Complexes of rhodium and iridium derived from 2,5-bis(pyrazol-1′-yl)-1,4-dihydroxybenzene

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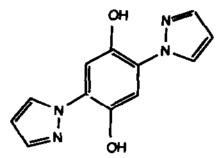
Abstract

The behaviour of the ligand 2,5-bis(pyrazol-1′-yl)-1,4-dihydroxybenzene (H_2LL) towards Rh^I, Ir^I, Rh^{III} and Ir^{III} complexes is reported. This compound with two OH groups might act as a neutral ligand (H_2LL), as a monoanionic ligand (HLL^-) or as a dianionic ligand (LL^{2-}). Complexes of all the three kinds have been isolated. In the case of H_2LL, the compounds are not organometallic complexes but clathrates. The crystal and molecular structure of the host–guest complex $[\{(\eta^5\text{-}C_5Me_5)RhCl\}_2(\mu\text{-}Cl)_2]$–$H_2LL$ (**6a**) is reported. Both the host and the guest have crystallographic C_i symmetry. No metal–H_2LL chemical bonds are present, and van der Waals interactions between host and guest molecules govern the crystal packing. An heterobimetallic derivative $[IrRh(\eta^5\text{-}C_5Me_5)Cl_2(LL)]$ (**7c**) has been isolated.

Key words: Rhodium; Iridium; Pyrazolyl; Clathrate; Crystal structure; Nuclear magnetic resonance

1. Introduction

The interest in polypyrazole ligands in coordination chemistry has been growing rapidly in recent years [1]. We report here the behaviour of 2,5-bis(pyrazol-1′-yl)-1,4-dihydroxybenzene (H_2LL) towards the complexes of rhodium(I) and iridium(I) $[\{Rh(\mu\text{-}Cl)(COD)\}_2]$ and $[\{Ir(\mu\text{-}Cl)(COD)\}_2]$ (COD = 1,5-cyclooctadiene) and the complexes of rhodium(III) and iridium(III) $[\{(\eta^5\text{-}C_5Me_5)RhCl\}_2(\mu\text{-}Cl)_2]$ and $[\{(\eta^5\text{-}C_5Me_5)IrCl\}_2(\mu\text{-}Cl)_2]$ (C_5Me_5 = pentamethylcyclopentadienyl). The ^1H and ^{13}C NMR properties of the different species are discussed and also the crystal and molecular structure of a (1 : 1) host–guest complex $[\{(\eta^5\text{-}C_5Me_5)RhCl\}_2(\mu\text{-}Cl)_2]$–$H_2LL$ (**6a**).



(H_2LL)

2. Experimental details

IR spectra were obtained with a Perkin–Elmer 1330 spectrometer. ^1H and ^{13}C NMR spectra were recorded at 298 K on a Bruker AC-200 spectrometer at 200.13 MHz for ^1H and at 50.32 MHz for ^{13}C. Chemical shifts are in ppm relative to tetramethylsilane, and coupling constants in hertz. The spectra were recorded with digital resolutions of 0.3 and 0.6 Hz per point respectively.

The ^{13}C solid state spectra were obtained on the same spectrometer working under conditions of cross-

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polarization (CP) and magic angle spinning (MAS), using a 7 mm Bruker DAB 7 probe head with rotation frequencies of about 3.5–4.5 kHz. The standard CP–MAS pulse sequence was applied with a 7 ms ^1H 90° pulse width, 3–5 ms contact pulses and 5 s repetition time, the spectral width being 20000 Hz. All chemical shifts are given with respect to the spectrometer reference frequency which was calibrated with the glycine signal at 176.1 ppm.

H_2LL was prepared as described previously [2] starting from pyrazole and *p*-benzoquinone.

2.1. Preparation of Rh^I and Ir^I complexes

2.1.1. $[Rh_2Cl_2(COD)_2(H_2LL)]$ (1a)

The addition of 41.9 mg (0.173 mmol) of H_2LL to a suspension of 84.6 mg (0.174 mmol) of $[\{Rh(\mu\text{-}Cl)(COD)\}_2]$ [3] in 5 cm^3 of dichloromethane gave a yellow solution. After stirring under dinitrogen for 1 h, the solution was vacuum concentrated to about 1 cm^3. The addition of 2 cm^3 of hexane completed the precipitation of a yellow solid, which was filtered off and air dried.

2.1.2. $[Rh_2Cl_2(CO)_4(H_2LL)]$ (2a)

The addition of 42.4 mg (0.175 mmol) of H_2LL to a suspension of 69.1 mg (0.178 mmol) of $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ [4] in 5 cm^3 of acetone gave a greenish-yellow solution. After stirring under dinitrogen for 2 h, the solution was vacuum concentrated to about 1 cm^3. The addition of 5 cm^3 of hexane completed the precipitation of a yellow solid, which was filtered off and air dried.

2.1.3. [Rh(COD)(HLL)] (3a)

To a solution of 117.5 mg (0.384 mmol) of [Rh(acac)(COD)] [5] in 10 cm^3 of acetone, 93.0 mg (0.384 mmol) of H_2LL were added. The resulting yellow suspension was stirred for 6 h and then vacuum concentrated to half-volume. The addition of 5 cm^3 of hexane completed the precipitation of a yellow solid which was filtered off and air dried.

2.1.4. $[Ir_2(COD)_2(LL)]$ (4b)

To a solution of 85.0 mg (0.215 mmol) of [Ir(acac)(COD)] [6] in 5 cm^3 of acetone, 26.8 mg (0.111 mmol) of H_2LL were added. After stirring for 5 min a yellow solid began to precipitate. The resulting suspension was stirred for 2 h under dinitrogen and the solid was then filtered off, washed with acetone and air dried.

2.1.5. $[Rh_2(CO)_4(LL)]$ (5a)

To a solution of 64.6 mg (0.250 mmol) of $[Rh(acac)(CO)_2]$ [7] in 5 cm^3 of dichloromethane, 31.1 mg (0.128 mmol) of H_2LL were added. Instantaneously a yellow solid precipitated. The suspension was stirred for 1 h under dinitrogen and the precipitation was completed by slow addition of hexane. The solid was filtered off, washed with hexane and air dried.

Alternatively, **5a** can be prepared by bubbling carbon monoxide (atmospheric pressure; room temperature) for 1 h through a suspension of the diolefin complex **3a** in dichloromethane.

2.2. Preparation of Rh^{III} and Ir^{III} complexes

2.2.1. $[Rh_2(\eta^5\text{-}C_5Me_5)_2Cl_4(H_2LL)]$ (6a)

To a red solution of 109.6 mg (0.177 mmol) of $[\{(\eta^5\text{-}C_5Me_5)RhCl\}_2(\mu\text{-}Cl)_2]$ [8] in 10 cm^3 of chloroform or acetone, 46.0 mg (0.190 mmol) of H_2LL were added. The colour of the solution remained unchanged. After stirring for 4 h, the solution was vacuum concentrated until 1 cm^3 and slow addition of hexane completed the precipitation of an orange solid, which was filtered off and air dried.

2.2.2. $[Ir_2(\eta^5\text{-}C_5Me_5)_2Cl_4(H_2LL)]$ (6b)

To a solution of 111.0 mg (0.139 mmol) of $[\{(\eta^5\text{-}C_5Me_5)IrCl\}_2(\mu\text{-}Cl)_2]$ [8] in 20 cm^3 of chloroform, 36.3 mg (0.150 mmol) of H_2LL were added. The resulting red solution was stirred under reflux for 3 h. After vacuum concentration to half-volume, slow addition of hexane completed precipitation of an orange solid, which was filtered off, washed with hexane and air dried.

2.2.3. $[Rh_2(\eta^5\text{-}C_5Me_5)_2Cl_2(LL)]$ (7a)

To a solution of 129.0 mg (0.150 mmol) of complex **6a** in 10 cm^3 of dichloromethane, 3 cm^3 of a methanolic solution of KOH (0.132 N) were added. The resulting dark-red solution was stirred for 4 h. After removal of KCl and extraction with 5 cm^3 twice of dichloromethane, the red solution was vacuum concentrated to half-volume and slow addition of hexane completed the precipitation of a red solid, which was filtered off, washed with hexane and air dried.

2.2.4. $[Ir_2(\eta^5\text{-}C_5Me_5)_2Cl_2(LL)]$ (7b)

The addition of 38.6 mg (0.159 mmol) of H_2LL to a solution of 150.4 mg (0.326 mmol) of $[Ir(\eta^5\text{-}C_5Me_5)Cl(acac)]$ [9] in 10 cm^3 of acetone gave a yellow precipitate after stirring for 5 h under dinitrogen. The solid was filtered off, washed with hexane and air dried.

2.2.5. $[IrRh(\eta^5\text{-}C_5Me_5)_2Cl_2(LL)]$ (7c)

To a suspension of the complex $[Ir(\eta^5\text{-}C_5Me_5)Cl(HLL)]$ (**8b**) (43.5 mg, 0.072 mmol) in 10 cm^3

of acetone, a solution of [Rh(η^5-C_5Me_5)Cl(acac)] [9] (28.0 mg, 0.075 mmol) in the same amount of solvent was added. The slow precipitation of an orange solid was observed. This was filtered off, washed with hexane and air dried.

*2.2.6. [Rh(η^5-C_5Me_5)Cl(HLL)] (**8a**)*

To a solution of 178.5 mg (0.480 mmol) of [Rh(η^5-C_5Me_5)Cl(acac)] in 10 cm^3 of dichloromethane, 116.3 mg (0.479 mmol) of H_2LL were added. The slow precipitation of an orange solid was observed. After stirring for 48 h, the solid was filtered off, washed with hexane and air dried.

*2.2.7. [Ir(η^5-C_5Me_5)Cl(HLL)] (**8b**)*

To a solution of 71.0 mg (0.154 mmol) of [Ir(η^5-C_5Me_5)Cl(acac)] in 5 cm^3 of acetone, 37.3 mg (0.154 mmol) of H_2LL were added. The resulting yellow suspension was stirred for 5 h, and then the solid was filtered off, washed with hexane and air dried.

The microanalytical data, yields and selected IR frequencies are gathered in Table 1.

2.3. X-Ray analysis

Table 2 summarizes the crystal data and selected parameters of the X-ray analysis. The structure was solved by the Patterson and Fourier methods. Both 2,5-bis(pyrazol-1'-yl)-1,4-dihydroxybenzene and [{(η^5-C_5Me_5)RhCl}$_2$(μ-Cl)$_2$] were located in two crystallographic symmetry centres at (0, 0, 0) and ($\frac{1}{2}$, $\frac{1}{2}$, 1) respectively. The hydrogen atom positions were obtained from difference synthesis. All non-hydrogen atoms were refined anisotropically while the hydrogen atoms of H_2LL were refined isotropically and those of C_5Me_5 were kept fixed during refinement. The highest thermal displacement parameters are those displayed by the methyl groups in a similar way to those shown by the complex [{(η^5-C_5Me_5)RhX}$_2$(μ-X)$_2$] (X = Cl or Br) [10, 11]. The final atomic coordinates are given in Table 3. The atomic scattering factors were taken from ref. 12. All calculations, including the numerical absorption correction, were carried out on a Vax 6410 computer using the XRAY80 system [13], and the PARST [14] and PESOS [15] programs.

3. Results and discussion

3.1. Syntheses

2,5-Bis(pyrazol-1'-yl)-1,4-dihydroxybenzene (H_2LL) was formed by the nucleophilic addition of pyrazole to 1,4-benzoquinone in dioxane together with 2-(pyrazol-1'-yl)-1,4-dihydroxybenzene and 2,3-bis(pyrazol-1'-yl)-1,4-dihydroxybenzene in the relative proportions indicated in Scheme 1. The separation of these derivatives yielded pure H_2LL [2].

The reaction of [{Rh(μ-Cl)(COD)}$_2$] or [{Rh(μ-Cl)(CO)$_2$}$_2$] with H_2LL in a 1:2 or 1:1 molar ratio gave yellow air-stable solid complexes [Rh_2Cl_2(COD)$_2$-(H_2LL)] (**1a**) and [Rh_2Cl_2(CO)$_4$(H_2LL)] (**2a**) (Scheme 2). When the same reaction was attempted with [{Ir(μ-Cl)(COD)}$_2$], no definite product could be identified. Using [Rh(acac)(COD)] (acac = acetyl acetonate) and H_2LL in 1:1, 1:2 or 2:1 molar ratios, only [Rh(COD)(HLL)] (**3a**) was isolated. However, 1 mol of H_2LL reacted with 2 mol of [Ir(acac)(COD)] to yield [Ir_2(COD)$_2$(LL)] (**4b**). The compound [Rh_2(CO)$_4$(LL)] (**5a**) was also prepared from H_2LL and [Rh(acac)(CO)$_2$] in dichloromethane at room temperature. Reaction of **3a** with carbon monoxide at room temperature and atmospheric pressure afforded **5a**.

TABLE 1. Microanalytical data, yields and selected IR frequencies

Compound	Molecular formulae (molecular weight)	Analyses, found (%) (calc. (%)) C	H	N	Yield (%)	IR (Nujol) (cm^{-1})
1a	$C_{28}H_{34}N_4O_2Cl_2Rh_2$ (735.3)	46.0 (45.74)	4.8 (4.66)	7.8 (7.62)	78	3100–2500 (ν(OH)), 250 (ν(RhCl))
2a	$C_{16}H_{10}N_4O_6Cl_2Rh_2$ (631.0)	31.1 (30.45)	1.5 (1.6)	9.2 (8.88)	71	3280 (ν(OH)), 2080, 2010 (ν(CO)), 310 (ν(RhCl))
3a	$C_{20}H_{21}N_4O_2Rh$ (452.3)	53.6 (53.11)	4.9 (4.68)	12.9 (12.39)	66	3000–2500 (ν(OH))
4b	$C_{28}H_{32}N_4O_2Ir_2$ (841.0)	40.6 (40.0)	4.0 (3.84)	6.7 (6.66)	72	—
5a	$C_{16}H_8N_4O_6Rh_2$ (558.1)	35.4 (34.43)	1.6 (1.44)	10.7 (10.04)	50	2060, 1990 (ν(CO))
6a	$C_{32}H_{40}N_4O_2Cl_4Rh_2$ (860.3)	44.5 (44.67)	4.9 (4.69)	6.6 (6.51)	79	3200–3000 (ν(OH)), 280, 245w (ν(RhCl))
6b	$C_{32}H_{40}N_4O_2Cl_4Ir_2$ (1038.9)	37.0 (37.00)	(3.85) (3.88)	5.3 (5.39)	84	3200–3000 (ν(OH)), 290, 245w (ν(IrCl))
7a	$C_{32}H_{38}N_4O_2Cl_2Rh_2$ (787.4) [a]	48.0 (48.81)	4.9 (4.86)	7.0 (7.12)	87	1700–1670, 265w (ν(RhCl))
7b	$C_{32}H_{38}N_4O_2Cl_2Ir_2$ (966.0)	40.9 (39.79)	4.1 (3.97)	6.3 (5.80)	69	1700–1670, 270w (ν(IrCl))
7c	$C_{32}H_{38}N_4O_2Cl_2RhIr$ (876.71)	42.6 (43.84)	4.5 (4.37)	6.4 (6.39)	47	1700–1670, 265w (ν(MCl))
8a	$C_{22}H_{24}N_4O_2ClRh$ (514.8)	50.0 (51.32)	4.9 (4.70)	10.7 (10.88)	76	3500 (ν(OH))
8b	$C_{22}H_{24}N_4O_2ClIr$ (604.1)	42.9 (43.74)	40 (4.00)	9.2 (9.28)	69	3500 (ν(OH)), 285w (ν(IrCl))

[a] Mass spectra, $M^{+\cdot}$, 786 (100%), 788 (64%), 790 (10%); w, weak.

When 2,5-bis(pyrazol-1′-yl)-1,4-dihydroxybenzene reacted with di-μ-chloro-dichlorobis(pentamethylcyclopentadienyl)dirhodium(III) and di-μ-chloro-dichlorobis(pentamethylcyclopentadienyl)diiridium(III), complexes of the general formulae $[M_2(\eta^5\text{-}C_5Me_5)_2Cl_4(H_2LL)]$ (**6a**) and (**6b**) were obtained (Scheme 3). Treatment of **6a** with 2 mol of potassium hydroxide afforded $[Rh_2(\eta^5\text{-}C_5Me_5)_2Cl_2(LL)]$ (**7a**). With $[M(\eta^5\text{-}C_5Me_5)Cl(acac)]$, H_2LL yielded complexes $[M(\eta^5\text{-}C_5Me_5)Cl(HLL)]$ (**8a**, **8b**) or $[Ir_2(\eta^5\text{-}C_5Me_5)_2Cl_2(LL)]$ (**7b**), depending on the reaction conditions.

The reaction of **8b** with $[Rh(\eta^5\text{-}C_5Me_5)Cl(acac)]$ yielded heterometallic derivatives such as $[RhIr(\eta^5\text{-}C_5Me_5)_2Cl_2(LL)]$ (**7c**).

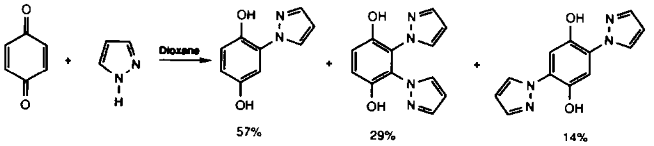
TABLE 2. Crystal data and refinement parameters at room temperature

Crystal data	
Chemical formula	$C_{20}H_{30}Cl_4Rh_2 \cdot C_{12}H_{10}N_4O_2$
M_r	860.3
Crystal system	
space group	Triclinic $P\bar{1}$
a (Å)	12.3313(10)
b (Å)	8.7128(6)
c (Å)	8.7797(6)
α (°)	104.800(6)
β (°)	104.873(5)
γ (°)	89.778(7)
Z	1
V (Å^3)	879.5(1)
D_c (Mg m^{-3})	1.624
Radiation	Cu Kα
Wavelength (Å)	1.5418
Absorption coefficient (mm^{-1})	109.18
Number of reflections for lattice parameters:	81
θ range for lattice parameters (°)	2–45
Temperature (K)	295
Crystal description	Prism
Crystal colour	Dark red
Crystal size (mm × mm × mm)	0.13 × 0.18 × 0.45
Data collection	
Diffractometer type	Four-circle Philips PW1100, bisecting geometry, graphite monochromator
Collection method	ω–2θ scans
Scan width	1.6°
Absorption correction type	analytical
Absorption correction T_{min}; T_{max}	0.088; 0.363
θ_{max} (°)	65
Number of standard reflections (interval)	2 (90 minimum)
Variation in standards	No variation
Number of independent reflections	2997
Number of observed reflections	2952
Criterion for observed	$I > 3\sigma(I)$
Refinement	
Treatment of hydrogen atoms	Isotropic
Refinement	Least squares on F_o; full matrix
Number of parameters refined	219[a]
Number of reflections used in refinement	2952
R	0.049
wR	0.057
Weighting scheme:	Empirical as to give no trends in $\langle \omega\Delta^2 F\rangle$ *vs.* $\langle \lvert F_o \rvert \rangle$ and $\langle (\sin\theta)/\lambda \rangle$
Maximum thermal factor (Å^2)	$U_{11}[C(18)] = 0.28(2)$
$(\Delta\rho)_{max}$ (electrons Å^{-3})	1.5 near Rh atom

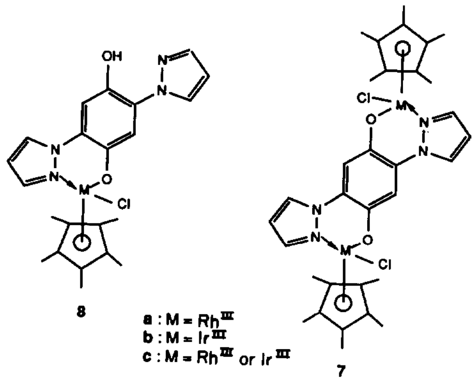
[a] See Section 2.

TABLE 3. Final atomic coordinates

Atom	x	y	z	Atom	x	y	z
Rh(1)	0.13922(3)	0.06529(4)	0.13693(4)	O(9)	0.5255(5)	0.3994(7)	0.6887(5)
Cl(2)	0.0528(1)	−0.0288(2)	−0.1586(1)	C(10)	0.2007(5)	0.2878(7)	0.1147(8)
Cl(3)	0.1711(1)	−0.2030(1)	0.1495(2)	C(11)	0.2904(5)	0.1832(8)	0.1426(12)
N(1)	0.3589(4)	0.6206(5)	0.7567(5)	C(12)	0.2990(6)	0.1574(9)	0.2970(14)
N(2)	0.3819(4)	0.6022(7)	0.6088(6)	C(13)	0.2130(8)	0.2340(9)	0.3603(8)
C(3)	0.3039(6)	0.6746(9)	0.5274(8)	C(14)	0.1524(5)	0.3174(6)	0.2452(7)
C(4)	0.2321(6)	0.7427(9)	0.6192(8)	C(15)	0.1641(11)	0.3501(10)	−0.0327(12)
C(5)	0.2680(5)	0.7062(8)	0.7649(7)	C(16)	0.3631(10)	0.1237(14)	0.0336(22)
C(6)	0.4304(4)	0.5589(6)	0.8780(6)	C(17)	0.3835(11)	0.0662(14)	0.3850(25)
C(7)	0.5792(5)	0.3955(7)	0.9618(6)	C(18)	0.1874(17)	0.2386(15)	0.5193(10)
C(8)	0.5109(5)	0.4514(7)	0.8407(6)	C(19)	0.0546(7)	0.4193(9)	0.2581(13)



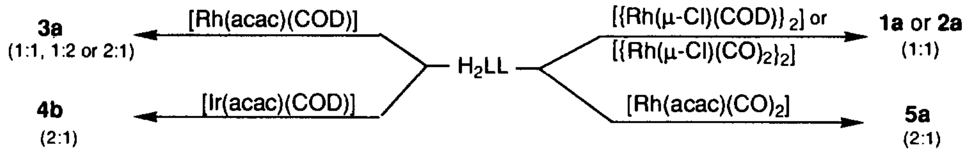
Scheme 1.



3.2. NMR analysis

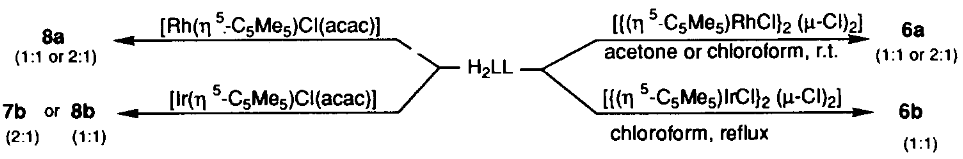
All foregoing complexes are insoluble in the usual NMR solvents such as deuteriochloroform or hexadeuteriodimethylsulphoxide (*cf.* **5a**, **7b** and **7c**) which made the determination of the NMR spectra very difficult.

However, we obtained some chemical shifts and coupling constants in solution and in the solid state, and these data are gathered in Tables 4 and 5. (Note that the numbering used in the NMR discussion is different from systematic IUPAC numbering.) To assign the NMR resonances, the criteria established in refs. 2 and 16 were used.



The molar ratios M/ H_2LL are indicated in brackets

Scheme 2.



The molar ratios M/ H_2LL are indicated in brackets

Scheme 3.

It is convenient to discuss the NMR data of the compounds in three groups: (i) derivatives of H_2LL (**1a**, **2a**, **6a** and **6b**); (ii) derivatives of HLL^- (**3a**, **8a** and **8b**) and (iii) derivatives of LL^{2-} (**4b**, **5a**, **7a**, **7b** and **7c**). **a** corresponds to Rh derivatives, **b** to Ir derivatives, and **c** to mixed Rh–Ir derivatives.

Compounds of series **a** behave in solution (Tables 4 and 5) as equimolar mixtures of H_2LL and the corresponding cyclooctadiene or cyclopentadienyl metal complexes (for instance **1a** [Rh(μ-Cl)(COD)$_2$], **6a** [{η^5-C_5Me_5)RhCl}$_2$]). In the solid state (Table 5), the resonances of **6a** are shifted to higher frequency compared with those of H_2LL (pyrazole carbon atoms, +3.9 ppm; hydroquinone carbon atoms, +1.9 ppm) which may be related to the conformation of H_2LL in clathrate **6a**, less planar than in the free H_2LL (see crystallographic discussion).

Compounds of series **c** are also symmetrical (the only exception, **7c**, was too insoluble in $CDCl_3$ to be studied). The effects of coordination on the ^{1}H NMR spectra are weak and dependent on the metal. The OH resonances disappear and ^3J(H(3)–H(4)) and ^4J(H(3)–H(5)) increase from 1.8 to 2.2 Hz and from less than 0.5 to 0.7 Hz. In the ^{13}C NMR spectra in solution (Table 5), the effects on the pyrazole carbon atoms are also very weak (only C(5) changes from 126.8 ppm in **1a** to 128.9 ppm in **4b**). The hydroquinone carbon resonances are much more shifted on complexation by 4–5 ppm to higher frequencies.

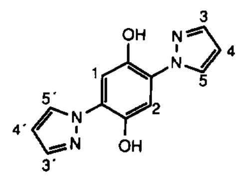
The most interesting series is the HLL^- derivatives (series (ii)), which behave as an interacting mixture of the other two series (for instance, in the ^{1}H NMR spectra, H(1)–H(2) appear at 7.14 ppm in H_2LL derivatives and at 6.99 ppm in HLL^- derivatives). The OH signals, which consistently appear at 11.15 ppm in series (i) are shifted to 10.7 ppm (**3a**) or to 10.9 ppm (**8a**, **8b**). Since this chemical shift is a measure of the hydrogen bond strength, it appears that the complexation involving one OH group of H_2LL weakens the hydrogen bonding of the other half. Compound **3a** behaves in the ^{13}C NMR spectrum (Table 5) as intermediate between **1a** and **4b**; the pyrazole carbon atoms have almost identical chemical shifts (less than 0.5 ppm change) whereas the hydroquinone carbon atoms C(1) and C(2) of **3a** appear closer (in **3a**, 110.4 ppm; 111.0 ppm; in **1a**, 107.6 ppm; in **4b**, 113.1 ppm).

In summary, the NMR results are consistent with the proposed structures.

TABLE 4. ^{1}H NMR chemical shifts δ and coupling constants J in $CDCl_3$ at room temperature

Compound	^{1}H NMR, δ (ppm)					
	H(3)–H(3)′	H(4)–H(4)′	H(5)–H(5)′	H(1) or H(2)	OH	Others
H_2LL [a]	7.74 (^3J = 1.8 Hz)	6.53	7.98 (^3J = 2.6 Hz)	7.14	11.14	–
1a	7.74 (^3J = 1.8 Hz)	6.53	7.98 (^3J = 2.5 Hz)	7.14	11.15	1.75; 2.50; 4.23
3a	7.74 (^3J = 1.8 Hz)	6.53	7.98 (^3J = 2.6 Hz)	6.97	10.74	
	7.70 (^3J = 2.1 Hz)	6.47	7.91 (^3J = 2.5 Hz)	6.88	–	4.35; 3.53; 2.50; 1.88
4b [b]	7.52 (^3J = 2.3 Hz)	6.55	8.09 (^3J = 2.7 Hz)	6.91	–	4.12; 3.53; 2.31; 1.70
6a [c]	7.74 (^3J = 1.8 Hz)	6.53	7.98 (^3J = 2.6 Hz)	7.14	11.14	1.62
7a	7.85 (^3J = 2.2 Hz, ^4J = 0.7 Hz)	6.62	7.94 (^3J = 2.5 Hz, ^4J = 0.7 Hz)	7.13	–	1.50
8a	7.74 (^3J = 1.9 Hz)	6.53	7.94 (^3J = 2.6 Hz)	7.00	10.87	
	7.84 (^3J = 2.3 Hz, ^4J = 0.7 Hz)	6.61	8.02 (^3J = 2.8 Hz, ^4J = 0.7 Hz)	7.13	–	1.52
8b	7.74 (^3J = 1.9 Hz)	6.52	7.99 (^3J = 2.7 Hz)	7.00	10.91	
	7.76 (^3J = 2.2 Hz, ^4J = 0.8 Hz)	6.59	7.59 (^3J = 2.9 Hz, ^4J = 0.8 Hz)	7.18	–	1.49

[a] The spectrum of compound **2a** shows only signals belonging to H_2LL.
[b] Compound **5a** is insoluble in $CDCl_3$.
[c] The spectrum of compound **6b** is identical with that of **6a**.



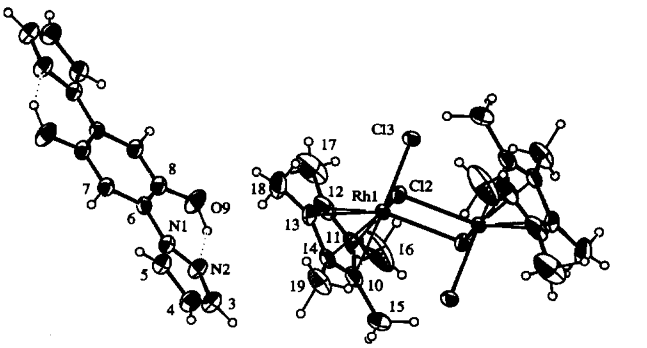


Fig. 1. An ORTEP [17] view of the molecular structure. Ellipsoids are drawn at a 30% probability level.

3.3. *Crystal structure of [{(η^5-C_5Me_5RhCl}$_2$ (μ-Cl)$_2$]-H_2LL (6a)*

The atom labelling and two views of the crystal packing are shown in Figs. 1 and 2, and Table 6 lists selected bond lengths and angles.

If C(10–14) (the centroid of the C_5Me_5 ring) is considered to occupy the central position of three *fac* octahedral sites, then the angles around the Rh atom are consistent with a slightly distorted octahedral coordination, the so-called "three-legged piano stool". The angles C(10–14)–Rh–Cl and Cl–Rh–Cl are in the ranges 124.7(1)–128.3(1)° and 84.2(1)–90.1(1)° (ideal values are 125.3° and 90.0°). The intermetallic Rh $\cdots$ Rh distance of 3.6412(5) Å excludes any metal–metal interaction. Each Rh atom is η^5 bonded to a pentamethylpentadienyl, the longer C–C bonds in the ring corresponding to the shorter Rh–C coordination distance (Table 3). No significant differences have been found between the Cl–Rh distances and those previously reported for [{(η^5-C_5Me_5)RhCl}$_2$(μ-Cl)$_2$] [10]. As far as the H_2LL molecule is concerned, the OH group is involved in an intramolecular hydrogen bond with the pyrazole ring; the phenyl ring is approximately −13.2(8)° out of the plane of the pyrazole ring. In free H_2LL this angle was −6.8(3)° [2]. So H_2LL shows a lesser degree of delocalization in the host–guest complex compared with the free H_2LL [2]. These differences in delocalization are apparent in the shortening of the N(2)–C(3) and C(8)–O(9) distances resulting from the greater twist about the N(1)–C(6) bond (1.306(9) Å, 1.354(7) Å and −13.2(8)° *vs.* 1.332(4) Å, 1.383(3) Å and −6.8(3)° respectively). The molecules in the crystal are only stabilized by van der Waals

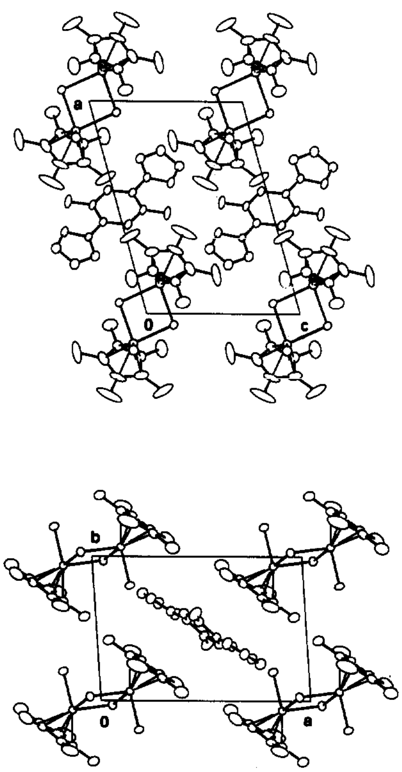
TABLE 5. ^{13}C nuclear magnetic resonance chemical shifts δ and coupling constants J

Compound	^{13}C NMR δ (ppm)							
	C(3)–C(3)′	C(4)–C(4)′	C(5)–C(5)′	C(1) or C(2)	C–O	C–Pz	Others	Conditions
H_2LL	139.1 (^1J = 188.5 Hz, ^3J = 8.2 Hz, ^2J = 6.0 Hz)	107.0 (^1J = 179.5 Hz, ^2J = 9.8 Hz, ^2J = 8.0 Hz)	126.8 (^1J = 189.1 Hz, ^2J = 9.3 Hz, ^3J = 4.6 Hz)	107.6 (^1J = 158.8 Hz, ^3J = 7.3 Hz)	142.1	123.3	–	$CDCl_3$
H_2LL	139.1	106.3	127.2	108.4	140.7	121.6	–	Solid CP–MAS
1a [a]	139.1	107.0	126.8	107.6	142.1	123.3	30.9; 78.7 [b]	$CDCl_3$
3a	138.9	106.6	127.0	110.4	142.1	123.3	84.1; 74.5	$CDCl_3$
	139.7	107.5	129.0	111.0	151.1	127.0	30.9; 29.9	
4b	140.2	107.7	128.9	113.1	146.9	126.8	68.7; 56.2 32.1; 30.5	$CDCl_3$
5a	140.0 144.5	108.3	130.7	114.0	147.9	126.8	192.0	Solid CP–MAS
6a	143.2	109.9	131.2	109.9	143.2	123.4	10.0; 95.1	Solid CP–MAS
7a	143.4	110.1	130.2	115.1	151.3	129.8	10.5; 95.1	Solid CP–MAS

[a] Compound **2a** is insoluble in $CDCl_3$.
[b] $^1J(^{103}Rh)$ = 14.0 Hz.

TABLE 6. Selected geometrical parameters (Å, °)

Rh(1)–Cl(2)	2.458(1)	Rh(1)–Cl(3)	2.395(1)
Rh(1)–Cl(2)′	2.451(1)	Rh(1)–C(10–14)	1.756(3)
Rh(1)–C(10)	2.157(7)	C(10)–C(11)	1.443(9)
Rh(1)–C(11)	2.115(8)	C(11)–C(12)	1.408(16)
Rh(1)–C(12)	2.125(7)	C(12)–C(13)	1.409(13)
Rh(1)–C(13)	2.111(6)	C(13)–C(14)	1.446(10)
Rh(1)–C(14)	2.147(5)	C(10)–C(14)	1.390(10)
N(1)–N(2)	1.370(7)	N(1)–C(6)	1.417(7)
N(2)–C(3)	1.306(9)	C(6)–C(7)′	1.397(8)
C(3)–C(4)	1.380(11)	C(6)–C(8)	1.405(8)
C(4)–C(5)	1.360(10)	C(8)–C(7)	1.371(8)
C(5)–N(1)	1.350(8)	C(8)–O(9)	1.354(7)
Cl(2)–Rh(1)–Cl(3)	90.1(1)	N(2)–N(1)–C(5)	110.8(5)
Cl(2)–Rh(1)–C(10–14)	124.7(1)	N(1)–N(2)–C(3)	105.1(5)
Cl(2)–Rh(1)–Cl(2)′	84.2(1)	N(2)–C(3)–C(4)	111.6(6)
Cl(3)–Rh(1)–C(10–14)	128.3(1)	C(3)–C(4)–C(5)	106.1(6)
Cl(3)–Rh(1)–Cl(2)′	89.8(1)	C(4)–C(5)–N(1)	106.4(6)
C(10–14)–Rh(1)–Cl(2)′	126.6(1)	C(6)–C(8)–O(9)	123.0(5)
N(2)–N(1)–C(6)	119.8(4)	N(1)–C(6)–C(7)′	119.7(5)
C(5)–N(1)–C(6)	129.3(5)	N(1)–C(6)–C(8)	121.4(4)
N(2)–N(1)–C(6)–C(8)	−13.2(8)	C(6)–C(8)–O(9)–H(9)	12(6)
Intramolecular contact			
O(9)–H(9)···N(2)	0.97(9)	2.593(8) 1.81(9)	135(8)



(a)

(b)

Fig. 2. Crystal packing (a) along the *b* axis and (b) along the *c* axis. The hydrogen atoms have been omitted for clarity.

forces, a phenomenon which has been described as a lattice clathrate [18]. Thus **6a** is a new example of a molecular solid [18], a family of not very common but interesting structures. A search in the CSD [19] reveals compound bis{dichloro-[(η^5-pentamethylcyclopentadienyl)(neopentylamino(*p*-tolyl)methylenerhodium-(III)]}bis(μ^2-chloro)chloro(η^5-pentamethylcyclopentadienyl)rhodium [20] as the only other co-crystallization derivative containing $[\{(\eta^5\text{-}C_5Me_5)RhCl\}_2\text{-}(\mu\text{-}Cl)_2]$.

The only noticeable difference in IR spectra (Nujol) between **6a** and an equimolar physical mixture of its two components is found in the Rh–Cl region (280–310 cm^{-1}).

4. Conclusion

H_2LL is not a good ligand, most probably because of strong intramolecular hydrogen bonding between the phenolic groups and the lone electron pairs of the ring nitrogen atoms [2a]. However, its monoanion HLL^- and its dianion LL^{2-} show versatile coordination properties towards rhodium and iridium in oxidation states I and III. The absence of lone pairs in H_2LL makes this compound, like tetraarylporphyns [18], suitable for the preparation of solid solutions.

5. Supplementary material available

Tables giving additional crystallographic anisotropic thermal parameters, hydrogen parameters and structure factors for the lattice clathrate **6a** (9 pages) can be obtained from the authors or, other than structure factors, from the Cambridge Crystallographic Data Centre.

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