions with triphenylphosphine are also described.

Results and discussion

Diolefin complexes

In benzene or chloroform aliphatic diamines (LL) cleave the chlorine bridges in $[\text{Rh}(\text{diolefin})\text{Cl}]_2$ dimers ($\text{Rh}/\text{LL} = 2/1$), to give products which depend on the nature of the *N*-substitution in the diamine. Thus, when aliphatic diamines with at least two methyl groups on the diamino *N*-donor atoms, such as: *N,N'*-dimethylethylenediamine (*N,N'*-Me₂en), *N,N*-dimethylethylenediamine (*N,N*-Me₂en) and *N,N,N',N'*-tetramethylethylenediamine (tmen) are used, asymmetric cleavage occurs and ion-pair complexes are formed (eq. 1):



When an excess of diamine ligand is used ($\text{Rh}/\text{LL} = 1/1$), the same ion-pair complexes are the only products.

The complexes I–V thus obtained are yellow; their analytical data, molar conductivities and yields are listed in Table 1. The conductivities in acetone support an ionic formulation though the *N,N*- or *N,N'*-Me₂en complexes have lower

TABLE 1
ANALYTICAL CONDUCTIVITY DATA AND YIELDS FOR DIOLEFIN COMPLEXES

Compound	Found (calcd.) (%)			Λ_M (ohm ⁻¹ cm ² mol ⁻¹)	Yield (%)
	C	H	N		
$[\text{Rh}(\text{COD})(N,N'\text{-Me}_2\text{en})][\text{Rh}(\text{COD})\text{Cl}_2]$ (I)	42.26 (41.32)	6.30 (6.24)	5.26 (4.81)	58 ^a	84
$[\text{Rh}(\text{COD})(N,N\text{-Me}_2\text{en})][\text{Rh}(\text{COD})\text{Cl}_2]$ (II)	41.83 (41.32)	6.21 (6.24)	5.09 (4.81)	48 ^a	74
$[\text{Rh}(\text{COD})(\text{tmen})][\text{Rh}(\text{COD})\text{Cl}_2]$ (III)	43.35 (43.36)	6.56 (6.61)	4.95 (4.59)	102 ^a	73
$[\text{Rh}(\text{NBD})(N,N\text{-Me}_2\text{en})][\text{Rh}(\text{NBD})\text{Cl}_2]$ (IV)	39.04 (39.36)	5.23 (5.10)	4.92 (5.10)	52 ^a	28
$[\text{Rh}(\text{NBD})(\text{tmen})][\text{Rh}(\text{NBD})\text{Cl}_2]$ (V)	42.01 (41.61)	5.72 (5.58)	4.57 (4.85)	101 ^a	55
$\text{Rh}(\text{Cl})(\text{COD})(\text{en})$ (VI)	37.89 (39.16)	6.64 (6.57)	8.55 (9.13)	133 ^b	62
$\text{Rh}(\text{Cl})(\text{COD})(1,3\text{-pn})$ (VII)	39.69 (41.20)	6.73 (6.91)	8.31 (8.73)	66 ^b	69
$\text{Rh}(\text{Cl})(\text{COD})(1,2\text{-pn})$ (VIII)	40.66 (41.20)	6.43 (6.91)	8.09 (8.73)	86 ^b	75
$\text{Rh}(\text{Cl})(\text{COD})(\text{stien})$ (IX)	56.01 (57.58)	5.98 (6.15)	6.15 (6.10)	62 ^b	82
$\text{Rh}(\text{Cl})(\text{COD})(N\text{-Me-en})$ (X)	40.80 (41.20)	6.62 (6.91)	8.17 (8.73)	66 ^b	80
$\text{Rh}(\text{Cl})(\text{NBD})(\text{en})$ (XI)	36.03 (37.19)	5.48 (5.54)	9.52 (9.64)	48 ^b	31
$\text{Rh}(\text{Cl})(\text{NBD})(1,2\text{-pn})$ (XII)	38.22 (39.42)	5.78 (5.91)	9.40 (9.19)	9 ^a ; 76 ^b	63
$[\text{Rh}(\text{NBD})(\text{en})(\text{PPh}_3)]\text{BPh}_4$ (XIII)	73.29 (73.23)	6.38 (6.10)	3.31 (3.35)	93 ^a	45

^a Acetone solutions. ^b Methanol solutions.

TABLE 2
IR DATA FOR DIOLEFIN COPMLEXES (cm⁻¹)

Compound	$\nu(\text{N-H})$	$\Delta\nu(\text{N-H})$	$\delta(\text{N-H})$	$\nu(\text{Rh-Cl})$
I	3165s	155	—	258m, 250m
II	3210s, 3170m	160, 130	1575w	260m, 250m
III	—	—	—	258s, 245s
IV	3220s, 3180m	150, 120	1570w	275m, 255m
V	—	—	—	270s, 258sh
VI	3160s, 3060s	210, 225	1590s	265s
VII	3160s, 3070s	215, 220	1585w	260m, 245m
VIII	3165s, 3070s	205, 220	1588m	270m
IX	3120s, 3040s	230, 240	1590s	258m, 245m
X	3200m, 3150s	170, 150	1594m	270w, 245w
XI	3170s, 3080s	200, 205	1580m	308m, 245w
XII	3160s, 3075s	210, 215	1578s	305m, 240m
XIII	3330m, 3310m	40, 60	1580m	—
	3275m, 3260m	10, 25	1573m	

conductivities than would be expected for 1:1 electrolytes [12], and there may be some association in solution.

IR data are listed in Table 2. All the complexes show two bands in the far IR due to the $\nu(\text{Rh-Cl})$ vibration, as expected for the $[\text{Rh}(\text{diolefin})\text{Cl}_2]^-$ anions [7], along with the bands due the $\nu(\text{N-H})$ vibrations displaced towards lower frequencies as expected for coordinated diamine ligands. The ^1H NMR spectra of the complexes show three groups of resonances, around 4.2, 2.5, and 1.8 ppm, respectively, for the compounds containing COD as diolefinic ligand and two groups of resonances, around 3.9 and 1.2 ppm, for those containing NBD. The coordinated diamine ligands show singlets for the CH_3 resonances in the range 2.3–2.5 ppm. The CH_2 groups of *N,N'*-Me₂en and tmen show singlets and those of *N,N*-Me₂en two triplets in the 2.5–2.9 ppm region.

When $[\text{Rh}(\text{diolefin})\text{Cl}]_2$ cleavage reactions are performed with primary aliphatic diamines ($\text{Rh/LI} = 2/1$), such as ethylenediamine (en), 1,2-propylenediamine (1,2-pn), 1,3-propylenediamine (1,3-pn) and 1,2-diphenylethylenediamine (stien), or with *N*-methylethylenediamine (*N*-Me-en), symmetric cleavage occurs and only neutral pentacoordinated $\text{Rh}(\text{Cl})(\text{diolefin})(\text{LL})$ complexes are formed. Consequently, 1/1 Rh/LL ratios are required for the starting dimers to react completely, according to eq. 2:

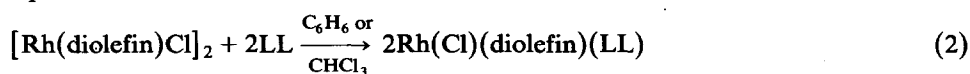


Table 1 presents analyses, molar conductivities, and yields of the isolated yellow complexes (VI–XII). All the complexes are very slightly soluble or insoluble in common organic solvents except alcohols. The conductivity of $\text{Rh}(\text{Cl})(\text{NBD})(1,3\text{-pn})$ in acetone shows it to be a neutral species. The conductivity values for methanol solutions (all but one of the complexes were insoluble in acetone) are rather high probably due to some chlorine dissociation in this more polar solvent [8], leading to ionic tetracoordinated species.

The IR spectra of these compounds (Table 2) show one or two bands in the far IR due to $\nu(\text{Rh-Cl})$, thus confirming that the chlorine is bonded to the rhodium

atom in the solid state. Bands due to bonded diamino groups are also present, and the absorptions due to uncoordinated *N*-donor ligands are totally absent. All these data indicate pentacoordination in the solid state for rhodium, which probably has a trigonal bipyramidal environment, the most frequent situation for rhodium(I) pentacoordinated compounds, but a square-pyramidal structure cannot be totally excluded [13]. It should be noted that the decrease in $\nu(\text{N-H})$ upon coordination is much more pronounced in these complexes with primary diamines than in reported cationic $[\text{Rh}(\text{diolefin})(\text{LL})]\text{ClO}_4$ complexes [14], suggests the presence of some $\text{N-H} \cdots \text{Cl}$ hydrogen bonding. Unfortunately, the insolubility of these compounds precluded molecular weight or NMR measurements.

From the results we conclude that the nature of the products obtained in the reaction between $[\text{Rh}(\text{diolefin})\text{Cl}]_2$ and aliphatic diamines depends mainly on the degree of *N*-substitution on the *N*-donor atoms.

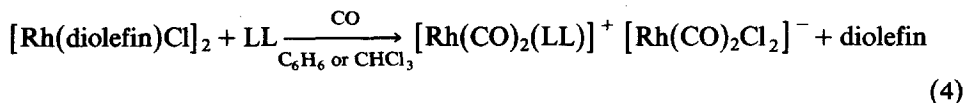
The reaction of $[\text{Rh}(\text{NBD})\text{Cl}]_2$ with ethylenediamine and triphenylphosphine yields a pentacoordinated ionic complex, which was isolated as tetraphenylborate salt, according to eq. 3:



Analytical and conductivity data for this yellow ionic compound XIII are presented in Table 1. Its IR spectrum (Table 2) shows bands due to coordinated diamine that are split, probably due to crystal lattice effects, and their displacements upon coordination are markedly lower than those in pentacoordinated complexes not containing phosphines (VI, XI). When $[\text{Rh}(\text{COD})\text{Cl}]_2$ was used as starting material no pentacoordinated complexes were obtained, and this is in line with previous observations [15] that norbornadiene shows a higher tendency than cyclooctadiene to give pentacoordinated species. Other diamines gave only mixtures of $[\text{Rh}(\text{diolefin})(\text{LL})]\text{BPh}_4$ and $[\text{Rh}(\text{diolefin})(\text{PPh}_3)]\text{BPh}_4$ as revealed by the IR spectra of the products.

Carbonylated complexes

When the reactions between $[\text{Rh}(\text{diolefin})\text{Cl}]_2$ and aliphatic diamines ($\text{Rh}/\text{LL} = 2/1$) were performed under carbon monoxide, only carbonylated ion-pair $[\text{Rh}(\text{CO})_2(\text{LL})]^+ [\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ complexes were obtained, irrespective of the *N*-donor ligand employed. Similar behaviour was observed with phenanthroline type ligands [7] (Eq. 4):



The complexes obtained (XIV–XXI), along with their analytical results, conductivity data, colours and yields are shown in Table 3. They are slightly soluble or insoluble in acetone, insoluble in chlorinated solvents, and soluble in alcohols to give yellow solutions; they behave as 1 : 1 electrolytes in methanol or acetone. The IR spectra (Table 4) show at least four bands in the $\nu(\text{C}\equiv\text{O})$ region, two in the far IR due to $\nu(\text{Rh}-\text{Cl})$ for mutually *cis* Cl atoms, and several bands from the coordinated diamino groups with $\Delta\nu(\text{N-H})$ in the range $75\text{--}180 \text{ cm}^{-1}$.

Both, the colour changes upon dissolution and the complexity of the IR spectra may indicate metal–metal interactions in the solid state, as is rather common for d^8

TABLE 3
ANALYTICAL AND CONDUCTIVITY DATA, COLOURS AND YIELDS FOR CARBONYL COMPLEXES

Compound	Found (calcd.) (%)			$\Lambda_{M_2}^{-1}$ (ohm ⁻¹ cm ² mol ⁻¹)	Yield (%)	Colour
	C	H	N			
[Rh(CO) ₂ (en)[Rh(CO) ₂ Cl ₂] ₂] (XIV)	15.32 (16.05)	2.09 (1.79)	5.70 (6.24)	100 ^a ; 85 ^b	78	dark blue
[Rh(CO) ₂ (1,3-pn)[Rh(CO) ₂ Cl ₂] ₂] (XV)	17.24 (18.16)	2.89 (2.17)	5.66 (6.05)	75 ^b	81	red
[Rh(CO) ₂ (1,2-pn)[Rh(CO) ₂ Cl ₂] ₂] (XVI)	19.10 (18.16)	2.57 (2.17)	7.11 (6.05)	108 ^b	85	dark blue
[Rh(CO) ₂ (N-Me-en)[Rh(CO) ₂ Cl ₂] ₂] (XVII)	18.83 (18.16)	2.33 (2.17)	6.04 (6.05)	76 ^a	63	red
[Rh(CO) ₂ (stien)[Rh(CO) ₂ Cl ₂] ₂] (XVIII)	35.74 (35.96)	2.94 (2.68)	4.85 (4.66)	100 ^a	71	yellow
[Rh(CO) ₂ (N,N'-Me ₂ en)[Rh(CO) ₂ Cl ₂] ₂] (XIX)	18.85 (20.14)	2.93 (2.53)	5.15 (5.87)	100 ^a	44	red
[Rh(CO) ₂ (N,N-Me ₂ en)[Rh(CO) ₂ Cl ₂] ₂] (XX)	19.88 (20.14)	2.66 (2.53)	5.97 (5.87)	104 ^a	47	orange
[Rh(CO) ₂ (tmen)[Rh(CO) ₂ Cl ₂] ₂] (XXI)	23.46 (23.78)	3.42 (3.19)	5.57 (5.54)	116 ^a	59	orange-yellow

^a Acetone solution. ^b Methanol solution.

TABLE 4
SPECTROSCOPIC DATA FOR CARBONYL COMPLEXES

Compound	IR (cm ⁻¹)			UV (nm)	
	$\nu(\text{N-H})$	$\nu(\text{C}\equiv\text{O})$	$\nu(\text{Rh-Cl})$	MeOH solution	Nujol mull
XIV	3280m, 3210m	2100s, 2040s 1990sh, 1980m	310m, 280m	332, 266 203	585, 400
XV	3260m, 3190m 3120m, 3060m	2095s, 2060m 2030s, 1980m	310m, 275m	333, 265 204	568
XVI	3270s, 3200s 3120s, 3030s	2095s, 2060sh 2035s, 2015sh 1980m	305m, 275m	341, 266 204	568
XVII	3290m, 3255s 3200s, 3140s 3120s	2085s, 2035s 2010sh, 1980m	312m, 285m	330, 266 204	540
XVIII	3230s, 3180s 3120m, 3100m	2085s, 2070s 2035s, 2020s 1995s, 1985sh	315m, 280m	333, 261	428
XIX	3160s	2098s, 2060s 2040s, 1995s	305m, 280m	329, 250 217	505
XX	3230m, 3190m	2100s, 2080s 2020s, 1995s	315m, 280m	333, 261 218	460
XXI	—	2080s, 2060s 2020s, 1980s	320m, 290m	331, 260 206	376

metal carbonyl complexes [9,10,16]. The electronic spectra of the solid complexes (Nujol mulls) and their methanol solutions (Table 4) suggest a columnar structure with stacked square-planar anions and cations. From these electronic spectra the metal-metal interaction appears to be stronger for the complexes containing primary amines, except for the complex containing stien, that contains two phenyl groups on the carbon atoms, and the weakest interaction is that in the compound containing tmen; it thus seems that the interaction depends mainly on the steric requirements of the diamine.

Experimental

[Rh(COD)Cl]₂ [5] and [Rh(NBD)Cl]₂ [17] compounds were prepared by published methods. The C, H and N microanalysis were carried out with a Perkin-Elmer 240 C microanalyzer. Conductivities were measured in ca. 2.5×10^{-4} M solutions with a Metrohm E 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. Electronic spectra were recorded with a Varian 634-S spectrophotometer, Proton NMR spectra were recorded at room temperature with a XL-200 Varian spectrometer with tetramethylsilane as internal standard and deuteriochloroform as solvent.

[Rh(diolefin)(LL)]⁺ [Rh(diolefin)Cl₂]⁻ complexes

To a C₆H₆ solution of the dimer [Rh(COD)Cl]₂ (0.06 mmol) was added an equimolar amount of *N*-donor ligand LL (0.06 mmol). Precipitation of the expected complex immediately occurred. The yellow solids were filtered off, washed with

C_6H_6 , and air-dried. The complexes with norbornadiene as diolefinic ligand were prepared analogously from $[Rh(NBD)Cl]_2$, but under N_2 .

$[Rh(Cl)(diolefin)(LL)]$ complexes

These complexes were prepared by the above method but with 2/1 $[Rh(diolefin)Cl]_2/LL$ ratios.

$[Rh(NBD)(en)(PPh_3)]BPh_4$

When ethylenediamine (0.12 mmol) was added under N_2 to a suspension of $[Rh(NBD)Cl]_2$ (0.06 mmol) in MeOH total dissolution occurred. The solution was cooled to $-10^\circ C$ and triphenylphosphine (0.12 mmol) and sodium tetraphenylborate (0.12 mmol) were added. The yellow complex which separated was filtered off, washed with cold MeOH, and air-dried.

$[Rh(CO)_2(LL)]^+ [Rh(CO)_2Cl_2]^-$ complexes

CO at atmosphere pressure for 30 min was bubbled through stirred C_6H_6 or $CHCl_3$ suspensions or solutions containing equimolar amounts of $[Rh(COD)Cl]_2$ and N -donor ligand (LL). The yellow, red, or dark blue solids obtained were filtered off, washed with the same solvent, and air-dried.

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