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N-Substituted imidazole derivatives of rhodium(I) and iridium(I) with and without metal–metal interaction. Crystal structure of *cis*-$(CO)_2RhCl$(*N*-methylimidazole)

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Abstract

Bridge splitting reactions with *N*-methylimidazole (Rim, R = Me) or *N*-benzylimidazole (Rim, $R = PhCH_2$) gave *cis*-L_2MCl(Rim) complexes (M = Rh, Ir, $L_2 = (CO)_2$, 1,5-cyclooctadiene; M = Rh, L_2 = (*p*-tosylmethyl isocyanide)$_2$ or (CO)$(PPh)_3$). M · · · M interactions in the dicarbonyl complexes are revealed by an X-ray diffraction study of *cis*-$(CO)_2RhCl$(*N*-methylimidazole). The molecular units pack in the crystal as infinite chains along the *c*-axis with intermetallic distances Rh · · · Rh of 3.2833(5) Å.

Introduction

In pursuance of our interest in both the chemistry of diazoles [1] and the metal–metal interactions, especially in rhodium or iridium derivatives [2–4], it was decided to investigate some derivatives of imidazoles (Him). These were chosen as ligands because they are flat compounds, with basic character [5], and are likely to allow metal–metal interactions of the type observed in dicarbonyl(β-diketonato)-metal(I), where the metal is rhodium or iridium [3,6]. In these related square-planar derivatives containing a planar bidentate ligand with suitable bite and a $(OC)_2M$ moiety, planarity of the coordination environment and of the resulting molecules is generally assured, so that the possibility of stacking up molecules of the complex

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through metal–metal interactions depends upon the geometrical properties of the chelating ligand. On the other hand replacement of a chelating anion by a halide plus a neutral donor ligand, such as a chloride plus an amine or nitrile, are expected to give compounds in which the plane of the neutral ligand lies normal to the coordination plane, so minimizing intramolecular steric repulsion: this is often found in square-planar pyrazole or imidazole adducts, such as (cod)RhCl(pyrazole) [7]. However, the closely related *cis*-$(CO)_2RhCl$(pyrazole) complex [7] shows a weak interaction (Rh ··· Rh 3.4522(4) Å [7]), but no interaction was reported in the case of *cis*-$(CO)_2RhCl(L)$ where L is either allopurinol-*N*9 or 9-methylallopurinol-*N*8 [8], although these two are planar ligands. It thus seemed of interest to prepare and investigate some rhodium(I) and iridium(I) complexes containing *N*-substituted derivatives of imidazoles in order to provide additional data. With these derivatives, *N*-methyl- and *N*-benzyl-imidazole (Rim, R = CH_3, $PhCH_2$), any effect of hydrogen bonding on the possible metal–metal interaction is removed, and the resulting information may be of more general interest than that collected for *cis*-$(CO)_2RhCl$(amine), where the amine may include ammonia [9], aniline [9], pyrazole [7], or nucleobases [8].

Results and discussion

(a) Preparation and reactivity. The bridge-splitting reaction shown below afforded the compounds I–IV, from which the corresponding carbonyls, V–VIII, were then obtained in nearly quantitative yields:

$$\tfrac{1}{2}[(cod)M(\mu\text{-}Cl)]_2 + Rim \longrightarrow (cod)MCl(Rim)$$

	I	II	III	IV
M	Rh	Rh	Ir	Ir
R	Me	$PhCH_2$	Me	$PhCH_2$

$$(cod)MCl(Rim) + 2\,CO \longrightarrow cis\text{-}(CO)_2MCl(Rim) + cod$$

	V	VI	VII	VIII
M	Rh	Rh	Ir	Ir
R	Me	$PhCH_2$	Me	$PhCH_2$

Compound VI was also obtained from *N*-benzylimidazolium chloride and dimeric dicarbonylchlororhodium(I), instead of the expected $[RimH]^+[(CO)_2RhCl_2]^-$, which would be comparable, with for example the corresponding (stable) tetrathiafulvalenium salt [10]. All the compounds except VII and VIII, are stable in solution, and the *M*-imidazole bond seems to be reasonably stable, because from some of them additional imidazole derivatives could be obtained. By replacing the chloride by an azide ligand, or by displacement of a carbonyl ligand by a triphenylphosphine or of 1,5-cyclooctadiene by two isocyanides the complexes *cis*-$(CO)_2RhN_3(PhCH_2im)$ (IX), $(CO)(PPh_3)RhCl(Mem)$ (X) or *cis*-$(R'NC)_2RhCl(Meim)$ (XI), respectively, were formed. Complex $[(R'NC)_4Rh]Cl$ (XII) was also prepared for purpose of comparison (R′ = *p*-tosylmethyl).

The compounds were identified by elemental analyses and molecular weight

Table 1

Analytical data [a] for the compounds

Compound	Analyses (%)			Yield (%)	Colour [b]	M
	C	H	N			
(cod)RhCl(Meim)	43.9	5.7	8.4	92	yellow	313
(I)	(43.8)	(5.5)	(8.5)			(329)
(cod)RhCl($PhCH_2im$)	53.4	5.7	6.6	91	yellow	392
(II)	(53.4)	(5.5)	(6.9)			(405)
(cod)IrCl(Meim)	35.0	4.4	6.7	95	yellow	539
(III)	(34.5)	(4.3)	(6.7)			(418)
(cod)Ir(Cl($PhCH_2im$)	43.6	4.7	5.7	92	yellow	537
(IV)	(43.8)	(4.5)	(5.7)			(494)
cis-$(CO)_2$RhCl(Meim)	25.9	2.2	10.2	84	green-golden	250
(V)	(26.1)	(2.2)	(10.1)			(276)
cis-$(CO)_2$RhCl($PhCH_2im$)	40.5	3.0	7.9	96	red-green	320
(VI)	(40.9)	(2.9)	(7.9)			(353)
cis-$(CO)_2$IrCl(Meim)	19.9	1.3	7.8	87	dark-blue-purple	–
(VII)	(19.7)	(1.6)	(7.7)			
cis-$(CO)_2$IrCl($PhCH_2im$)	32.8	2.4	6.2	81	dark-blue	–
(VIII)	(32.6)	(2.3)	(6.3)			
cis-$(CO)_2RhN_3(PhCH_2im)$	39.4	2.9	19.6	80	red-green	–
(IX)	(40.1)	(2.8)	(19.5)			
(CO)(PPh_3)RhCl(Meim)	53.8	4.3	5.6	82	yellow	500
(X)	(54.1)	(4.1)	(5.5)			(511)
cis-$(R'NC)_2$RhCl(Meim)	43.6	4.2	8.7	87	orange	590
(XI)	(43.2)	(3.9)	(9.2)			(611)
$[(R'NC)_4Rh]Cl$	46.7	4.1	6.1	98	dark-blue	–
(XII)	(47.0)	(3.9)	(6.1)			

[a] Required values are given in parentheses. [b] The compounds V–IX give yellow solutions.

Table 2

IR spectra of the compounds

Compound	Region around 2000 cm^{-1}		ν(C–H) [b]	Ring breathing vibration [b]	ν(M–Cl) [b]
	solution [a]	solid [b]			
I			3110	1515, 1540	370
II			3120	1495, 1515	360
				1535	
III			3105	1540, 1515	285
IV			3110	1495, 1500	290
				1515, 1535	
V	2005	1960, 1970, 1985, 1995	3130	1520, 1545	295
	2085	2000, 2040, 2060, 2075			
VI	2004	1985, 1996, 2003, 2052	3115	1495, 1505	310
	2082	2075		1525, 1530	
VII	1997	1950, 1965, 1975-2000	3120	1525, 1550	300
	2080	2030, 2050, 2075			
VIII	1986	1939, 1949-1998, 2032	3115	1495, 1530	320
	2070	2066		1540	
IX	2005	2000-2120	3160	1530, 1545	–
	2080				
	2040 [c]				
X	1970	1970	3135	1510, 1535	355

[a] Carbonyl stretching vibrations in CH_2Cl_2 solutions unless otherwise stated. [b] In nujol mulls. [c] Azide.

Table 3

^1H NMR chemical shifts [a] (ppm) [b] and coupling constants [c] for the compounds in $CDCl_3$, 293 K

Compound	Imidazole		CH_3 or CH_2	Aryl [d]		Others	
	H(2)	H(4),H(5)		$H^{o,p}$	H^m		
I	8.14	6.80, 6.73	3.65			C–H 5.21(m), 4.00(m)	CH_2 2.44(d,8.1), 1.79(d,8.1)
II	8.30	6.78, 6.73	5.04	7.45	7.13	C–H 4.60(m), 4.00(m)	CH_2 2.44(d,8.3), 1.79(d,8.3)
III	8.35	7.02, 6.90	3.70			C–H 4.30(m), 3.64(m)	CH_2 2.28(m), 1.64(m)
IV	8.51	7.02, 6.87	5.08	7.36	7.16	C–H 4.20(m), 3.70(m)	CH_2 2.26(br), 1.54(br)
V	8.08	7.17, 6.94	3.76				
VI	8.21	6.92, 7.21	5.13	7.38	7.19		
VII	8.21	7.32, 6.98	3.79				
VIII	8.32	7.33, 6.96	5.18	7.31			
X [e]	8.23	7.33, 6.88	3.69	7.75	7.38		
XI	8.13	6.84(d, 1.7)	3.70	A_2B_2 7.91, 7.4 $J(AB)_{ortho}$ 7.8		CH_3 2.46	CH_2 4.72 4.57

[a] Position of the center of the doublet (d), multiplet (m), if no indication is given the signal is singlet. [b] The chemical shifts are relative to Me_4Si. [c] The linewidth in Hz is given in parentheses. [d] All signals are broad. [e] Isomer more abundant.

determinations (Table 1). The infrared spectra show the expected CO and M–Cl stretching vibrations; in addition, as shown in Table 2, the presence of an imidazole ligand is confirmed by the appearance of the expected medium bands due to the

Table 4

$^{13}C\{^1H\}$ chemical shifts [a] (ppm) [b] and linewidth [c] for the compounds in $CDCl_3$, 293 K

Compound	Imidazole		CH_3 or CH_2	Aromatic ring	cod or $(CO)_2$
	C(2)	C(4),C(5)			
I	140.2	126.7, 120.4	34.3		82.5, 75.5 30.8
II	139.9	126.8, 119.4	51.7	134.0, 129.2, 128.7, 127.7	82.5, 75.5 30.8, 30.7
III	140.1	126.5, 120.7	34.6		67.1, 58.1 31.9, 31.1
IV	139.8	126.6, 119.9	52.1	134.0, 129.3, 128.9, 127.7	67.3, 58.2 31.9, 31.1
V	139.9	130.9, 121.1	34.7		183.8 (d, 66.2) 181.1 (d, 73.5)
VI	139.4	131.2, 120.0	52.2	133.9, 129.3, 129.1, 127.8	183.6 (d, 65.7) 181.1 (d, 74.1)
VII	139.9	131.2, 121.5	34.9		170.9 167.7
VIII	139.4	131.4, 120.4	52.4	134.0, 129.4, 129.3, 127.9	170.8 167.8
IX	139.8	131.1, 121.0	34.5		not observed

[a] Position of the singlet or center of the doublet (d). [b] The chemical shifts are relative to Me_4Si. [c] The linewidth in Hz is given in parentheses.

C–H stretching mode at ca. 3100 and the ring breathing vibration in the 1500–1550 cm^{-1} region. Supporting evidence comes from the NMR spectra (^1H in Table 3, $^{13}C\{^1H\}$ in Table 4 and $^{31}P\{^1H\}$ values in the Experimental). In the $^{13}C\{^1H\}$ spectra the two non-equivalent atoms of the carbonyl groups are split into doublets by coupling with ^{103}Rh. In the $^{13}C\{^1H\}$ spectra it is noteworthy that, relative to that for the corresponding ligand [11], the signal due to C(2) of the imidazole ring is always shifted by at least 2 ppm towards lower field, while the signal from the other carbon nucleus linked to the donor nitrogen, i.e. C(4), is shifted upfield in the carbonyl derivatives V–VIII, and downfield in the diolefin complexes I–IV.

Of the imidazole adducts described here, the diolefin complexes I–IV and $(CO)(PPh_3)RhCl(Meim)$ (X) are yellow in the solid state and in solution, while the dicarbonyl compounds V–IX are yellow in solution but have a different colour in the solid state giving red, green, or blue needles. As this change of colour is paralleled by a marked change in the pattern of carbonyl stretching frequencies, as shown in Table 2, metal–metal interaction seemed likely to be present in all cases, and was shown to be present by the X-ray diffraction study of V (see below). Such an interaction is possible because of the flatness of the ligands surrounding the coordination center; indeed, replacement of at least one carbonyl by a non planar ligand, such as triphenylphosphine or a diolefin, removes the possibility of the interaction. Coordination of a planar ligand, such as *N*-alkylimidazole, is a necessary condition for such interaction, but it is not in itself sufficient, as shown by the fact that *cis*-$(R'NC)_2RhCl(Meim)$ (XI) is orange both in the solid state and in solution whereas $[(R'NC)_4Rh]Cl$ (XII) is blue in the solid state and its colour in solution depends on the solvent used.

(b) Description of structure of V. Selected geometrical parameters for the complex are listed in Table 5. The rhodium atom is in a square-planar environment, the deviation of the metal atom from the coordination plane being 0.0036(3) Å. The methylimidazole ring is only 13.6(2)° away from coincidence with that coordination plane, in agreement with earlier observations [7].

Table 5

Selected geometrical parameters

(a) Bond distances (Å) and angles (°)			
Rh–N(1)	2.072(4)	N(1)–C(2)	1.327(7)
Rh–Cl	2.372(1)	C(2)–N(3)	1.338(7)
Rh–C(7)	1.836(6)	N(3)–C(4)	1.357(8)
Rh–C(8)	1.825(6)	C(4)–C(5)	1.343(9)
C(7)–O(7)	1.141(7)	C(5)–N(1)	1.381(9)
C(8)–O(8)	1.173(8)	C(6)–N(3)	1.466(9)
Cl–Rh–N(1)	89.9(1)	N(1)–Rh–C(8)	178.3(2)
N(1)–Rh–C(7)	92.0(2)	Rh–C(7)–O(7)	178.5(5)
C(7)–Rh–C(8)	89.4(2)	Rh–C(8)–O(8)	177.5(5)
C(8)–Rh–Cl	88.7(2)	Cl–Rh–C(7)	177.7(2)
(b) Least-square planes (deviations (Å) in brackets and dihedral angle (°))			
i: C(7),C(8),Cl,N(1)		[Rh: −0.0036(3)	
ii: N(1),C(2),N(3),C(4),C(5)		[C(6): −0.03(1)]	
dihedral angle i, ii 13.6(2)			

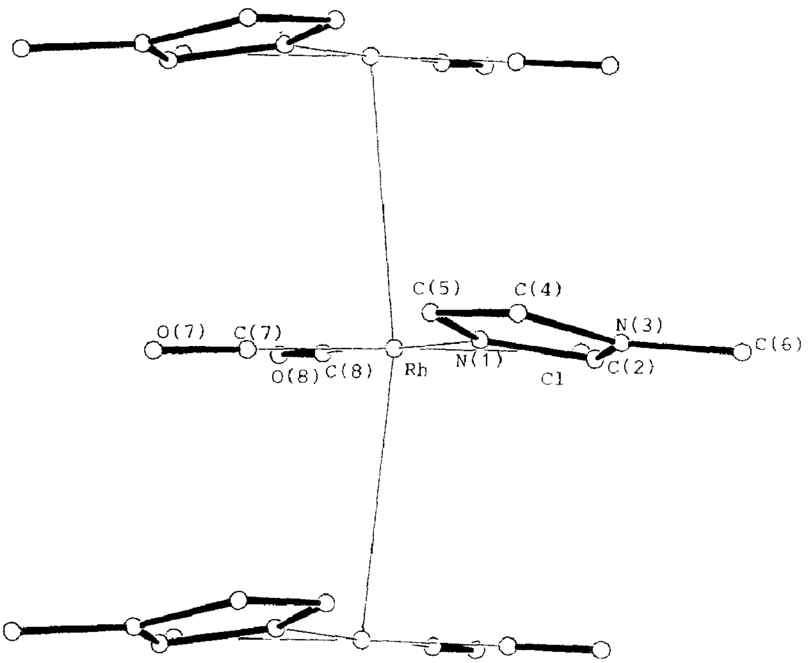


Fig. 1. Stacking arrangement along the *c*-axis of the title complex together with numbering scheme.

The molecular packing in the crystal is shown in Fig. 1 [12]. The units are stacked along the *c*-axis to form slightly zig-zag chains (169.21(2)° of metal atoms, with Rh ··· Rh $(x, \frac{1}{2}-y, z \pm \frac{1}{2})$ 3.2833(5) Å). This arrangement is similar to the that in a triazolaterhodium complex [2], with Rh ··· Rh 3.425(4) Å and Rh ··· Rh ··· Rh 177.6(3)°, and in the complex *cis*-$(CO)_2RhCl$(pyrazole) [7], with an intermetallic distance of Rh ··· Rh 3.4522(4) Å and an angle equal to 171.4(4)°.

Chains are linked through Cl ··· H–C contacts [13] of the type Cl ··· C(4)(*i*) 3.6887(7), Cl ··· H(4)(*i*) 2.83(8) Å, and C(4)(*i*)–H(4)(*i*) ··· Cl 158(6)°, $(i = -\frac{1}{2} + x, y, \frac{1}{2} - z)$. Similar observations were made in reference 7, with a Cl ··· N(2)(*ii*) distance of 3.296 Å and Cl ··· H(1)(*ii*) 2.748 Å, N(2)(*ii*)–H(1)(*ii*) ··· Cl 133°, $(ii = 2 - x, -y, 2 - z)$.

A remarkable feature of the structure described here is that the disposition, the square-planar coordinated species in the stacks adopt an approximately staggered conformation (about 55°), whereas with *cis*-$(CO)_2RhCl$(pyrazole) [7] the square-planar species are in a somehow eclipsed disposition (see Fig. 2 and 3) [14].

The strength of the M ··· M interaction in V, like that in several dicarbonylrhodium(I) or -iridium(I) *β*-diketonates, *cis*-$(CO)_2M(RCO)_2CH$, is shown by the value of the M ··· M distance, 3.27 Å for M = Rh and R = Me [3b], 3.20 Å for M = Ir and R = Me [6], and 3.28 Å in the present case. In addition, it should be noted that the interaction between the *β*-diketonates does not require any special rearrangement of the ligand around the metal. In contrast, in the case of V the Meim ligand lies parallel to the coordination plane, whereas there is a general tendency of planar heterocyclic ligands to arrange themselves normally to the coordination plane, in order to reduce intramolecular steric repulsion, e.g. in the cases of (cod)RhCl(pyrazole) and $[(Ph_2PCH_2)_2Pt(pyrazole)_2]$ [15]. Therefore, the

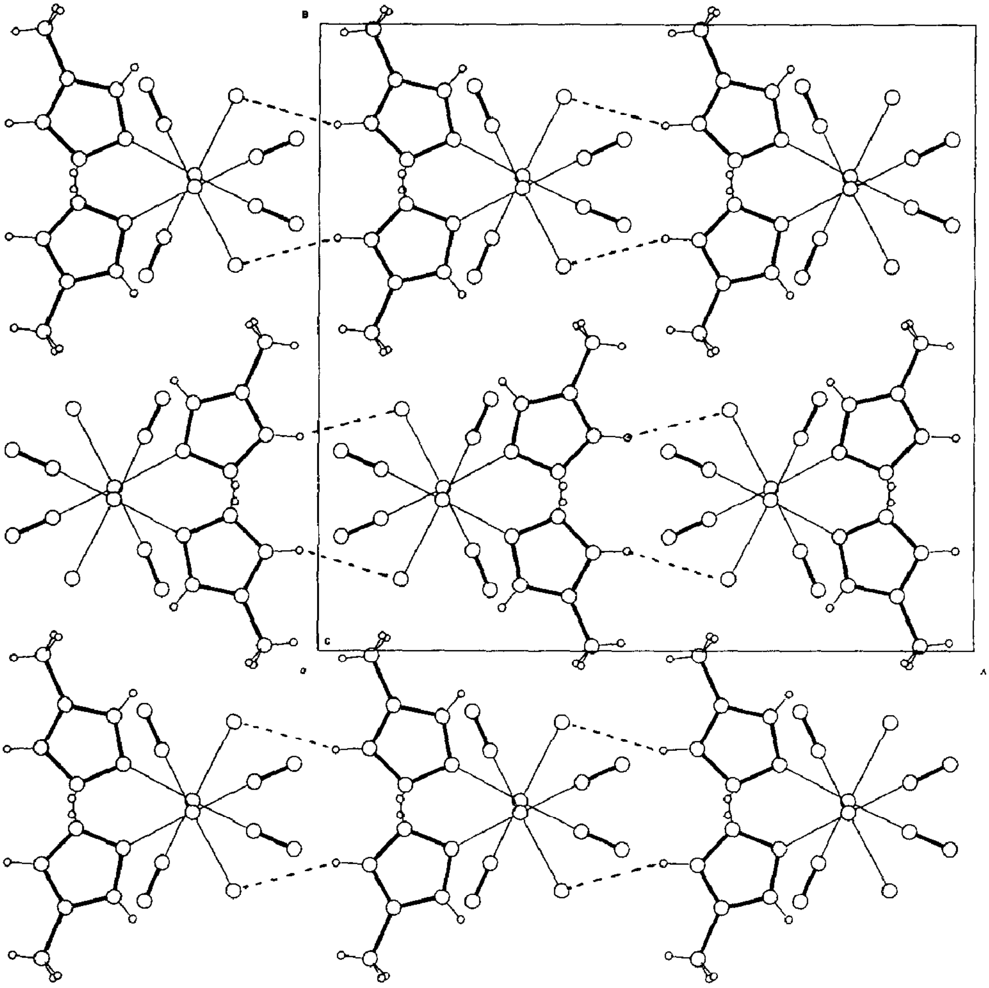


Fig. 2. Molecular packing of the title compound projected along the *c*-axis showing the Cl · · · H–C contacts and the disposition of the planar coordinations.

energy of the M · · · M interaction, although small at least in the case where M is gold [16], seems in the present case to be sufficient to overcome intramolecular steric repulsion.

In addition, the magnitude of the Rh · · · Rh interaction must be roughly proportional to the donor ability of the ligands surrounding the coordination center. Indeed, in the series of β-diketonates mentioned above the longest Rh · · · Rh interaction was found for $R = CF_3$ (3.34 Å [3b]); moreover, in the case of *cis*-$(CO)_2RhCl(L)$ complexes the interaction decreases on going from the more strongly donating ligand (L = imidazole, V, 3.28 Å) to the less strongly donating ligand (L = pyrazole, 3.45 Å [7]), and is not found in the case of some purines in which the donor nitrogen is located on the pyrazole ring (L = allopurinol-*N*9 or 9-methylallopyrinol-*N*8 [8]); similarly, with imidazole the Rh–N bond distance seems to be at a minimun, the values being 2.072(4), 2.090(4), 2.088(2) and 2.105(3) Å for imidazole, pyrazole, allopyrinol-*N*9 and 9-methylallopurinol-*N*8, respectively. Although these distances may be related to the basic character of the donor as measured by their pK_a's (2.52, 7.1 and 7.3 for pyrazole, imidazole and *N*-methylimidazole, respectively), it should be remembered that rhodium(I) differs from the proton in being a soft acceptor, and that the analysis should be carried out using more appropriate parameters, for example the Gutmann donor number, or in terms of Drago's theory, since aromatic nitriles, which are not considered to be basic, give *cis*-$(CO)_2$RhX(nitrile) complexes [17] with Rh · · · Rh interactions (X = Cl or Br).

Even so the fact that there is a weak Rh · · · Rh interaction in *cis*-$(CO)_2$RhCl(L) where L is pyrazole but none when L is allopyrinol-*N*9 or 9-methylallopurinol-*N*8 requires some comment. The weak donor character of the pyrazole ring should not make much electron density available on the orbitals, perpendicular to the coordination plane, required in order to allow good M · · · M interactions. However, reconsideration of the data [7] relating to *cis*-$(CO)_2$RhCl(pyrazole) shows that the weak intermolecular hydrogen bonding, shown by broken lines in Fig. 3, may explain why the pyrazole lies in the coordination plane, thus allowing Rh · · · Rh intramolecular

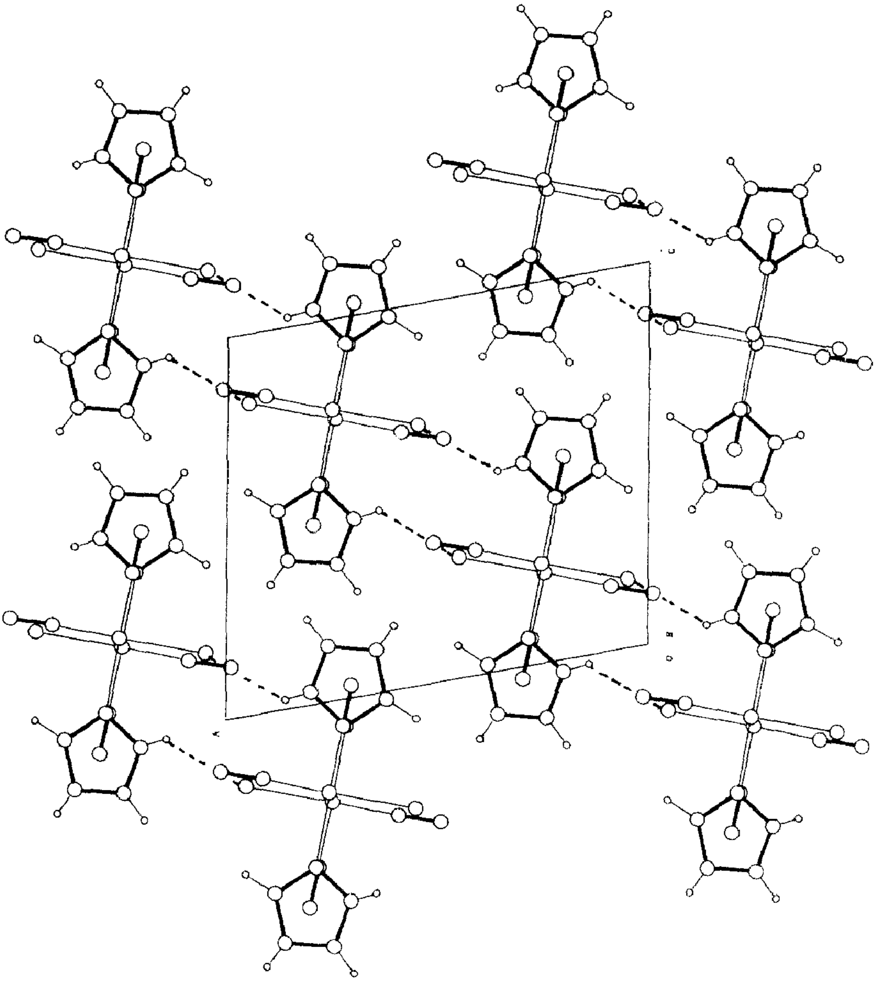


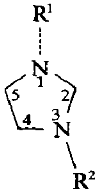
Fig. 3. Molecular packing of the complex *cis*-$(CO)_2$RhCl(pyrazole) [7] projected along the *b*-axis showing the Cl · · · H–N contacts and the disposition of the planar coordinations.

interactions. Furthermore the infrared spectrum (solid state, Nujol mull) provided independent supporting evidence for such a hydrogen bond, viz. a strong N–H stretching vibration centered at 3200 cm^{-1}. Nevertheless, on this evidence it cannot be concluded that H-bonding, which is present in most of the *cis*-$(CO)_2RhCl$(amine) complexes investigated by Vallarino [9] as well as *cis*-$(CO)_2RhCl$(pyrazole), is the determining factor in making M · · · M interaction possible. The ancillary position of hydrogen bonding is illustrated by the following observation: no Rh · · · Rh interaction was reported in the presence of either intra- or inter-molecular H-bonding, as shown in the cases of *cis*-$(CO)_2RhCl(L)$ where L is either allopurinol-*N*9 or 9-methylallopurinol-*N*8. Indeed, the single crystal X-ray structure of the latter complex shows a Cl · · · H–N^1 (*i*) bond (3.17 Å) which keeps the heterocyclic ring at an angle of 65.5 ° to the coordination plane, and for the former planar compound a Cl · · · H–N^8 distance of 3.01 Å can be calculated from the published data.

As far as the imidazole group is concerned, we have compared its structure with that of others from the Cambridge Structural Data Base [18], as shown in Table 6 (the names correspond to the codes given in the CSDB files). In all these compounds [19–21] there is some delocalization in the N(1)–C(2) and C(2)–N(3) bonds, which have the shortest distances, and the C(2)–N(1)–C(5), C(2)–N(3)–C(4) and N(3)–C(4)–C(5) angles are the smallest in the four compounds. Comparison with data for the free imidazole molecule [19] shows that the N(3)–C(4) and C(4)–C(5) distances are shorther in the methyl-substituted compounds.

Table 6

Comparison of bond distances (Å) and angles (°) in the imidazole ring



	Imazolo6	Barmim	Mpyrhe	This work
R^1	H	CH_3	H	CH_3
R^2	–	–	Rh	Rh
1–2	1.323(1)	1.288(3)	1.335(6)	1.327(7)
2–3	1.347(1)	1.338(3)	1.337(7)	1.338(7)
3–4	1.369(1)	1.347(3)	1.361(8)	1.357(8)
4–5	1.368(1)	1.335(3)	1.364(8)	1.343(9)
5–1	1.375(1)	1.363(3)	1.376(6)	1.381(9)
2–1–5	105.1(1)	104.9(3)	106.3(4)	103.5(5)
1–2–3	111.9(1)	112.2(3)	110.0(5)	112.1(5)
2–3–4	107.1(1)	106.6(3)	108.6(5)	107.5(5)
3–4–5	106.0(1)	106.2(3)	106.3(5)	105.9(6)
4–5–1	109.8(1)	110.1(3)	108.8(5)	111.1(6)
1–1–2	–	126.1(3)	–	126.4(5)
1–1–5	–	127.2(3)	–	126.1(5)
2–3–2	–	–	126.4(4)	127.6(4)
2–3–4	–	–	125.2(3)	128.9(4)

Experimental

General

The reactions were carried out at room temperature. Evaporation was always carried out under reduced pressure. Solvents were purified by standard methods. Elemental analyses were carried out with a Perkin–Elmer 240B microanalyser. Infrared spectra (range 4000–200 cm^{-1}) were recorded on a Perkin–Elmer 783 spectrophotometer using Nujol mulls between polyethylene sheets or dichloromethane solutions in cells with sodium chloride windows. Abscissa expansion was used in the carbonyl region. Molecular weights were determined with a Knauer osmometer using chloroform solutions. ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra were recorded with $CDCl_3$ solutions at room temperature on a Varian XL 200 spectrophotometer, with $SiMe_4$ as internal or 85% H_3PO_4 as external standard.

Preparation of compounds

(cod)RhCl(Rim) (R = Me, PhCH$_2$) (I,II). To a solution of [(cod)Rh(μ-Cl)]$_2$ (150 mg, 0.3 mmol) in 25 ml of dichloromethane was added Rim (R = Me, 0.024 ml; R = $PhCH_2$, 48.1 mg). The colour of the solutions immediately changed from orange-yellow to pale-yellow. After 30 min stirring, the solution was concentrated to ca. 2 ml; Slow addition of hexane (20 ml) gave a yellow microcrystalline solid, which was filtered off, washed with hexane, and air-dried.

(cod)IrCl(Rim) (R = Me, PhCH$_2$) (III, IV). To a suspension of [(cod)Ir(μ-Cl)]$_2$ (170 mg, 0.25 mmol) in acetone (20 ml) under nitrogen, was added dropwise a solution of Rim (R = Me, 0.02 ml; R = $PhCH_2$, 43 mg) in 5 ml of acetone. The starting material dissolved and after 30 min stirring the solution was evaporated to ca. 2 ml and pentane (15 ml) was added. The yellow complex which separated was filtered off, washed with pentane, and vacuum-dried.

cis-(CO)$_2$MCl(Rim) (M = Rh, Ir; R = Me, PhCH$_2$) (V–VIII). Dry carbon monoxide was slowly bubbled through a concentrated solution of (cod)MCl(Rim) (0.3 mmol) in deoxygenated dichloromethane (ca. 5 ml). After 15 min the initially yellow solutions had become pale yellow, and hexane (5 ml) was added. Bubbling was continued for 2 h and small amounts of hexane were added to complete the crystallization of the dicarbonyl compounds, which were filtered off, washed with cold hexane (5 ml), and air-dried.

cis-(CO)$_2$RhN$_3$(PhCH$_2$im) (IX). To a solution of *cis*-(CO)$_2$RhCl(PhCH$_2$im) (100 mg, 0.28 mmol) in 20 ml of methanol, was added a slight excess of NaN_3 (19.5 mg, 0.3 mmol). The colour of the solution changed from yellow to orange-yellow. After 30 min stirring the solution was evaporated to dryness. The residue was extracted with dichloromethane (20 ml), and the extract filtered through kieselguhr and evaporated to ca. 2 ml. Pentane (15 ml) was added, and complex IX which separated was filtered off, washed with pentane, and air-dried.

(CO)(PPh$_3$)RhCl(Meim) (X). To a solution of *cis*-(CO)$_2$RhCl(Meim) (205 mg, 0.74 mmol) in diethyl ether (20 ml) was added dropwise a solution of PPh_3 (194.5 mg, 0.74 mmol) in diethyl ether (8 ml). The yellow complex X separated spontaneously. After 30 min stirring the suspension was concentrated to ca. 10 ml and the solid then filtered off, washed with cold pentane (10 ml), and vacuum dried. ^{31}P{^{1}H} NMR: δ 43.3 (d, 153 Hz) (major product) and 46.4 (d, 179 Hz) (minor product) (ca. 13/1).

cis-(R'NC)$_2$RhCl(Meim) (R' = p-tosylmethyl) (XI). To a solution of (cod)RhCl(Meim) (200 mg, 0.61 mmol) in acetone (20 ml) was added dropwise a solution of R'NC (234 mg, 1.22 mmol) in acetone (10 ml). During the addition a dark blue solid separated and then redissolved to give an orange solution. After 30 min stirring the solution was evaporated to ca. 2 ml, and slow addition of hexane (15 ml) gave an orange solid, which was filtered off, washed with hexane, and vacuum-dried.

[(R'NC)$_4$Rh]Cl (R' = p-tosylmethyl) (XII). Solid R'NC (200 mg, 1.02 mmol) was added to a solution of [(cod)Rh(μ-Cl)]$_2$ (56.1 mg, 0.11 mmol) in acetone/methanol (1/1, 20 ml). The colour of the solution changed inmediately from yellow to dark blue. After 30 min stirring the solution was evaporated to dryness. Addition of diethyl ether gave dark blue microcrystalline solid, which was filtered off, washed with diethyl ether (15 ml), and vacuum dried.

Structure and determination of cis-(CO)$_2$RhCl(Meim)

Crystal data. $C_6H_6N_2O_2RhCl$, orthorhombic, space group *Pbca*, $M = 276.48$, *a* 17.4572(10), *b* 16.6550(12), *c* 6.5375(2) Å (determined by least-squares fit of the angular positions of 75 reflections with $5° < \theta < 45°$, Cu-K_α radiation, λ 1.5418 Å), *V* 1900.8(2) Å^3, D_c 1.932 g cm^{-3}, $Z = 8$, $F(000) = 1072$, μ 172.67 cm^{-1} (empirical absorption correction [22] were appplied. Maximum and minimum transmission factors: 1.312 and 0.470 respectively).

Plate shaped crystal 0.43 × 0.13 × 0.02 mm, in size, and with a metallic glister, was used to collect 1614 independent reflections (up to θ 65°), 1284 of which were considered as observed ($I > 3\sigma(I)$). A Philips PW 1100 diffractometer was employed, using bisecting geometry and Cu-K_α graphite monochromatized radiation with ω–2θ scans of width 1.6°. No decay was observed for two standard reflections were monitored every 90 minutes.

Solution and refinement

The structure was solved by Patterson and direct difference methods [23], and refined by full-matrix least-squares procedures on F_{obs}. Weights were chosen empirically using functions of the type $w = K/f(F_o)g(\sin\theta/\lambda)$, with K ensuring that

Table 7

Final atomic parameters

Atom	*x*	*y*	*z*
Rh	0.19004(2)	0.25927(2)	0.23043(5)
Cl	0.1270(1)	0.3854(1)	0.2288(3)
C(7)	0.2359(3)	0.1601(3)	0.2245(9)
O(7)	0.2629(3)	0.0977(3)	0.2210(8)
C(8)	0.0965(4)	0.2106(3)	0.2206(9)
O(8)	0.0351(3)	0.1819(3)	0.2168(9)
N(1)	0.2949(2)	0.3172(3)	0.2474(7)
C(2)	0.3092(3)	0.3946(4)	0.2190(10)
N(3)	0.3833(3)	0.4122(3)	0.2458(7)
C(4)	0.4199(4)	0.3430(4)	0.2957(13)
C(5)	0.3660(4)	0.2855(4)	0.2929(13)
C(6)	0.4182(5)	0.4921(5)	0.2332(19)

$\langle w\Delta^2F\rangle \sim 1$, and to give no trends in $\langle w\Delta^2F\rangle$ vs. $\langle F_o\rangle$ and $\langle \sin\theta/\lambda\rangle$. Hydrogen atoms were located from a difference synthesis. The refinement converged to $R = 0.031$ ($R_w = 0.036$). The final difference synthesis showed peaks no greater than 0.5 e$\AA^{-3}$ near the rhodium atom. Final atomic coordinates for the non-hydrogen atoms are given in Table 7, and the numbering scheme in Fig. 1 [12].

The scattering atomic factors were taken from ref. 24. All calculations were done on a VAX 11/750, mostly by use of the X-RAY 76 system [25].

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