

## IMIDAZOLATE BRIDGED POLYNUCLEAR RHODIUM(I) COMPLEXES. X-RAY STRUCTURE OF $[\text{Rh}(2\text{-Meimidazolate})(\text{CO})_2]_4$

A. TIRIPICCHIO, M. TIRIPICCHIO CAMELLINI,

*Istituto di Chimica Generale ed Inorganica, Università di Parma, Centro di Studio per la Strutturistica Diffraattometrica del C.N.R., Via M.D'Azeglio 85, Parma (Italy)*

R. USON, L.A. ORO, M.A. CIRIANO and M.T. PINILLOS

*Departamento de Química Inorgánica, Universidad de Zaragoza, Zaragoza (Spain)*

(Received August 3rd, 1981)

### Summary

The synthesis and properties of polynuclear complexes of general formulae  $[\text{M}(\text{RIm})(\text{diolefin})]_x$ ,  $[\text{M}(\text{RIm})(\text{CO})_2]_x$  and  $[\text{M}(\text{RIm})(\text{CO})\text{L}]_x$  ( $\text{M} = \text{Rh}, \text{Ir}$ ;  $\text{RIm} = \text{imidazolate}, 2\text{-methylimidazolate}, 2\text{-benzylbenzimidazolate}$ ;  $\text{L} = \text{PPh}_3$  or  $\text{P}(\text{OPh})_3$ ) are reported. The crystal structure of the novel complex  $[\text{Rh}(2\text{-MeIm})(\text{CO})_2]_4$  ( $2\text{-MeIm} = 2\text{-methylimidazolate}$ ) has been determined by X-ray methods. The crystals are orthorhombic, space group  $P2_12_12_1$ , with  $Z = 4$  in a unit cell of dimensions  $a$  19.427(12),  $b$  13.419(8),  $c$  12.346(9) Å. The structure has been solved by combined Patterson and direct methods and refined by full-matrix least-squares to  $R = 0.043$  for 937 independent observed reflections. It consists of discrete tetrameric complexes in which each Rh atom is in a nearly *cis* square planar arrangement, bonded to two carbon atoms of carbonyl groups and to two nitrogen atoms of two 2-methylimidazolate ligands, each of which, acting as an *exo*-bidentate ligand, bridging two metal atoms, so that the four bridging 2-MeIm ligands and the four Rh atoms form a multiatomic ring.

### Introduction

The synthesis and properties of dinuclear rhodium(I) complexes with pyrazolate-type ligands have been described [1–5]. In contrast, the coordination chemistry of the imidazolate anion ( $\text{Im}^-$ ) with this metal has been little studied, but Japanese patents have revealed that the complex  $[\text{Rh}(\text{Im})(\text{COD})]_2$  is an active catalyst for the hydroformylation of olefins [6,7].

In this paper we report the preparation of polynuclear rhodium and iridium complexes of the types  $[\text{M}(\text{RIm})(\text{diolefin})]_x$ ,  $[\text{M}(\text{RIm})(\text{CO})_2]_x$  and  $[\text{M}(\text{RIm})-$

(CO)L]<sub>x</sub> (M = Rh, Ir; RIm = imidazolate type ligands; L = PPh<sub>3</sub> or P(OPh)<sub>3</sub>). The structure of the tetranuclear complex [Rh(2-MeIm)(CO)<sub>2</sub>]<sub>4</sub> (2-MeIm = 2-methylimidazolate) has been determined by single-crystal X-ray diffraction.

## Results and discussion

### a) Diolefin complexes

The reaction of complexes of the type Rh(acac)(diolefin) (diolefin = 1,5-cyclooctadiene (COD) [8], tetrafluorobenzobarrelene (TFB) [9]) of Ir(acac)-(COD) [10] with imidazole (HIm), 2-methylimidazole (H2-MeIm) and 2-benzylbenzimidazole (HbbIm) in acetone gives complexes of the type [M(RIm)(diolefin)]<sub>x</sub> (eq. 1)



Table 1 lists the analytical data for the isolated complexes. The complex [Rh(Im)(COD)]<sub>3</sub> has been previously prepared by reaction of [RhCl(COD)]<sub>2</sub> with imidazole and butyllithium [6]. The molecular weight measurements indicate that *x* has a value of 3 (see Table 1) for [Rh(RIm)(COD)]<sub>x</sub> complexes but a value between 2 and 3 for the [Rh(bbIm)(COD)]<sub>x</sub> complex. The experimental values decrease with dilution, suggesting that there is dissociation of the complexes in solution, and so the results are not completely reliable guide to the nuclearity of the complexes. The low solubility of the TFB complexes prevented determination of their molecular weights by osmometry.

### b) Carbonyl complexes

The [M(RIm)(COD)]<sub>x</sub> complexes react with carbon monoxide with formation of complexes of the type [M(RIm)(CO)<sub>2</sub>]<sub>x</sub>. Since the displacement reaction was very slow for the [Rh(bbIm)(COD)]<sub>x</sub> complex, the dicarbonyl deriva-

TABLE 1  
ANALYTICAL DATA FOR THE DIOLEFIN COMPLEXES

Complex	Analysis (found (calcd.) (%))			Mol. wt. (CHCl <sub>3</sub> ) (found (calcd.))	Yield (%)
	C	H	N		
[Rh(Im)(COD)] <sub>x</sub>	47.76 (47.33)	5.39 (5.42)	10.07 (10.03)	861 (834 <sup>a</sup> )	90
[Rh(2-MeIm)(COD)] <sub>x</sub>	49.33 (49.33)	5.84 (5.86)	9.45 (9.59)	913 (877 <sup>a</sup> )	88
[Rh(Im)(TFB)] <sub>x</sub>	46.30 (45.48)	2.35 (2.29)	7.15 (7.07)	—	65
[Rh(2-MeIm)(TFB)] <sub>x</sub>	47.88 (46.85)	3.21 (2.70)	6.98 (6.81)	—	62
[Rh(bbIm)(COD)] <sub>x</sub>	63.21 (63.16)	5.48 (5.78)	6.60 (6.69)	985 (837 <sup>b</sup> , 1255 <sup>a</sup> )	88
[Ir(Im)(COD)] <sub>x</sub>	35.57 (35.95)	4.05 (3.84)	7.54 (7.62)	1151 (1102 <sup>a</sup> )	83
[Ir(2-MeIm)(COD)] <sub>x</sub>	38.07 (37.78)	4.51 (4.49)	7.42 (7.34)	1198 (1144 <sup>a</sup> )	88

<sup>a</sup> *x* = 3. <sup>b</sup> *x* = 2.

tive was prepared from  $\text{Rh}(\text{acac})(\text{CO})_2$  [8] by the reaction shown in eq. 2



All the complexes were isolated as microcrystalline solids. Their IR spectra in dichloromethane show two strong  $\nu(\text{CO})$  bands, as expected for *cis*-dicarbonyl structures [11]. The  $[\text{M}(2\text{-MeIm})(\text{CO})_2]_x$  derivatives can be specifically formulated as tetramers on the basis of molecular weight measurements.

When a stoichiometric amount of triphenylphosphine or triphenylphosphite was added to dichloromethane solutions of  $[\text{M}(\text{RIm})(\text{CO})_2]_x$  complexes, the corresponding monocarbonyl derivatives are formed. They show one strong  $\nu(\text{CO})$  absorption in the 1990–1975  $\text{cm}^{-1}$  range. Table 2 lists some data for the carbonyl derivatives. Again, the molecular weight values decrease with dilution.

In all the complexes reported in this paper the imidazolate type group should act as an *exo*-bidentate ligand.

#### Crystal structure of the complex $[\text{Rh}(2\text{-MeIm})(\text{CO})_2]_4$

The crystal structure of the compound  $[\text{Rh}(2\text{-MeIm})(\text{CO})_2]_4$  consists of tetrameric rhodium complexes, separated by normal Van der Waals contact distances. A view of the structure of the tetramer with the atomic numbering is shown in Fig. 1; selected bond distances and angles are given in Table 3.

Each of the four Rh atoms is in a nearly square planar arrangement, and is bonded to two carbon atoms of carbonyl groups and two nitrogen atoms of two 2-methylimidazolate ligands. The two similar ligands are *cis* coordinated to

TABLE 2  
ANALYTICAL DATA FOR THE CARBONYL COMPLEXES

Complex	Analysis (found (calcd.) (%))			Mol. wt. ( $\text{CHCl}_3$ ) (found (calcd.))	$\nu(\text{CO})$ ( $\text{CH}_2\text{Cl}_2$ ) ( $\text{cm}^{-1}$ )	Yield (%)
	C	H	N			
$[\text{Rh}(\text{Im})(\text{CO})_2]_x$	27.29 (26.57)	1.53 (1.34)	12.61 (12.39)	818 (678 <sup>a</sup> , 904 <sup>c</sup> )	2087, 2013	89
$[\text{Rh}(\text{Im})(\text{CO})(\text{PPh}_3)]_x$	58.38 (57.41)	4.47 (3.94)	5.81 (6.09)	1466 (1381 <sup>a</sup> )	1983	80
$[\text{Rh}(2\text{-MeIm})(\text{CO})_2]_4$	30.17 (30.02)	2.23 (2.10)	11.84 (11.67)	974 (960 <sup>c</sup> )	2078, 2010	82
$[\text{Rh}(2\text{-MeIm})(\text{CO})(\text{PPh}_3)]_x$	59.04 (58.24)	4.63 (4.25)	5.57 (5.91)	1414 (1423 <sup>a</sup> )	1975	83
$[\text{Rh}(2\text{-MeIm})(\text{CO})\{\text{P}(\text{OPh})_3\}]_x$	52.33 (52.89)	4.01 (3.86)	5.18 (5.36)	1553 (1567 <sup>a</sup> )	2000	85
$[\text{Rh}(\text{bbIm})(\text{CO})_2]_x$	51.57 (52.48)	3.21 (3.02)	7.73 (7.65)	1193 (1099 <sup>a</sup> , 1465 <sup>c</sup> )	2090, 2025	80
$[\text{Rh}(\text{bbIm})(\text{CO})(\text{PPh}_3)]_x$	66.30 (66.00)	4.51 (4.36)	4.59 (4.66)	1393 (1201 <sup>b</sup> , 1801 <sup>a</sup> )	1980	87
$[\text{Ir}(\text{Im})(\text{CO})_2]_x$	19.13 (19.05)	1.16 (0.96)	8.67 (8.88)	940 (946 <sup>a</sup> )	2070, 2000	87
$[\text{Ir}(\text{Im})(\text{CO})\{\text{P}(\text{OPh})_3\}]_x$	43.79 (44.22)	3.50 (3.04)	4.70 (4.69)	—	1990	40
$[\text{Ir}(2\text{-MeIm})(\text{CO})_2]_4$	22.06 (21.88)	1.65 (1.53)	8.89 (8.51)	1307 (1317 <sup>c</sup> )	2065, 1990	89

<sup>a</sup>  $x = 3$ . <sup>b</sup>  $x = 2$ . <sup>c</sup>  $x = 4$ .

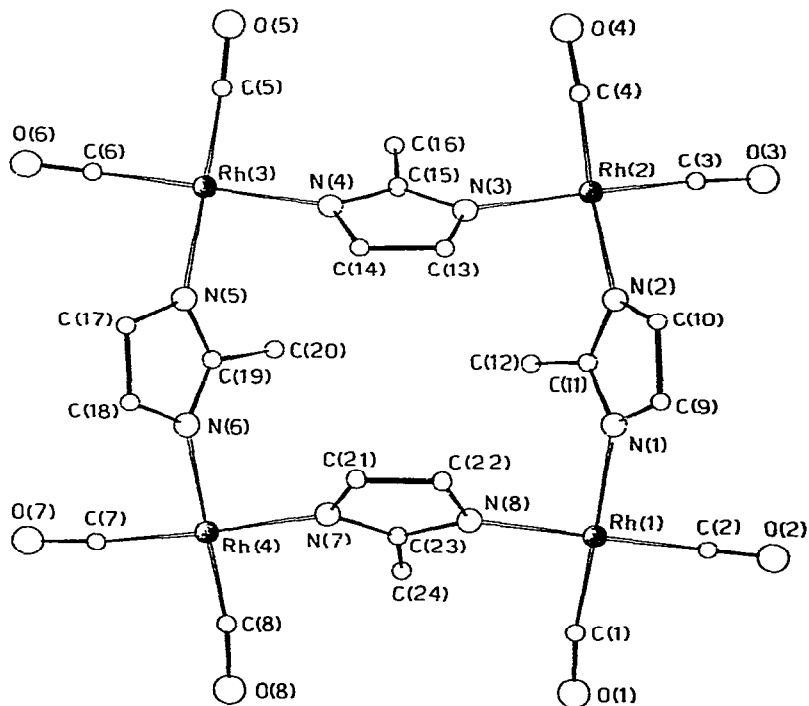


Fig. 1. View of the molecular shape of the tetrameric complex  $[\text{Rh}(2\text{-MeIm})(\text{CO})_2]_4$  with the atomic numbering scheme.

the metal. Each 2-MeIm anion, acting as an *exo*-bidentate ligand, bridges two rhodium atoms, so that the four bridging ligands together with the four metal atoms, form a multiatomic ring. The conformation of the tetramer is shown in Fig. 2. The mean plane passing through the metal atoms leaves Rh(1), Rh(2), Rh(3) and Rh(4) out of this by  $-0.09$ ,  $0.09$ ,  $-0.09$  and  $0.09$  Å, whereas all the nitrogen atoms are displaced to the same side with respect to this plane [displacements of N(1), N(2), N(3), N(4), N(5), N(6), N(7) and N(8):  $-0.67$ ,  $-0.50$ ,  $-0.45$ ,  $-0.55$ ,  $-0.59$ ,  $-0.47$ ,  $-0.38$  and  $-0.48$  Å].

The lengths of the Rh—N bonds, ranging from 2.00 to 2.11 Å, mean value 2.06 Å, agree with those found in the dimeric complexes  $[\text{Rh}(\text{Pz})(\text{CO})\text{P}(\text{OPh})_3]_2$ , ranging from 2.07 to 2.11 Å, mean value 2.08 Å [4], and

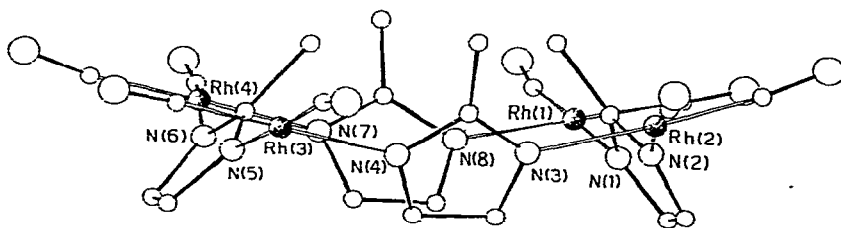


Fig. 2. View of the complex  $[\text{Rh}(2\text{-MeIm})(\text{CO})_2]_4$  showing the conformation of the tetramer.

TABLE 3

SELECTED BOND DISTANCES (Å) AND ANGLES (°) WITH e.s.d.'s IN PARENTHESES

<i>a) In the Rh coordination sphere</i>			
Rh(1)—N(1)	2.07(1)	Rh(3)—N(4)	2.08(1)
Rh(1)—N(8)	2.07(1)	Rh(3)—N(5)	2.06(1)
Rh(1)—C(1)	1.80(2)	Rh(3)—C(5)	1.85(2)
Rh(1)—C(2)	1.86(3)	Rh(3)—C(6)	1.85(2)
Rh(2)—N(2)	2.03(2)	Rh(4)—N(6)	2.00(2)
Rh(2)—N(3)	2.11(2)	Rh(4)—N(7)	2.01(1)
Rh(2)—C(3)	1.78(2)	Rh(4)—C(7)	1.82(2)
Rh(2)—C(4)	1.81(2)	Rh(4)—C(8)	1.68(3)
N(1)—Rh(1)—N(8)	87.4(6)	N(4)—Rh(3)—N(5)	87.6(5)
N(8)—Rh(1)—C(1)	90.8(8)	N(5)—Rh(3)—C(6)	91.2(8)
C(1)—Rh(1)—C(2)	89.6(9)	C(6)—Rh(3)—C(5)	87.9(9)
C(2)—Rh(1)—N(1)	92.2(9)	C(5)—Rh(3)—N(4)	93.3(7)
N(2)—Rh(2)—N(3)	88.6(6)	N(6)—Rh(4)—N(7)	86.6(6)
N(3)—Rh(2)—C(4)	95.1(9)	N(7)—Rh(4)—C(8)	90.3(9)
C(4)—Rh(2)—C(3)	87.0(9)	C(8)—Rh(4)—C(7)	93.5(9)
C(3)—Rh(2)—N(2)	89.7(8)	C(7)—Rh(4)—N(6)	89.5(8)
<i>b) In the carbonyls</i>			
C(1)—O(1)	1.17(2)	C(5)—O(5)	1.13(2)
C(2)—O(2)	1.08(3)	C(6)—O(6)	1.10(2)
C(3)—O(3)	1.18(2)	C(7)—O(7)	1.18(2)
C(4)—O(4)	1.19(2)	C(8)—O(8)	1.23(2)
Rh(1)—C(1)—O(1)	169(2)	Rh(3)—C(5)—O(5)	166(2)
Rh(1)—C(2)—O(2)	178(2)	Rh(3)—C(6)—O(6)	178(2)
Rh(2)—C(3)—O(3)	172(2)	Rh(4)—C(7)—O(7)	169(2)
Rh(2)—C(4)—O(4)	176(2)	Rh(4)—C(8)—O(8)	167(2)
<i>c) In the 2-methylimidazolate ligands</i>			
N(1)—C(9)	1.38(2)	N(5)—C(17)	1.42(2)
C(9)—C(10)	1.43(2)	C(17)—C(18)	1.37(2)
N(2)—C(10)	1.35(2)	N(6)—C(18)	1.46(2)
N(2)—C(11)	1.38(2)	N(6)—C(19)	1.31(2)
N(1)—C(11)	1.40(2)	N(5)—C(19)	1.36(2)
C(11)—C(12)	1.55(2)	C(19)—C(20)	1.60(2)
N(3)—C(13)	1.38(2)	N(7)—C(21)	1.40(2)
C(13)—C(14)	1.37(2)	C(21)—C(22)	1.37(2)
N(4)—C(14)	1.38(2)	N(8)—C(22)	1.38(2)
N(4)—C(15)	1.37(2)	N(8)—C(23)	1.38(2)
N(3)—C(15)	1.33(2)	N(7)—C(23)	1.35(2)
C(15)—C(16)	1.47(2)	C(23)—C(24)	1.51(2)
C(11)—N(1)—C(9)	110(1)	C(19)—N(5)—C(17)	106(1)
N(1)—C(9)—C(10)	105(1)	N(5)—C(17)—C(18)	105(2)
C(9)—C(10)—N(2)	109(1)	C(17)—C(18)—N(6)	111(2)
C(10)—N(2)—C(11)	109(1)	C(18)—N(6)—C(19)	102(1)
N(2)—C(11)—N(1)	107(2)	N(6)—C(19)—N(5)	116(1)
C(9)—N(1)—Rh(1)	128(1)	C(17)—N(5)—Rh(3)	125(1)
C(11)—N(1)—Rh(1)	122(1)	C(19)—N(5)—Rh(3)	128(1)
C(22)—N(8)—Rh(1)	122(1)	C(14)—N(4)—Rh(3)	125(1)
C(23)—N(8)—Rh(1)	133(1)	C(15)—N(4)—Rh(3)	127(1)
N(1)—C(11)—C(12)	126(2)	N(5)—C(19)—C(20)	120(1)
N(2)—C(11)—C(12)	126(2)	N(6)—C(19)—C(20)	124(1)
C(15)—N(3)—C(13)	112(1)	C(23)—N(7)—C(21)	104(1)
N(3)—C(13)—C(14)	104(2)	N(7)—C(21)—C(22)	110(1)
C(13)—C(14)—N(4)	110(2)	C(21)—C(22)—N(8)	108(1)
C(14)—N(4)—C(15)	107(1)	C(22)—N(8)—C(23)	105(1)
N(4)—C(15)—N(3)	107(1)	N(9)—C(23)—N(7)	114(1)
C(15)—N(3)—Rh(2)	127(1)	C(21)—N(7)—Rh(4)	126(1)
C(13)—N(3)—Rh(2)	121(1)	C(23)—N(7)—Rh(4)	131(1)
C(10)—N(2)—Rh(2)	125(1)	C(18)—N(6)—Rh(4)	126(1)
C(11)—N(2)—Rh(2)	126(1)	C(19)—N(6)—Rh(4)	132(1)
N(3)—C(15)—C(16)	128(2)	N(7)—C(23)—C(24)	125(1)
N(4)—C(15)—C(16)	125(2)	N(8)—C(23)—C(24)	121(1)

$[\text{Rh}(\text{3,5-Me}_2\text{Pz})(\text{CS})(\text{PPh}_3)]_2$ , ranging from 2.07 to 2.14 Å, mean value 2.10 Å [5], with pyrazolate ligands. All the carbonyls are terminal, the Rh—C—O angles ranging from 166 to 178°; the Rh—C bond distances (mean value 1.81 Å) are quite normal. The four 2-methylimidazolate rings are perfectly planar.

## Experimental

C, H and N analysis were carried out with a Perkin-Elmer 240 B microanalyzer. IR spectra were recorded on a Perkin-Elmer 599 spectrophotometer using Nujol mulls between polyethylene disks and in dichloromethane solution between NaCl disks (for the carbonyl complexes). Molecular weights were measured with ca.  $2 \times 10^{-3}$  M  $\text{CHCl}_3$  solutions with a Perkin-Elmer 115 osmometer.

All reactions were carried out in air and at room temperature unless otherwise stated, using 0.1–0.2 mmol of the starting materials.

### *Preparation of complexes of the $[\text{Rh}(\text{RIm})(\text{diolefin})]_x$ type*

On mixing a solution of HRIm (imidazole, 2-methylimidazole, 2-benzylbenzimidazole) in acetone with the stoichiometric amount (1 : 1) of Rh-(acac)(diolefin) in the same solvent the products separated as yellow solids. After concentration of the solution and stirring for 20 min the solids were filtered off, washed with methanol, and air-dried.

### *Preparation of complexes of the $[\text{Ir}(\text{RIm})(\text{COD})]_x$ type*

Thallium acetylacetonate was reacted with a stoichiometric amount (2 : 1) of  $[\text{IrCl}(\text{COD})]_2$  in acetone under argon for 20 min. The resulting thallium(I) chloride was removed by filtration and a stoichiometric amount (1 : 1) of the corresponding HRIm (imidazole, 2-methylimidazole) in acetone was then added to the filtrate. The products precipitated as yellow solids. After vacuum-evaporation of the solution they were filtered off, washed with methanol, and vacuum-dried.

### *Preparation of complexes of the $[\text{M}(\text{RIm})(\text{CO})_2]_x$ type*

Bubbling of carbon monoxide through a solution of the corresponding complex  $[\text{M}(\text{RIm})(\text{COD})]_x$  (M = Rh, Ir; RIm = Im, 2-MeIm) in dichloromethane for 20 min gave a yellow solution. Vacuum-evaporation followed by addition of methanol gave the products as microcrystalline solids, which were filtered off, washed with methanol, and air-dried.

### *Preparation of $[\text{Rh}(\text{bbIm})(\text{CO})_2]_x$*

A solution of Rh(acac)(CO)<sub>2</sub> (0.052 g, 0.2 mmol) in dichloromethane was reacted with 2-benzylbenzimidazole (0.042 g, 0.2 mmol) for 0.5 h. The solution was evaporated to dryness and the residue was recrystallized from methanol/water to give a yellow solid, which was filtered off, washed with methanol/water and then with cold methanol, and air-dried.

*Preparation of complexes of the  $[M(RIm)(CO)(PR_3)]_x$  type*

Carbon monoxide was bubbled through a dichloromethane solution of the corresponding complex  $[M(RIm)(COD)]_x$  ( $M = Rh, Ir$ ;  $RIm = Im, 2-MeIm$ ) for 20 min. A stoichiometric amount of P-donor ligand ( $PPh_3, P(OPh)_3$ ) was added and the resulting solution was stirred for 15 min. Addition of hexane to the concentrated solution gave the products as yellow solids, which were filtered off, washed with hexane and vacuum-dried.

The iridium complex  $[Ir(Im)(CO)\{P(OPh)_3\}]_x$  is air-sensitive, and was prepared under argon.

TABLE 4

FRACTIONAL ATOMIC COORDINATES ( $\times 10^4$ ) WITH e.s.d.'s IN PARENTHESES FOR THE NON-HYDROGEN ATOMS

Atom	x/a	y/b	z/c
Rh(1)	3800(2)	-4011(2)	7998(3)
Rh(2)	3839(2)	431(3)	6942(3)
Rh(3)	3949(2)	1528(2)	11815(3)
Rh(4)	3727(2)	-2920(3)	12892(3)
O(1)	3289(18)	-5963(28)	8761(29)
O(2)	3507(18)	-4766(32)	5812(35)
O(3)	3303(14)	131(22)	4723(25)
O(4)	3570(17)	2617(29)	6712(30)
O(5)	3707(20)	3563(35)	10975(32)
O(6)	3657(16)	2307(25)	13998(28)
O(7)	3312(17)	-2545(25)	15180(29)
O(8)	3363(18)	-4997(29)	13106(33)
N(1)	4140(14)	-2650(20)	7409(19)
N(2)	4102(15)	-1031(27)	6985(28)
N(3)	4118(16)	536(26)	8592(25)
N(4)	4173(14)	952(23)	10288(23)
N(5)	4166(13)	137(20)	12436(19)
N(6)	4055(14)	-1506(26)	12811(24)
N(7)	3971(16)	-3022(24)	11315(23)
N(8)	4014(16)	-3480(25)	9537(23)
C(1)	3528(21)	-5190(34)	8550(32)
C(2)	3623(29)	-4486(47)	6611(58)
C(3)	3557(20)	284(32)	5577(33)
C(4)	3690(24)	1751(38)	6770(40)
C(5)	3716(23)	2765(35)	11274(33)
C(6)	3754(19)	2012(33)	13182(36)
C(7)	3532(24)	-2743(37)	14319(37)
C(8)	3578(27)	-4149(42)	12935(47)
C(9)	4692(17)	-2472(24)	6738(27)
C(10)	4668(17)	-1430(29)	6517(26)
C(11)	3756(21)	-1772(30)	7536(26)
C(12)	3112(19)	-1635(33)	8258(33)
C(13)	4701(21)	72(30)	8978(32)
C(14)	4708(20)	305(32)	10055(30)
C(15)	3778(19)	1015(26)	9370(28)
C(16)	3130(20)	1575(32)	9277(30)
C(17)	4661(21)	-64(33)	13254(34)
C(18)	4608(19)	-1068(33)	13453(31)
C(19)	3818(21)	-731(24)	12281(26)
C(20)	3179(20)	-772(29)	11462(30)
C(21)	4575(18)	-2660(28)	10837(28)
C(22)	4588(19)	-2915(30)	9759(30)
C(23)	3645(19)	-3481(29)	10490(29)
C(24)	2939(19)	-3943(29)	10554(29)

*X-ray data collection for the complex [Rh(2-MeIm)(CO)<sub>2</sub>]<sub>4</sub>*

A yellow-gold prismatic crystal of the complex [Rh(2-MeIm)(CO)<sub>2</sub>]<sub>4</sub>, having approximate dimensions 0.13 × 0.15 × 0.25 mm, was used for data collection. Preliminary cell parameters were first determined from rotation and Weissenberg photographs and then refined from a least-squares procedure of  $\theta$  values for 17 reflections accurately measured on a single-crystal automated Siemens AED diffractometer (using the Nb-filtered Mo- $K_{\alpha}$  radiation). Crystal data are: C<sub>24</sub>H<sub>24</sub>N<sub>8</sub>O<sub>8</sub>Rh<sub>4</sub>,  $M = 964.12$ , orthorhombic,  $a$  19.427(12),  $b$  13.419(8),  $c$  12.346(9) Å,  $V$  3218(3) Å<sup>3</sup>,  $Z = 4$ ,  $d_{\text{calc.}}$  1.99 g/cm<sup>3</sup>,  $\mu(\text{Mo-}K_{\alpha}) = 20.40$  cm<sup>-1</sup>; space group  $P2_12_12_1$  (from systematic absences).

A complete set of intensity data was collected within the angular range  $2.5 \leq \theta \leq 25^\circ$ . The  $\theta/2\theta$  scan technique was used with a variable scan rate ranging from 2.5 to 10°/min. A standard reflection was remeasured after every 20 reflections as a check on crystal and instrument stability. No significant change in the measured intensities of these reflections was observed during data collection. A total of 3213 independent reflections were measured of which 937 only were employed in the analysis having  $I \geq 2\sigma(I)$ ; the remaining 2276 were considered unobserved. The intensities were corrected for Lorentz and polarization factors, but no absorption correction was applied because of the very low value of  $\mu r$ . The first absolute scale and the mean temperature factor were determined by the Wilson's method.

*Structure determination and refinement*

The structure was solved by combined Patterson and direct methods. Refinement was carried out by full-matrix least-squares using the SHELX system of computer programs [12], with initially isotropic and then anisotropic thermal

TABLE 5

CALCULATED FRACTIONAL ATOMIC COORDINATES ( $\times 10^4$ ) FOR THE HYDROGEN ATOMS

Atom	$x/a$	$y/b$	$z/c$
H(9)	5063	-3006	6443
H(10)	5044	-1022	6048
H(121)	2957	-2348	8581
H(122)	2698	-1327	7780
H(123)	3232	-1134	8916
H(13)	5068	-373	8532
H(14)	5076	26	10637
H(161)	2992	1874	10059
H(162)	2727	1084	8997
H(163)	3195	2178	8707
H(17)	5005	460	13637
H(18)	4931	-1477	14009
H(201)	2971	-1518	11447
H(202)	3349	-569	10659
H(203)	2786	-257	11728
H(21)	4971	-2244	11253
H(22)	4982	-2707	9184
H(241)	2741	-3865	11367
H(242)	2972	-4724	10349
H(243)	2599	-3571	9993



TABLE 6

THERMAL PARAMETERS ( $\times 10^4$ ) WITH e.s.d.'s IN PARENTHESES FOR THE NON-HYDROGEN ATOMS <sup>a</sup>

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Rh(1)	680(23)	349(19)	588(24)	27(20)	-9(26)	-45(19)
Rh(2)	612(23)	343(21)	496(23)	65(18)	81(27)	35(20)
Rh(3)	641(22)	370(20)	556(26)	-10(19)	-59(23)	6(18)
Rh(4)	768(30)	389(21)	479(21)	49(20)	34(24)	25(19)

Atom	$U$	Atom	$U$	Atom	$U$	Atom	$U$
O(1)	1076(123)	N(3)	612(94)	C(5)	708(138)	C(15)	352(101)
O(2)	1159(133)	N(4)	515(88)	C(6)	601(118)	C(16)	558(116)
O(3)	775(92)	N(5)	377(78)	C(7)	723(153)	C(17)	697(126)
O(4)	934(112)	N(6)	568(71)	C(8)	1085(176)	C(18)	649(120)
O(5)	1350(142)	N(7)	485(90)	C(9)	391(88)	C(19)	481(117)
O(6)	930(113)	N(8)	506(88)	C(10)	422(93)	C(20)	534(120)
O(7)	901(111)	C(1)	545(121)	C(11)	263(141)	C(21)	445(104)
O(8)	1179(121)	C(2)	856(201)	C(12)	716(123)	C(22)	522(109)
N(1)	314(76)	C(3)	534(124)	C(13)	609(120)	C(23)	468(108)
N(2)	573(94)	C(4)	832(156)	C(14)	581(112)	C(24)	645(108)

<sup>a</sup> The anisotropic parameters (for the Rh atoms only) are in the form:  $\exp[-2\pi^2(h^2a^*U_{11} + \dots + 2hka^*b^*U_{12})]$

parameters for the Rh atoms only (in view of the limited number of observed reflections). The hydrogen atoms were placed in their geometrically calculated positions and included in the final structure factor calculations with isotropic thermal parameters. The final  $R$  value was 0.043 for the observed reflections only. The function minimized in the least-squares calculations was  $\sum w|\Delta F|^2$ ; unit weights were used in the first cycles of refinement, the weight calculated as  $w = K/[\sigma^2(F_o) + gF_o^2]$  with  $K = 0.306$  and  $g = 0.005$  was chosen in the final cycles. The atomic scattering factors (corrected for the anomalous dispersion of Rh) were taken from the International Tables [13]. Final atomic coordinates for the non-hydrogen atoms and for the hydrogen atoms (in the calculated positions) are given in Tables 4 and 5, respectively. The thermal parameters are given in Table 6. A list of observed and calculated structure factors is available from the authors on request.

Calculations were performed on the CYBER 7600 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna, with financial support from the University of Parma.

## References

- 1 S. Trofimenko, *Inorg. Chem.*, **10** (1971) 1372.
- 2 N.F. Borkett and M.I. Bruce, *J. Organometal. Chem.*, **65** (1974) C51.
- 3 F. Bonati, *Chim. Ind. (Milan)*, **62** (1980) 323.
- 4 R. Usón, L.A. Oro, M.A. Ciriano, M.T. Pinillos, A. Tiripicchio and M. Tiripicchio Camellini, *J. Organometal. Chem.*, **205** (1981) 247.
- 5 R. Usón, L.A. Oro, M.A. Ciriano, D. Carmona, A. Tiripicchio and M. Tiripicchio Camellini, *J. Organometal. Chem.*, **206** (1981) C14.
- 6 K. Noriaki, K. Saeki and Y. Toda, *Japan Kokai*, **76**, 141, 866; *Chem. Abstr.*, **86** (1977) 171604e.
- 7 M. Tanaka, K. Saeki and N. Kihara, *Japan Kokai*, **77**, 83, 311; *Chem. Abstr.*, **87** (1977) 200792t.

- 8 F. Bonati and G. Wilkinson, *J. Chem. Soc.*, (1964) 3156.
- 9 D.M. Roe and A.G. Massey, *J. Organometal. Chem.*, 28 (1971) 273.
- 10 S.D. Robinson and B.L. Shaw, *J. Chem. Soc.*, (1965) 4997.
- 11 R. Usón, L.A. Oro, C. Claver and M.A. Garralda, *J. Organometal. Chem.*, 105 (1976) 365.
- 12 G.M. Sheldrick, *SHELX System of Computing Programs*, University of Cambridge, 1976.
- 13 *International Tables for X-Ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, 1974.