Rhodium(I) complexes with unsymmetric aliphatic diamines. Crystal structure of [Rh(C$_8$H$_{12}$)(C$_7$N$_2$H$_{16}$)][RhCl$_2$(C$_8$H$_{12}$)] and [Rh(C$_8$H$_{12}$)(C$_7$N$_2$H$_{16}$)]ClO$_4$

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

Elena Pinilla
Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense, Madrid (Spain)

and M. Angeles Monge*
Laboratorio de Difracción de Rayos X, Universidad Complutense e Instituto de Ciencias de Materiales, Sede D, C.S.I.C., Madrid (Spain)

Abstract

Reactions of [Rh(COD)Cl]$_2$ with unsymmetric aliphatic diamines (LL′) have been studied. The 1:1 ligand:dimer reactions yield ionic products [Rh(C$_8$H$_{12}$)(LL′)][RhCl$_2$(C$_8$H$_{12}$)] that in solution are in equilibrium with the respective binuclear compounds {[RhCl$_2$(C$_8$H$_{12}$)]$_2$(μ-LL′)}. The X-ray structure of [Rh(C$_8$H$_{12}$)(C$_7$N$_2$H$_{16}$)][RhCl$_2$(C$_8$H$_{12}$)] is presented. When the reactions are performed in media saturated with CO, carbonylated ion-pair complexes are obtained. The 2:1 ligand:dimer reactions afford neutral tetracoordinated [Rh(COD)(LL′)Cl] compounds bonded through the primary amino group, and show rapid interchange of olefinic protons at room temperature. The synthesis and properties of cationic complexes of general formulae [Rh(COD)(LL′)]ClO$_4$ and [Rh(CO)(PPh$_3$)(LL′)]ClO$_4$ are also discussed. Cyclooctadiene compounds show association processes in acetone solution, though they are monomeric in the solid state. The X-ray structure of [Rh(C$_8$H$_{12}$)(C$_7$N$_2$H$_{16}$)]ClO$_4$ indicates the existence of hydrogen bonding between the oxygens in the perchlorate anion and the primary amino group in the cation.

Introduction

It is well known that potentially bidentate N-donor ligands cleave easily the chlorine bridges in [Rh(COD)Cl]$_2$ complexes to give different types of products, depending on the ligands and/or the stoichiometric ratios employed. Thus, some bis(pyrazolyl)methane derivatives may give dinuclear [Rh$_2$Cl$_2$(diolefin)$_2$(μ-LL)] [1, 2] compounds irrespective of the stoichiometric ratios used, while others give mononuclear cationic tetracoordinated [1] or neutral pentacoordinated complexes [2] when Rh:LL = 1:1. α-Diimines may give dinuclear compounds [3] or ion-pair [Rh(diolefin)(LL)]$^+$-[Rh(diolefin)Cl$_2$]$^-$ complexes [4], nevertheless, it has been suggested that in solution both forms exist in equilibrium. Substituted phenanthrolines [5, 6] and aliphatic diamines [7] (Rh:LL = 2:1) may give ion-

pair complexes or neutral pentacoordinated species. When Rh:LL = 1:1, α-diimines [4], substituted phenanthrolines [5, 8] and chelating aminomethylpyridines [9] give tetracoordinated cationic species. Non-chelating ligands such as some aminomethylpyridines [9], pyrazyne [10], pyrimidine [11] and 4,4′-bipyrazole type ligands [12] afford dinuclear neutral complexes with bridging LL groups (Rh:LL = 2:1), while tetracoordinated monomeric neutral compounds are formed when Rh:LL = 1:1 and LL = aminopyridines [9], pyridazine [10], benzotriazole derivatives [13] or imidazole type ligands [8, 14], where LL act as monodentate. Some of the aforementioned ligands may give carbonylated neutral species similar to the analogous diolefinic compounds [10, 12–14], but in other cases only cation–anion [Rh(CO)$_2$(LL)]$^+$-[Rh(CO)$_2$Cl$_2$]$^-$ species are obtained [1, 2, 6, 7, 15], probably due to high stability of the carbonylated anion.

---

*Authors to whom correspondence should be addressed.

We report now the reaction between [Rh(COD)Cl]₂ and unsymmetric aliphatic diamines containing one primary and one cyclic tertiary amino group, LL', using different stoichiometric ratios. The behaviour of solutions of the obtained compounds, their reactions with carbon monoxide and the study of cationic complexes containing these ligands are described. Crystal structures of representative compounds are also reported.

Experimental

The preparation of the metal complexes was carried out at room temperature under nitrogen by standard Schlenk techniques. [Rh(COD)Cl]₂ [16] and [Rh(COD)₂]ClO₄ [17] were prepared as previously reported.

Microanalyses were 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) and ³¹P (H₃PO₄ external standard) spectra were measured from CDCl₃ solutions at variable temperature in 5 mm tubes. Molecular weights were measured with a Knauer cryoscopic unit using benzene as solvent.

Preparation of [Rh(COD)(LL')][Rh(COD)Cl₂] complexes

To a CH₂Cl₂ solution of [Rh(COD)Cl]₂ (0.06 mmol), was added an equimolar amount (0.06 mmol) of the corresponding ligand. The addition of hexane or diethyl ether, gave yellow complexes that were filtered off, washed with hexane and vacuum dried. Yields 46–60%.

Preparation of [Rh(CO)₂(LL')] [Rh(CO)₂Cl₂] complexes

Carbon monoxide at room temperature was bubbled for 30 min through dichloromethane solutions prepared as indicated previously, whereupon their colour darkened. Subsequent addition of hexane or diethyl ether, gave the corresponding reddish complexes that were filtered off, washed with hexane and vacuum dried. Yields 30–76%.

Preparation of Rh(COD)(LL')Cl complexes

To a CH₂Cl₂ solution of [Rh(COD)Cl]₂ (0.06 mmol), was added a double amount (0.12 mmol) of the corresponding ligand. The addition of hexane or diethyl ether, gave yellow complexes that were

filtered off. The products were washed with hexane, recrystallized from dichloromethane/diethyl ether and vacuum dried. Yields 56%.

Preparation of [Rh(COD)(LL')]ClO₄ compounds

These complexes were prepared by adding an slight excess of ligand (0.15 mmol) to a dichloromethane solution of [Rh(COD)₂]ClO₄ (0.12 mmol). The yellow products which were formed immediately, were precipitated by addition of diethyl ether, filtered off, washed with diethyl ether and vacuum dried. Yields 62–75%.

Preparation of [Rh(CO)(PPh₃)(LL')]ClO₄ compounds

Carbon monoxide at room temperature was bubbled for 5 min through a dichloromethane solution of the corresponding [Rh(COD)(LL')]ClO₄ compound (0.09 mmol), during which the colour of the solution darkened. Addition of triphenylphosphine (0.09 mmol) gave yellow solutions. Subsequent addition of diethyl ether precipitated the complexes which were filtered off, washed with diethyl ether and vacuum dried. Yields 66–90%.

X-ray structure determinations

Crystals of both compounds were mounted in a kappa diffractometer. The cell dimensions refined by least-squares fitting the values of 25 reflections. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Rh and Cl were taken from the International Tables for X-Ray Crystallography [18].

[Rh(C₈H₁₂)(C₇N₂H₁₆)][RhCl₂(C₈H₁₂)]

A summary of the fundamental crystal data is given in Table 1. The crystals were yellow, fibrous and polysynthetically twinned. The structure was solved by Patterson and Fourier methods. An empirical absorption correction [19] was applied at the end of isotropic refinement. The maximum and minimum absorption correction factors were 1.012 and 0.941, respectively.

We have observed a very important non-resolvable positional disorder in the cyclooctadiene bonded to RhI and the structure was refined within space groups P1 and P1̄. In P1̄ all the anisotropic thermal parameters determinants were positive, in P1 some of them became negative, the standard deviations were larger and the disorder remained. Hence, the space group P1̄ was retained.

Final refinement employed fixed isotropic factors and coordinates for H atoms. In order to prevent bias on (F) versus (Fₒ) or (sin θ/λ), the last steps

TABLE 1. Crystal and refinement data for [Rh(C$_8$H$_{12}$)(C$_7$N$_2$H$_{16}$)][RhCl$_2$(C$_8$H$_{12}$)]

Formula	RhC$_{23}$Cl$_2$N$_2$H$_{40}$
M_r	621.30
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	8.954(2)
b (Å)	10.842(2)
c (Å)	13.745(4)
α (°)	83.13(2)
β (°)	76.73(2)
γ (°)	70.18(2)
V (Å^3)	1220.5(5)
Z	2
$F(000)$	632
ρ_{calc} (g cm^{-3})	1.69
Temperature (°C)	22
μ (cm^{-1})	15.66
Crystal dimensions (mm)	0.2×0.2×0.3
Diffractometer	Enraf-Nonius CAD4
Radiation	graphite-monochromated Mo Kα (λ=0.71069 Å)
Scan technique	$\omega/2\theta$
Data collected	(-10, -12, 0) to (10, 12, 16)
Reflections collected	4672
Unique data	4288
Unique data (I)$\geqslant 3\sigma(I)$	2885
R_{int} (%)	1.3
Standard reflections	3/186
RF (%)	10.4
R_wF (%)	14.6
Average shift/error	0.03

TABLE 2. Coefficients for the weighting scheme in [Rh(C$_8$H$_{12}$)(C$_7$N$_2$H$_{16}$)][RhCl$_2$(C$_8$H$_{12}$)]

	a	b	c	d
$|F_o|<33$	4.91	-0.04		
$33<|F_o|<231$	3.01	0.02		
$(\sin\theta)/\lambda<0.60$ A^{-1}			2.50	-3.31

of the refinement were calculated by Pesos [20] with weights $w=w_1w_2$ where $w_1=1/(a+b|F_o|)^2$ and $w_2=1/(c+d\,(\sin\theta)/\lambda)$ and the coefficients shown in Table 2.

[Rh(C$_8$H$_{12}$)(C$_7$N$_2$H$_{16}$)]ClO$_4$

A summary of the fundamental crystal data is given in Table 3. The crystals are yellow and prismatic. The structure was solved by Multan [21] and Fourier methods. An empirical absorption correction [19] was applied at the end of the isotropic refinement. The oxygen atoms of the perchlorate anions were refined isotropically because of some non-resolvable disorder from thermal motion.

TABLE 3. Crystal and refinement data for [Rh(C$_8$H$_{12}$)(C$_7$N$_2$H$_{16}$)]ClO$_4$

Formula	RhC$_{15}$ClN$_2$O$_4$H$_{28}$
Crystal system	monoclinic
Space group	$C2/c$
a (Å)	20.356(6)
b (Å)	19.437(6)
c (Å)	11.035(7)
β	122.50(3)
V (Å^3)	3682(3)
Z	8
$F(000)$	1808
ρ_{calc} (g cm^{-1})	1.58
Temperature (°C)	22
μ (cm^{-1})	10.78
Crystal dimensions (mm)	0.4×0.2×0.2
Diffractometer	Enraf-Nonius CAD4
Radiation	graphite-monochromated Mo Kα (λ=0.71069 Å)
Scan technique	$\omega/2\theta$
Data collected	(-24, 0, 0) to 24, 23, 13)
Reflections collected	7286
Unique data	6683
Unique data (I)$\geqslant 2\sigma(I)$	2849
R_{int} (%)	0.7
Standard reflections	3/233
RF (%)	5.4
R_wF (%)	5.7
Average shift/error	0.02

Final refinement employed fixed isotropic factors and coordinates for H atoms, except H21 and H22, that have been located in a final difference synthesis and refined. No trend in F versus F_o or $(\sin\theta)/\lambda$ was observed.

Most of the calculations were carried out with the XRAY80 system [22].

Results and discussion

[Rh(COD)Cl]$_2$ reacts with unsymmetric aliphatic diamines (LL'), such as N-(2-aminoethyl)piperidine (am-pip), N-(2-aminoethyl)pyrrolidine (am-pyrr) or 2-(aminomethyl)-1-ethylpyrrolidine (amme-etpyrr) in 1:1 molar ratio (Rh:LL'=2:1) to give yellow complexes of formula Rh$_2$Cl$_2$COD$_2$(LL'). Their analytical, IR and conductivity data are listed in Table 4. These complexes show two bands due to the ν(N–H) vibrations displaced towards lower frequencies as expected for coordinated primary amino groups and these displacements are similar to those observed for cation–anion compounds containing other diamines as ligands [7]. The bands due to ν(Rh–Cl) are also present. Surprisingly, these complexes show very low conductivity values in acetone suggesting

TABLE 4. Analytical results, IR and conductivity data for chlorine complexes

Complex	Analysis: found (calc.) (%)			ν(N–H) (cm^{-1})	$\Delta\nu$(N–H) (cm^{-1})	ν(Rh–Cl) (cm^{-1})	ν(C≡O) (cm^{-1})	[a]Λ_0 (ohm^{-1} cm^2 mol^{-1})
	C	H	N					
[Rh(COD)(am-pip)][Rh(COD)Cl$_2$]	43.30 (44.45)	6.22 (6.44)	4.41 (4.50)	3210(m), 3170(m)	130, 90	260(m)		22
[Rh(COD)(am-pyrr)][Rh(COD)Cl$_2$]	42.88 (43.49)	6.33 (6.26)	4.62 (4.61)	3220(s), 3170(s)	130, 100	275(m), 260(s)		37
[Rh(COD)(amme-etpyrr)][Rh(COD)Cl$_2$]	43.96 (44.45)	6.50 (6.44)	4.39 (4.50)	3175(s), 3095(s)	175, 175	260(m)		58
[Rh(CO)$_2$(am-pip)][Rh(CO)$_2$Cl$_2$]	25.09 (25.53)	3.35 (3.09)	5.46 (5.41)	3220(m), 3100(m)	120, 160	290(m), 270(m)	2080(s), 2000(s, broad)	85
[Rh(CO)$_2$(am-pyrr)][Rh(CO)$_2$Cl$_2$]	23.55 (23.86)	3.01 (2.78)	5.17 (5.56)	3230(m), 3200(m)	120, 70	310(m), 290(m)	2070(s), 2055(s) 2010(s), 1985(s)	68
[Rh(COD)(am-pip)Cl][b]	48.02 (48.07)	7.38 (7.47)	7.24 (7.47)	3290(m), 3210(m)	50, 50	250(w)		9
[Rh(COD)(am-pyrr)Cl]	46.41 (46.60)	7.22 (7.21)	7.54 (7.76)	3240(m), 3210(m)	110, 60	270(m)		18

[a]Measured in acetone solution c. 2.5×10^{-4} M.   [b]MW (calc.): 418 (375). Measured in benzene solution by cryoscopy.

strong association in solution, specially for the complex containing am-pip.

To confirm the ionic nature of the solid complexes, the crystal structure of the compound containing am-pip was resolved. Atomic parameters are listed in Table 5. The crystal consists of [Rh(C$_8$H$_{12}$)(C$_7$N$_2$H$_{16}$)]$^+$ mononuclear cations and [RhCl$_2$(C$_8$H$_{12}$)]$^-$ mononuclear anions. Figure 1 shows the geometry of the cation and the anion [23]. The bond lengths and angles, with their standard deviations are given in Table 6, while the system of numbering of the atoms in the molecule is shown in Fig. 1. The calculation of the best plane [24] through Rh1N1N2S1S2 (S1 and S2 are the centres of the C9=C10 and C13=C14 bonds, respectively) showed that the coordination polyhedron around Rh1 is square-planar with a deviation of 0.039(2) Å for the rhodium atom. The C=C double bonds of C$_8$H$_{12}$ are nearly perpendicular to the coordination polyhedron, they form angles of 8(2) and 3(1)(°) with the normal of the Rh1N1N2S1S2 plane, respectively. The Rh2 atom shows a deviation of 0.005(3) Å of the plane Rh2CL1CL2S3S4 and the C1=C2 and C5=C6 double bonds form angles of 4(2) and 3(2)°, respectively with the coordination polyhedron.

The low conductivities values in acetone solution prompted us to study the solution behaviour of these complexes. The corresponding ^{1}H NMR spectra, in chloroform solution, show the expected signals due to the coordinated LL', nearly identical to those of the free ligands. In the complexes containing LL' = am-pip or am-pyrr, at room temperature, all the olefinic protons appear equivalent and show one signal around 4.2 ppm (Table 7). On lowering the

TABLE 5. Atomic parameters for [Rh(C$_8$H$_{12}$)(C$_7$N$_2$H$_{16}$)][RhCl$_2$(C$_8$H$_{12}$)]

Atom	x/a	y/b	z/c	U_{eq}[a]
Rh1	0.1748(2)	0.1968(2)	0.1695(1)	28(1)
Rh2	0.6156(2)	−0.2656(2)	0.2941(1)	34(1)
Cl2	0.6515(9)	−0.1097(7)	0.1600(6)	48(3)
Cl1	0.6318(10)	−0.4196(8)	0.1796(6)	52(3)
N1	0.219(2)	0.3828(17)	0.1665(12)	25(6)
N2	0.400(2)	0.1556(19)	0.0655(17)	37(7)
C1	0.525(4)	−0.114(3)	0.398(2)	52(12)
C2	0.691(4)	−0.163(3)	0.383(3)	57(14)
C3	0.790(6)	−0.261(6)	0.457(4)	94(28)
C4	0.738(5)	−0.379(4)	0.489(2)	68(16)
C5	0.658(5)	−0.414(3)	0.408(2)	55(14)
C6	0.501(4)	−0.361(3)	0.413(2)	54(12)
C7	0.371(4)	−0.267(3)	0.486(3)	71(14)
C8	0.412(5)	−0.149(4)	0.492(4)	86(20)
C9	0.180(6)	−0.001(4)	0.198(4)	87(0)
C10	0.115(3)	0.047(2)	0.109(2)	37(9)
C11	−0.069(3)	0.092(3)	0.119(2)	46(11)
C12	−0.172(4)	0.180(4)	0.211(3)	71(16)
C13	−0.072(4)	0.255(2)	0.241(3)	52(12)
C14	0.026(3)	0.207(3)	0.313(2)	36(8)
C15	0.043(5)	0.085(4)	0.366(2)	64(14)
C16	0.099(4)	−0.033(4)	0.293(3)	64(14)
C17	0.403(3)	0.338(3)	0.144(3)	55(12)
C18	0.470(3)	0.260(3)	0.060(3)	47(12)
C19	0.147(4)	0.459(3)	0.075(3)	52(12)
C20	0.174(6)	0.592(4)	0.057(4)	74(20)
C21	0.109(5)	0.673(3)	0.155(3)	64(15)
C22	0.179(5)	0.601(3)	0.234(2)	52(14)
C23	0.138(4)	0.468(3)	0.251(2)	49(12)

[a]$U_{eq} = (\frac{1}{3}) \Sigma (U_{ij} a^*_i a^*_j a_i a_j \cos(a_i a_j)) \times 10^3$.

temperature, the olefinic protons show four of five signals, one of them, at 4.25 ppm, corresponds to the [Rh(COD)Cl$_2$]$^-$ anion. Therefore an interchange
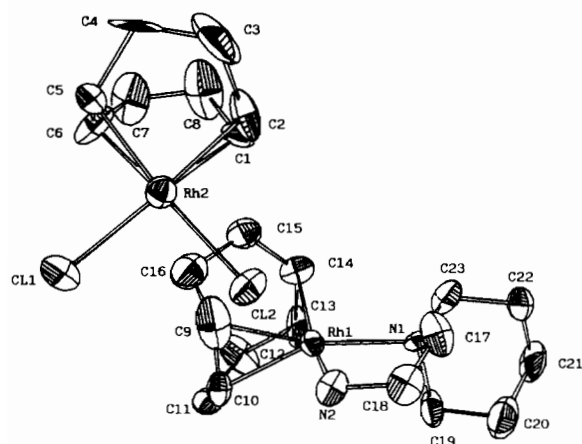
Fig. 1. View of the cation $[Rh(C_8H_{12})(C_7N_2H_{16})]^+$ and the anion $[RhCl_2(C_8H_{12})]^-$, depicting the atom-numbering scheme.

TABLE 6. Bond distances (Å) and angles (°) for $[Rh(C_8H_{12})(C_7N_2H_{16})][RhCl_2(C_8H_{12})]$ with e.s.d.s. in parentheses

Rh1–N1	2.17(2)	C3–C4	1.49(8)
Rh1–N2	2.13(2)	C4–C5	1.56(5)
Rh1–C9	2.12(5)	C5–C6	1.31(5)
Rh1–C10	2.17(3)	C6–C7	1.53(4)
Rh1–C13	2.11(3)	C7–C8	1.46(6)
Rh1–C14	2.10(2)	C9–C10	1.44(6)
Rh2–Cl2	2.389(8)	C9–C16	1.41(6)
Rh2–Cl1	2.376(9)	C10–C11	1.53(4)
Rh2–C1	2.13(3)	C11–C12	1.58(5)
Rh2–C2	2.10(4)	C12–C13	1.54(6)
Rh2–C5	2.10(3)	C13–C14	1.40(5)
Rh2–C6	2.08(3)	C14–C15	1.42(4)
N1–C17	1.52(3)	C15–C16	1.59(5)
N1–C19	1.56(4)	C17–C18	1.41(5)
N1–C23	1.46(3)	C19–C20	1.52(6)
N2–C18	1.45(3)	C20–C21	1.58(6)
C1–C2	1.38(5)	C21–C22	1.40(5)
C1–C8	1.55(5)	C22–C23	1.58(5)
C2–C3	1.57(6)		
C13–Rh1–C14	39(1)	C5–Rh2–C6	36(1)
C10–Rh1–C14	100(1)	C2–Rh2–C6	96(1)
C10–Rh1–C13	84(1)	C2–Rh2–C5	84(1)
C9–Rh1–C14	79(1)	C1–Rh2–C6	81(1)
C9–Rh1–C13	88(1)	C1–Rh2–C5	92(1)
C9–Rh1–C10	39(1)	C1–Rh2–C2	38(1)
N2–Rh1–C14	155.1(9)	Cl1–Rh2–C6	92(1)
N2–Rh1–C13	166(1)	Cl1–Rh2–C5	91(1)
N2–Rh1–C1	91(1)	Cl1–Rh2–C2	159(1)
N2–Rh1–C9	96(1)	Cl1–Rh2–C1	163(1)
N1–Rh1–C14	98(1)	Cl2–Rh2–C6	160(1)
N1–Rh1–C13	99(1)	Cl2–Rh2–C5	163(1)
N1–Rh1–C10	155(1)	Cl2–Rh2–C2	88(1)
N1–Rh1–C9	164(1)	Cl2–Rh2–C1	90(1)
N1–Rh1–N2	80(1)	Cl2–Rh2–Cl1	91.0(3)

process between anion and cation cyclooctadiene groups in solution seems likely, and this could occur via an associative process, similar to those suggested for complexes containing α-diimines [3, 4], such as

$[Rh(COD)(LL')][Rh(COD)Cl_2] \rightleftharpoons$
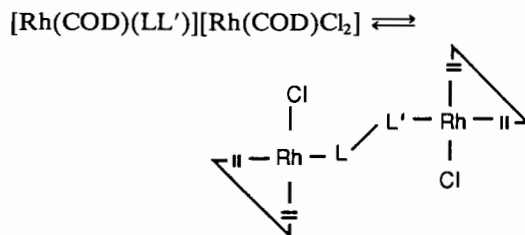
that could account for the low conductivity values in acetone solution. On the other hand, the complex containing amme-etpyrr, that shows the highest conductivity in acetone solution, shows a broad band at 4.22 ppm, due to the $[Rh(COD)Cl_2]^-$ anion, at room temperature.

When these reactions were performed under carbon monoxide, carbonylated ion-pair $[Rh(CO)_2(LL')][Rh(CO)_2Cl_2]$ complexes were obtained that behave as 1:1 electrolytes in acetone solution. Their IR spectra show the expected bands due to ν(N–H), ν(Rh–Cl) or ν(C≡O) (Table 4).

Reaction between $[Rh(COD)Cl]_2$ and am-pip or am-pyrr (Rh:LL' = 1:1) gives neutral $[Rh(COD)(LL')Cl]$ complexes (Table 4). Their IR spectra, show, along with the band due to ν(Rh–Cl), two bands due to the ν(N–H) vibrations displaced towards lower frequencies, that indicate coordination of the primary amino group. These displacements are markedly lower than those observed for pentacoordinated compounds containing other diamines as ligands [7] and suggest tetracoordination for the rhodium atom. The molecular weight measurement of Rh(COD)(am-pip)Cl in benzene solution indicates a monomeric nature in solution. ^{1}H NMR spectra at room temperature show only one signal due to olefinic protons but four signals at −50 °C (Table 7). This indicates interchange of olefinic protons that can occur via pentacoordinated species in those compounds with low conductivity values (i.e. LL' = am-pip). Complexes with higher conductivity values (i.e. LL' = am-pyrr) may interchange the olefinic protons via ionic intermediates.

Perchlorate complexes

The addition to dichloromethane solutions of $[Rh(COD)_2]ClO_4$ of a stoichiometric amount of LL' (Rh:LL' = 1:1) gives $[Rh(COD)(LL')]ClO_4$ derivatives whose analytical results, along with IR and conductivity data are collected in Table 8. These complexes are yellow and moderately air-stable solids. Their IR spectra show the ν(N–H) stretching frequencies to have decreased on coordination similarly

TABLE 7. NMR data

Complex	$\delta(=CH)$		$\delta^{31}P$	$^1J(^{103}Rh, ^{31}P)$
	$T = 16$ °C	$T = -50$ °C		
[Rh(COD)(am-pip)][Rh(COD)Cl₂]	4.17	4.52; 4.26ᵃ; 4.07; 3.77; 3.20(d, broad)		
[Rh(COD)(am-pyrr)][Rh(COD)Cl₂]	4.19	4.58; 4.25ᵃ; 4.14; 3.62		
[Rh(COD)(amme-etpyrr)][Rh(COD)Cl₂]	4.22ᵃ; 3.94	4.56; 4.20ᵃ; 4.47; 3.98; 3.81; 3.63		
[Rh(COD)(am-pip)Cl]	4.09	4.65; 4.40; 3.77; 3.20(d)		
[Rh(COD)(am-pyrr)Cl]	4.10	4.70; 4.49; 4.26; 3.57		
Et₄N[Rh(COD)Cl₂]	4.22ᵃ	4.20ᵃ		
[Rh(COD)(am-pip)]ClO₄	4.18; 3.83; 3.35; 3.10(br.)	4.12; 3.77; 3.31; 3.20(m)		
[Rh(COD)(am-pyrr)]ClO₄	4.22; 3.73; 3.38; 2.96	4.18; 3.67; 3.37; 3.1(m)		
[Rh(COD)(amme-etpyrr)]ClO₄	4.26(d); 3.90; 3.74; 3.38	4.32(d); 4.04; 3.81; 3.46		
[Rh(COD)(amet-mepyrr)]ClO₄	4.1-3.8(c.m.); 3.2(c.m.)	4.13; 3.8(m); 3.23		
[Rh(CO)(PPh₃)(am-pip)]ClO₄			45.47	152
[Rh(CO)(PPh₃)(am-pyrr)]ClO₄			45.40	150
[Rh(CO)(PPh₃)(amme-etpyrr)]ClO₄			44.23	152

ᵃ[Rh(COD)Cl₂]⁻ signal

TABLE 8. Analytical results, IR and conductivity data for perchlorate complexes

Complex	Analysis: found (calc.) (%)			ν(N–H) (cm⁻¹)	Δν(N–H) (cm⁻¹)	ν(C≡O) (cm⁻¹)	Conductivity data			
	C	H	N				ᵃΛ_0 (ohm⁻¹ cm² eq⁻¹)	ᵃA_{exp}	ᵇA_{theor} (1:1)	ᵇA_{theor} (2:1)
[Rh(COD)(am-pip)]ClO₄	40.51 (41.03)	6.18 (6.38)	6.42 (6.38)	3280(m), 3240(m)	60, 20		167	1524	616	1450
[Rh(COD)(am-pyrr)]ClO₄	38.63 (39.56)	6.29 (6.12)	6.42 (6.59)	3300(m), 3255(m)	50, 10		155	1141	596	1383
[Rh(COD)(amet-mepyrr)]ClO₄	40.85 (41.03)	6.29 (6.38)	6.43 (6.38)	3270(m), 3230(m)	80, 40		170	1468	622	1468
[Rh(COD)(amme-etpyrr)]ClO₄	40.26 (41.03)	6.85 (6.38)	6.47 (6.38)	3290(m), 3245(m)	60, 25		152	587	592	1370
[Rh(CO)(PPh₃)(am-pip)]ClO₄	49.88 (49.29)	4.96 (4.90)	4.34 (4.42)	3310(w), 3220(w)	30, 40	1980(s)	128	806	556	1250
[Rh(CO)(PPh₃)(am-pyrr)]ClO₄	49.31 (48.46)	4.78 (4.68)	4.33 (4.52)	3290(w), 3230(w)	60, 40	1980(s)	139	867	577	1302
[Rh(CO)(PPh₃)(amme-etpyrr)]ClO₄	49.66 (49.29)	4.87 (4.90)	4.42 (4.42)	3290(w), 3225(w)	60, 45	1965(m)	135	713	565	1283

ᵃMeasured in acetone solution. From Onsager's equation $\Lambda_e = \Lambda_0 - A\sqrt{c_e}$ plot.   ᵇCalculated according to ref. 27.

to other cationic rhodium(I) complexes containing aliphatic diamines [25]. The expected bands due to the coordinated olefin and the uncoordinated perchlorate anion (1100(s) and 620(s) cm⁻¹) are also present [26]. Although the X-ray structure of [Rh(COD)(am-pip)]ClO₄ (*vide infra*) indicates its monomeric structure in the solid state, measurements of the equivalent conductivities of the obtained complexes at different concentrations in acetone solutions gave plots of the Onsager equation $\Lambda_e = \Lambda_0 - A\sqrt{c}$ for which A values agree with those calculated for 2:1 electrolytes [27] for all cases except for et-pyrr. This suggests the formation of dinuclear cationic complexes with bridging LL' ligands in solution and has

also been observed for complexes with bis(pyrazolyl)methane ligands [2].

The ¹H NMR spectra in CDCl₃ solution show the resonances due to coordinated COD and the LL' ligands. The corresponding data for the olefinic protons are listed in Table 7. At room temperature, the complexes containing am-pip, am-pyrr or amme-etpyrr, show four groups of signals due to the four non-equivalent olefinic protons. The complex containing amet-mepyrr, where ligand chelation affords a six-membered ring, shows a complex pattern in the 4.1–3.2 region and could be related to ligand dissociation processes. At low temperatures the spectra remain unchanged.

In order to obtain further information about the nature of these complexes, the crystal structure of [Rh(COD)(am-pip)]ClO$_4$ was determined. Atomic parameters are listed in Table 9. The crystal consists of [Rh(C$_8$H$_{12}$)(C$_7$N$_2$H$_{16}$)]$^+$ mononuclear cations and perchlorate anions. A view of the cell down the c axis is depicted in Fig. 2. Figure 3 [23] shows the geometry of the cation and the perchlorate anion. The bond lengths and angles, with their standard deviations are given in Table 10, while the system

TABLE 9. Atomic parameters for [Rh(C$_8$H$_{12}$)-(C$_7$N$_2$H$_{16}$)]ClO$_4$

Atom	x/a	y/b	z/c	U_{eq}[a]
Rh	0.24515(3)	0.09428(3)	0.68342(6)	510(3)
Cl	0.85118(13)	0.12070(11)	0.3096(3)	748(12)
N1	0.1587(3)	0.1571(3)	0.6904(6)	531(29)
N2	0.1443(4)	0.0477(3)	0.5120(7)	683(36)
O1	0.8875(6)	0.1064(5)	0.4633(11)	1537(34)
O2	0.9022(6)	0.1629(5)	0.3017(10)	1439(32)
O3	0.7808(6)	0.1459(6)	0.2618(11)	1652(38)
O4	0.8500(4)	0.0540(4)	0.2545(8)	1003(21)
C1	0.3394(5)	0.1640(5)	0.8038(9)	673(43)
C2	0.3435(5)	0.1124(5)	0.8936(9)	781(46)
C3	0.4009(6)	0.0519(6)	0.9444(11)	1021(58)
C4	0.3747(8)	−0.0080(7)	0.8432(14)	1189(84)
C5	0.3126(5)	0.0089(5)	0.6936(10)	715(48)
C6	0.3172(4)	0.0594(4)	0.6124(9)	640(41)
C7	0.3853(6)	0.1058(6)	0.6594(12)	958(66)
C8	0.3871(6)	0.1676(5)	0.7376(12)	911(66)
C9	0.1781(5)	0.1789(5)	0.8364(9)	742(47)
C10	0.1175(6)	0.2266(5)	0.8350(10)	856(58)
C11	0.1039(6)	0.2882(5)	0.7427(12)	947(69)
C12	0.0830(6)	0.2671(5)	0.5972(11)	868(59)
C13	0.1450(5)	0.2197(4)	0.6041(9)	674(46)
C14	0.0884(5)	0.1108(4)	0.6247(10)	724(50)
C15	0.0729(5)	0.0806(4)	0.4865(10)	736(45)

[a]$U_{eq} = (\frac{1}{3})\Sigma(U_{ij}a^*_i a^*_j a_i a_j \cos(a_i a_j) \times 10^4$.
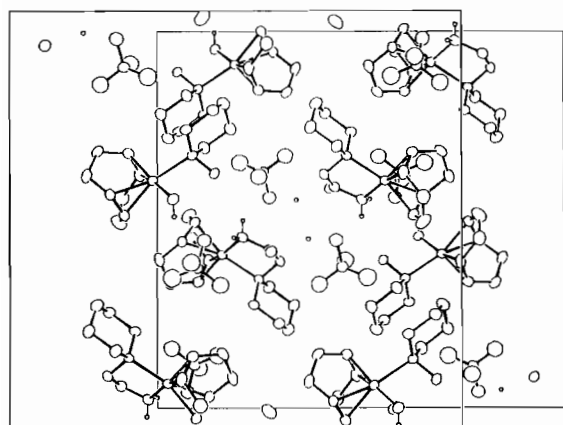
Fig. 2. View of [Rh(C$_8$H$_{12}$)(C$_7$N$_2$H$_{16}$)]ClO$_4$ cell down the c axis.
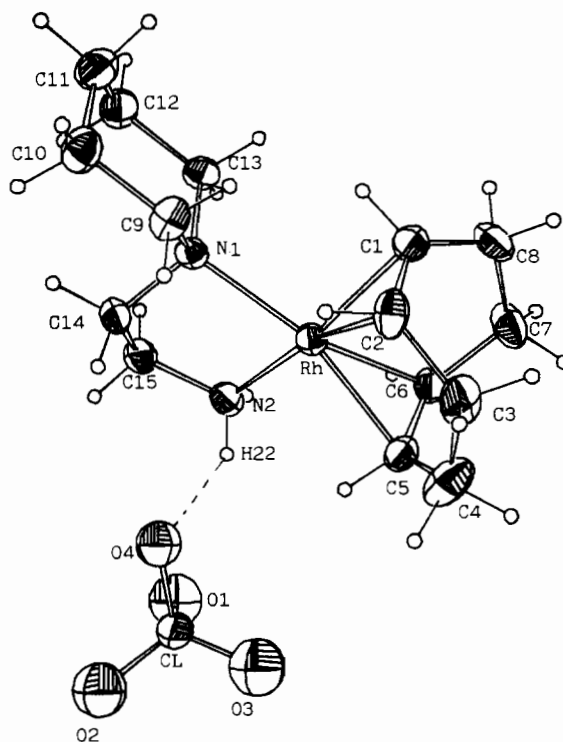
Fig. 3. View of [Rh(C$_8$H$_{12}$)(C$_7$N$_2$H$_{16}$)]ClO$_4$ showing the numbering schemes.

of numbering of the atoms in the molecule is shown in Fig. 3.

The calculation of the best plane [24] through RhN1N2S1S2 (S1 and S2 are the centres of the C1=C2 and C5=C6 bonds, respectively) showed that the coordination polyhedron is planar within the experimental error. The Rh–S1 and Rh–S2 distances 2.013(7) and 2.001(6) Å, respectively, are similar to other rhodium complexes [28–30]. The two coordinated C=C double-bond lengths are 1.37(1) and 1.37(1) Å. These values determined in this structure are comparable to the range of distances and angles observed for cyclooctadiene in other structures [30]. The carbon atoms participating in the bonding are virtually in a plane. The least-squares plane through the atoms C1C2C5C6 makes an angle of 90.9(3)° with the plane of the coordination polyhedron RhN1N2S1S2. The C=C double bonds are nearly perpendicular to the coordination polyhedron, they form angles of 6.4(5) and 5.7(4)° with the normal of the RhN1N2S1S2 plane, respectively.

The N2 of the C$_7$N$_2$H$_{16}$ ligand is hydrogen-bonded to the O4 of the perchlorate anion of the same unsymmetric unit and to the O1 of the nearest neighbour one. This fact could explain the longer bond distances of these two oxygen atoms (O1, O4) to the chlorine atom [30].

TABLE 10. Bond distances (Å) and angles (°) for [Rh(C$_8$H$_{12}$)(C$_7$N$_2$H$_{16}$)]ClO$_4$ with e.s.d.s. in parentheses

Rh–N1	2.176(7)	C4–C5	1.48(1)
Rh–N2	2.107(6)	C5–C6	1.37(1)
Rh–C1	2.132(8)	C6–C7	1.50(1)
Rh–C2	2.126(7)	C7–C8	1.47(2)
Rh–C5	2.12(1)	C9–C10	1.54(2)
Rh–C6	2.11(1)	C10–C11	1.50(2)
N1–C9	1.50(1)	C11–C12	1.49(2)
N1–C13	1.48(1)	C12–C13	1.53(2)
N1–C14	1.51(1)	C14–C15	1.50(2)
N2–C15	1.47(1)	Cl–O1	1.47(1)
C1–C2	1.38(1)	Cl–O2	1.36(1)
C1–C8	1.50(2)	Cl–O3	1.33(1)
C2–C3	1.53(2)	Cl–O4	1.427(8)
C3–C4	1.50(2)		

C5–Rh–C6	37.7(4)	Rh–C2–C1	71.3(5)
C2–Rh–C6	91.4(4)	C1–C2–C3	123.9(9)
C2–Rh–C5	82.5(4)	Rh–C2–C3	111.0(6)
C1–Rh–C6	82.2(4)	C2–C3–C4	115.2(9)
C1–Rh–C5	97.2(4)	C3–C4–C5	114(1)
C1–Rh–C2	37.9(3)	Rh–C5–C4	112.0(7)
N2–Rh–C6	93.7(3)	C4–C5–C6	125(1)
N2–Rh–C5	90.0(3)	Rh–C5–C6	71.0(6)
N2–Rh–C2	160.4(4)	Rh–C6–C5	71.3(6)
N2–Rh–C1	161.7(3)	C5–C6–C7	125.8(8)
N1–Rh–C6	158.3(3)	Rh–C6–C7	112.2(7)
N1–Rh–C5	162.0(3)	C6–C7–C8	115(1)
N1–Rh–C2	100.0(1)	C1–C8–C7	116(1)
N1–Rh–C1	95.4(3)	N1–C9–C10	114.3(7)
N1–Rh–N2	81.8(3)	C9–C10–C11	110(1)
Rh–N1–Cl6	103.0(5)	C10–C11–C12	111.0(9)
Rh–N1–Cl3	108.4(6)	C11–C12–C13	111.2(9)
Rh–N1–C9	116.5(5)	N1–Cl3–Cl2	113.1(8)
C13–N1–C14	112.5(6)	N1–C14–C15	110.5(8)
C9–N1–C14	108.7(7)	N2–C15–C14	109.2(8)
C9–N1–C13	108.0(6)	O3–Cl–O4	113.4(6)
Rh–N2–C15	111.8(6)	O2–Cl–O4	111.1(6)
Rh–C1–C8	109.2(6)	O2–Cl–O3	116.9(7)
Rh–C1–C2	70.8(6)	O1–Cl–O4	101.8(5)
C2–C1–C8	125.2(9)	O1–Cl–O3	107.1(8)
H21–N2–H22	109(9)	O1–Cl–O2	104.9(7)

Hydrogen bond geometry

X–H⋯Y	X⋯Y	X–H	H⋯Y	X–H⋯Y
N2–H21⋯O1	3.107(13)	0.867(87)	2.300(90)	154.5(6.5)
N2–H22⋯O4	3.010(13)	0.684(119)	2.326(118)	172.4(9.9)

The bubbling of carbon monoxide at room temperature through dichloromethane solutions of [Rh(COD)(LL')]ClO$_4$ complexes, brings about the formation of carbonylated species. Two CO bands characteristic of cis-dicarbonyl rhodium(I) complexes [25] are detected in the 2100–2000 cm^{-1} region of the spectra of the solutions. However attempts to isolate the solid dicarbonyl complexes have been unsuccessful because of the tendency of such complexes to form oils.

Treatment of dichloromethane solutions of the [Rh(COD)(LL')]ClO$_4$ complexes with carbon monoxide and subsequent addition of the stoichiometric amount of triphenylphosphine, leads to monocarbonylated complexes (eqn. (1)) that behave as 1:1 electrolytes in acetone solution and show the expected IR frequencies due to PPh$_3$ and LL' ligands and only one signal due to ν(C=O) below 2000 cm^{-1} (see Table 8)

$$[Rh(COD)(LL')]ClO_4 + PPh_3 \xrightarrow{CO}$$

$$[Rh(CO)(PPh_3)(LL')]ClO_4 + COD \quad (1)$$
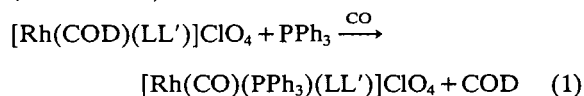
^{31}P NMR spectra of CDCl$_3$ solutions of the isolated complexes show only one doublet due to PPh$_3$ bonded to rhodium and the coupling constants and chemical shift values are collected in Table 7.

Supplementary material

Thermal parameters, hydrogen parameters and structural factors can be obtained from the authors on request.

Acknowledgement

References

1 P. Y. Leung and L. K. Peterson, J. Organomet. Chem., 219 (1981) 409.

2 L. A. Oro, M. Esteban, R. M. Claramunt, J. Elguero, C. Foces-Foces and F. H. Cano, J. Organomet. Chem., 276 (1984) 79.

3 H. Tom Dieck and J. Klaus, J. Organomet. Chem., 246 (1983) 301.

4 B. Crociani, F. di Bianca, M. Faci and T. Boschi, Inorg. Chim. Acta, 145 (1988) 253.

5 G. Clauti, G. Zassinovich and G. Mestroni, Inorg. Chim. Acta, 112 (1986) 103.

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

7 M. A. Garralda and L. Ibarlucea, J. Organomet. Chem., 311 (1986) 225.

8 G. Zassinovich, G. Mestroni and A. Camus, J. Organomet. Chem., 91 (1975) 379.

9 D. Brodzki and G. Pannetier, J. Organomet. Chem., 104 (1976) 241.

10 R. Halesha, G. K. N. Reddy, S. P. Sudhakar Rao and H. Manohar, J. Organomet. Chem., 252 (1983) 231.

11 R. Uson, L. A. Oro, M. Esteban, D. Carmona, R. M. Claramunt and J. Elguero, Polyhedron, 3 (1984) 213.

12 R. Uson, L. A. Oro, M. Esteban, A. M. Cuadro, P. Navarro and J. Elguero, *Transition Met. Chem.*, 7 (1982) 234.

13 L. A. Oro, M. T. Pinillos and C. Tejel, *J. Organomet. Chem.*, *280* (1985) 261.

14 F. Bonati, L. A. Oro, M. T. Pinillos, C. Tejel, M. C. Apreda, C. Foces-Foces and F. H. Cano, *J. Organomet. Chem.*, *369* (1989) 253.

15 E. Delgado-Laita and E. Sanchez-Muñoyerro, *Polyhedron, 3* (1984) 799.

16 J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, (1957) 4735.

17 R. Usón, L. A. Oro and F. Ibáñez, *Rev. Acad. Cienc. Zaragoza, 31* (1975) 169.

18 *International Tables for X-ray Crystallography,* Vol. IV, Kynoch Press, Birmingham, U.K., 1974, pp. 72–98.

19 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A, 39* (1983) 158.

20 M. Martinez-Ripoll and F. H. Cano, *PESOS program,* Instituto Rocasolano, CSIC, Serrano 119, 28006-Madrid, Spain, 1975.

21 P. Main, L. Lessinger, M. M. Germain and J. P. Declercq, *MULTAN*, a system of computer programs for the automatic solution of crystal structures from X-ray diffraction data, Universities of York, U.K., and Louvain, Belgium, 1980.

22 J. M. Stewart, *The XRAY80 System*, Computer Science Center, University of Maryland, College Park, MD, 1985.

23 C. K. Johnson, *ORTEP, Rep. ORNL-3794*, Oak Ridge National Laboratory, TN, 1965.

24 M. Nardelli, A. Musatti, P. Domiano and G. D. Andreetti, *Ric. Sci. Parte 2: Sez. A, 8* (1965) 807.

25 R. Usón, L. A. Oro, C. Claver and M. A. Garralda, *J. Organomet. Chem., 105* (1976) 365.

26 B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.,* (1961) 3091.

27 R. K. Bogess and D. A. Zatko, *J. Chem. Educ., 52* (1975) 649.

28 J. G. Leipoldt, S. S. Basson, G. J. Lamprecht, L. D. C. Bok and J. J. Schlebusch, *Inorg. Chim. Acta, 40* (1980) 43.

29 J. G. Leipoldt and E. C. Grobler, *Inorg. Chim. Acta, 72* (1983) 17.

30 R. G. Ball and N. C. Payne, *Inorg. Chem., 16* (1977) 1187.