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N-substituted imidazole derivatives of rhodium(I) and iridium(I). Crystal structure of the head-to-head dinuclear compound $[Ir_2(\mu\text{-}N\text{-benzylimidazolato-}N^3,C^2)_2(CO)_4]$

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Abstract

Complexes $[M_2(\mu\text{-Cl})_2(\text{diolefin})_2]$ (M = Rh or Ir; diolefin = cyclo-octa-1,5-diene (cod), norborna-2,5-diene (nbd)) react with lithium *N*-benzyl-2-imidazolate (LiBzim) to yield dinuclear $[M_2(\mu\text{-Bzim-}N^3,C^2)_2(\text{diolefin})_2]$ [M = Rh, diolefin = cod (**1**), nbd (**2**); M = Ir, diolefin = cod (**3**)]. Carbon monoxide reacts with diethyl ether suspensions of $[M_2(\mu\text{-Bzim-}N^3,C^2)_2(\text{diolefin})_2]$ to afford the tetracarbonyl complexes $[M_2(\mu\text{-Bzim-}N^3,C^2)_2(CO)_4]$ [M = Rh (**4**), Ir (**5**)]. In the crystal structure of dinuclear $[Ir_2(\mu\text{-Bzim-}N^3,C^2)_2(CO)_4]$, organocarbonyliridium(I), the Ir atoms exhibit different coordination environments: one Ir coordinates two CO groups and two N atoms of the imidazolate rings, and the other Ir coordinates two CO groups and two C atoms of the imidazolate rings.

Key words: Iridium; Rhodium; Imidazole

1. Introduction

An imidazole-N^3,C^2 is a planar bidentate ligand comparable to pyrazolate-*N,N'*. However, a *C*-derivative should be softer than an *N*-derivative. The difference in behaviour of *N*- and *C*-metallated imidazoles is consistent with a bigger *trans*-influence for *C*-imidazolyl than for *N*-imidazolyl. The formation of stable oligomers or polymers $[\{M(x-y)\}_n]$ of gold (I) is well established [1], where $(x-y)^-$ is a bidentate mononegative anion with suitable geometry, such as pyrazolate-*N,N'* and imidazolato-N^3,C^2_6. For example stable trimeric tris(μ-1-benzylimidazolato-N^3,C^2)gold was isolated and characterized.

In this context, structure and bonding in rhodium and iridium azolato complexes have attracted much interest in recent years [2,3], Pyrazolate type anions may be exobidentate *N,N'*, forming dinuclear structures [4]. In contrast, higher nuclearity is observed for related imidazolato-*N,N'* bridged complexes [5]. We decided to investigate the imidazolato-N^3,C^2 group as a mononegative, exobidentate ligand. This ligand is sterically comparable with a pyrazolato-*N,N'* group. However dinuclear systems with hetero-donor atoms are far more complex electronically and structurally than complexes with homo-donor groups.

Moreover the interaction between imidazoles and metals is interesting, because these heterocycles are corrosion inhibitors and some of the resulting compounds may have some relevance to anticorrosion mechanisms [6].

2. Results and discussion

Reaction of the chloro-bridged dimers $[M_2(\mu\text{-Cl})_2(\text{diolefin})_2]$ with a stoichiometric amount of lithium *N*-benzylimidazolate (LiBzim), in diethyl ether leads to the dinuclear complexes $[M_2(\mu\text{-Bzim-}N^3,C^2)_2(\text{diolefin})_2]$ [M = Rh, diolefin = cod (**1**), nbd (**2**); M = Ir, diolefin = cod (**3**)] as air-unstable orange (**1,2**) or red (**3**) solids, in nearly quantitative yield (reaction (1)). The compounds were characterized by elemental anal-

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† Deceased. This paper is dedicated to his memory.

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yses, infrared spectra, ^1H and $^{13}C\{^1H\}$ NMR data; complex **3** was also characterized by fast atom bombardment (FAB) mass spectroscopy.

$$[M_2(\mu\text{-Cl})_2(\text{diolefin})_2] + 2\text{LiBzim} \rightarrow [M_2(\mu\text{-Bzim-}N^3,C^2)_2(\text{diolefin})_2] + 2\text{LiCl} \quad (1)$$

It is worth noting that all attempts to prepare the dinuclear compounds **1**–**3** by reaction of n-butyllithium with the mononuclear complexes [MCl(cod)Bzim] [7] have been unsuccessful [8].

The presence of the metallated $Bzim^-$ in compounds **1**–**3** is shown by the absence of the resonance of the H^2 proton from their ^1H NMR spectra, and the displacement downfield of the signal due to the C^2 atom compared with that from the mononuclear [MCl(cod)(Bzim)] [7] derivatives, in their $^{13}C\{^1H\}$ spectra. In addition, in the $^{13}C\{^1H\}$ spectra of complexes **1** and **2** coupling between the C^2 atom of the imidazolate ring and one rhodium nucleus was detected ($J(^{13}C^2\text{–}^{103}Rh) \approx 50$ Hz).

The molecular weight of the iridium compound **3** was established by mass spectroscopy and corresponds to a dimeric structure (m/z 915).

Because of the asymmetry of the bridging ligands, dinuclear compounds of the type $[M_2(\mu\text{-Bzim-}N^3,C^2)_2(\text{diolefin})_2]$ can exist as two geometrical isomers (Fig. 1). The two asymmetrical bridging ligands could be oriented head-to-head (H-H) or head-to-tail (H-T). Judging by the ^1H and $^{13}C\ \{^1H\}$ NMR spectra of the compounds (Tables 1 and 2), only one of the possible isomers is present (*e.g.*, only one AB system is found for the diastereotopic CH_2 protons of $Bzim^-$ ligand in their ^1H NMR spectra).

The ^1H and $^{13}C\ \{^1H\}$ NMR spectra of the cod derivatives **1** and **3** are compatible with either H – H (C_s symmetry) or H – T (C_2 symmetry) isomers. However, the $^{13}C\ \{^1H\}$ spectrum of the nbd derivative **2** shows ten resonances for the nbd carbon atoms. It is evident this complex **2** exists, in solution, as the head-to-head isomer [9]. The hypothetical head-to-tail configuration has a C_2 symmetry axis that would result in only seven nbd signals.

As expected for the head-to-head isomer, spin correlation spectroscopy (COSY) of complex **2** shows two resonances, each corresponding to two methylene protons without geminal coupling between them. The methylene protons at δ 1.43 are coupled with two tertiary protons (δ 4.13, 3.63) and the other two at δ 1.26 are coupled with the other two isochronous tertiary protons (δ 3.83). The ^1H NMR spectra of complexes **1**–**3** do not change when the temperature is raised from 293 to 343 K, suggesting that isomerization processes do not occur.

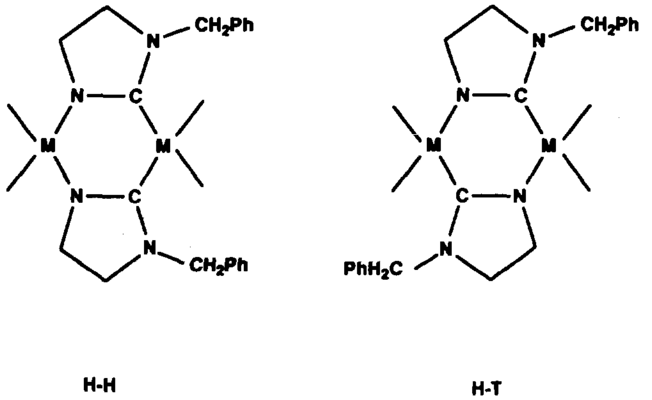


Fig. 1. Schematic structures for the dinuclear compounds: head-to-head (H-H) and head-to-tail (H-T) configurations.

The synthesis of the tetracarbonyl derivatives $[M_2(\mu\text{-Bzim-}N^3,C^2)_2(CO)_4]$ [M = Rh (**4**), Ir (**5**)] involves a straightforward reaction in diethyl ether between $[M_2(\mu\text{-benzylimidazolato-}N^3,C^2)_2(\text{diolefin})_2]$ and carbon monoxide. The complexes were isolated as yellow microcrystals in good yields, and their purity was ascertained by microanalysis. They are only moderately air-sensitive in the solid state.

The ^1H, $^{13}C\{^1H\}$ NMR spectra and IR spectra of **4** and **5** clearly indicate the presence of a single species in solution, either the head-to-head or the head-to-tail isomer. Their ^1H NMR spectra in C_6D_6 solution display sharp resonances due to the protons of the benzylimidazolato-ligands, the methylene groups appear as a sharp AB pattern. In the $^{13}C\{^1H\}$ NMR spectra all the expected signals are found. Again, the signal due to C^2 is displaced downfield by *ca.* 35 ppm compared with that from the corresponding free imidazole.

The IR spectra in cyclohexane solution of **4** and **5** show four ν(CO) bands at 1995, 2002, 2050 and 2072 or 1982, 1992, 2040 and 2060 cm^{-1}, respectively, consistent with either a C_s or C_2 symmetry [10].

A definitive assignment of head-to-head or head-to-tail geometry for complexes **4** and **5** seems impossible on the basis of the spectroscopic data. To assign unambiguously the structure, a crystallographic study of complex **5** was undertaken, revealing the molecule to be the head-to-head dinuclear species.

The asymmetric complexes $[M_2(\mu\text{-Bzim-}N^3,C^2)_2(CO)_4]$ present a rare opportunity to study the effects of a mixed-ligand environment on the chemistry of an important dimetal unit. Future work on these complexes will focus on the study of their reactivity towards coordinatively unsaturated molecules.

2.1. X-Ray crystal structure

The crystal contains discrete molecules with no intermolecular Ir · · · Ir interaction.

TABLE 1. ^1H NMR data (δ) for compounds 1–5

Compound	Imidazolate		Aryl			Diolefin		
	H^4	H^5	$H^{o,p}$	H^m	$>CH_2$ [a]	=CH	$>CH_2$	≥CH
1	6.34(d, 1.5)	6.91(d, 1.5)	6.96(m)	6.69(m)	5.12, 5.15 (15.5)	4.16(m, 2H) 4.48(m, 4H) 4.62(m, 2H)	1.86(m, 4H) 2.01(m, 2H) 2.17(m, 4H) 2.56(m, 4H) 2.74(m, 2H)	
2	6.34(d, 1.5)	6.95(d, 1.5)	7.00(m)	6.79(m)	4.98, 5.18 (15.5)	3.83(m, 2H) 4.13(m, 2H) 4.29(m, 2H) 4.77(m, 2H)	1.26(m, 2H) 1.43(m, 2H)	3.63(m, 1H) 3.83(m, 2H) 4.13(m, 1H)
3	6.37(d, 1.5)	7.00(d, 1.5)	6.96(m)	6.74(m)	5.08, 5.04 (15.9)	3.75(m, 2H) 4.01(m, 2H) 4.22(m, 2H) 4.25(m, 2H)	1.77(m, 2H) 1.80(m, 2H) 1.92(m, 2H) 2.04(m, 2H) 2.12(m, 2H) 2.47(m, 6H)	
4	6.77(d, 1.5)	6.97(d, 1.5)	7.24(m)	7.06(m)	5.11, 5.26 (15.0)			
5	6.88(d, 1.5)	7.07(d, 1.5)	7.28(m)	7.13(m)	5.20, 5.38 (15.2)			

s, d, t and m correspond to singlet, doublet, triplet and multiplet, respectively. The numbers in parentheses correspond to the coupling constants (Hz) or to the number of protons. [a] AB system.

The molecule is asymmetric and the benzyl groups are coordinated to the same iridium atom. One coordination centre has a C_2N_2 environment and the other a C_4 environment. Intramolecular interaction between the Ir atoms is excluded because of the long Ir(1) ··· Ir(2) separation, 3.5927(5) Å. The Ir atoms show approximately square planar coordination with the same average Ir–N and Ir–C distances, 2.071(5) and 2.07(1) Å respectively. These values compare well with the Ir–N distances, 2.02–2.10(3) Å found in $[Ir_2(\mu\text{-pz})_2(CO)_2(PPh_3)_2]$ [11], 2.07–2.10(2) Å in $[Ir_2(\mu\text{-pz})_2(CO)_2(PPh_3)_2] \cdot (C_6H_{14})$ [11] and 2.04–2.10(2) Å in $[Ir_2(\mu\text{-pz})_2Cl_2(CO)_2(PPh_3)_2] \cdot 2\ CH_2Cl_2$ [11]. Even though the Ir atoms exhibit different formal oxidation numbers in the complex [*i.e.* Ir(1) o.n = 0 and Ir(2) o.n = II], the oxidation state of both atoms is really I. The complex can be thought of as deriving from the interaction of two exobidentate mononegative imidazolate-N^3,C^2 anions with two iridium(I) centres, in a similar way as in the organogold oligomers [1]. The Ir–CO average distance *trans* to the nitrogen atoms (1.854(7) Å) is slightly smaller than the corresponding distance *trans* to the carbon atoms (1.886(8) Å), consistent with the previously quoted bigger *trans* influence

TABLE 2. $^{13}C\{^1H\}$ NMR data (δ) for compounds 1–5

Compound	Imidazolate					Diolefin			
	C^2	C^4	C^5	Aryl	$>CH_2$	$>C=$	$>CH_2$	≥CH	CO
1	186.0(d, 50.6)	140.1	117.8	126.8, 127.2, 128.6	52.4	76.9(d, 11.5) 80.2(d, 13.4) 83.8(d, 8.3) 86.1(d, 7.8)	31.3 31.6 31.8 32.0		
2	180.4(d, 54.8)	140.2	118.4	127.3, 127.4, 128.9	52.6	53.9(d, 9.7) 55.8(d, 10.6) 65.9(d, 7.4) 73.0(d, 7.4)	61.4(d, 7.9) 53.1(s, br)	51.7(d, 3.0) 52.4(d, 3.0) 54.3(d, 3.0) 66.5(d, 3.6)	
3	176.3	139.5	118.6	126.7, 126.8, 127.3, 128.6	52.4	59.7 64.8 70.7 71.7	32.2 32.4 32.6 33.0		
4	174.2(d, 51.0)	137.4	119.3	127.5, 127.7, 126.6, 130.9	53.3				186.2(d, 65.0) 189.8(d, 55.1)
5	171.6	137.0	120.4	127.8, 128.1, 128.7, 131.0	53.5				175.2 183.6

of C-imidazolyl. The Ir–CO distances compare well with the values 1.84–1.99(3) Å found in tri-μ-carbonylhexacarbonyl-μ_3-(1,3,5-trithiane)-*tetrahedro*-tetrairidium [12], 1.80–1.95(3) Å found in monocarbonyl-μ_3-(1,3,5-trithiane)-*tetrahedro*-tetrairidium [12], 1.879(7) Å found in $[Ru_3Ir(\mu\text{-}PPh_2)(\mu\text{-}CO)H_2(CO)_7(PPh_3)(PPh_3C_6H_4)]$ [13] and 1.83–1.91(2) Å found in $[Ir_2(\mu\text{-}C_5H_4NS)_2(CH_2I)I(CO)_4]$ [14].

TABLE 3. Interatomic distances (Å) and bond angles (deg) (with e.s.d.'s in parentheses)

Ir(1) ··· Ir(2)	3.5927(5)		
In the coordination spheres			
Ir(1)–N(3)	2.070(8)	Ir(2)–C(2)	2.057(9)
Ir(1)–N(3′)	2.071(7)	Ir(2)–C(2′)	2.086(9)
Ir(1)–C(6)	1.85(1)	Ir(2)–C(9)	1.89(1)
Ir(1)–C(7)	1.86(1)	Ir(2)–C(8)	1.88(1)
N(3)–Ir(1)–N(3′)	87.2(3)	C(2)–Ir(2)–C(2′)	84.2(3)
N(3)–Ir(1)–C(6)	89.8(4)	C(2)–Ir(2)–C(9)	91.9(4)
N(3)–Ir(1)–C(7)	177.0(4)	C(2)–Ir(2)–C(8)	175.0(4)
N(3′)–Ir(1)–C(6)	176.8(4)	C(2′)–Ir(2)–C(9)	175.9(4)
N(3′)–Ir(1)–C(7)	90.1(4)	C(2′)–Ir(2)–C(8)	92.3(4)
C(6)–Ir(1)–C(7)	93.0(4)	C(8)–Ir(2)–C(9)	91.5(5)
In the carbonyl groups			
C(6)–O(6)	1.13(1)	C(9)–O(9)	1.13(2)
C(7)–O(7)	1.12(1)	C(8)–O(8)	1.12(2)
Ir(1)–C(6)–O(6)	178(1)	Ir(2)–C(9)–O(9)	179(1)
Ir(1)–C(7)–O(7)	178(1)	Ir(2)–C(8)–O(8)	178(1)
In the benzyl-1-imidazole			
N(1)–C(2)	1.37(1)	N(1′)–C(2′)	1.35(1)
N(1)–C(10)	1.48(1)	N(1′)–C(10′)	1.46(1)
C(2)–N(3)	1.34(1)	C(2′)–N(3′)	1.34(1)
N(3)–C(4)	1.41(1)	N(3′)–C(4′)	1.39(1)
C(4)–C(5)	1.35(1)	C(4′)–C(5′)	1.34(1)
C(5)–N(1)	1.40(1)	C(5′)–N(1′)	1.36(1)
C(10)–C(11)	1.52(1)	C(10′)–C(11′)	1.51(2)
C(2)–N(1)–C(5)	110.5(8)	C(2′)–N(1′)–C(5′)	109.4(8)
C(2)–N(1)–C(10)	123.3(8)	C(2′)–N(1′)–C(10′)	127.0(8)
C(5)–N(1)–C(10)	125.3(8)	C(5′)–N(1′)–C(10′)	123.6(7)
N(1)–C(2)–N(3)	105.6(8)	N(1′)–C(2′)–N(3′)	107.6(7)
N(1)–C(2)–Ir(2)	132.3(7)	N(1′)–C(2′)–Ir(2)	129.3(7)
N(3)–C(2)–Ir(2)	121.8(7)	N(3′)–C(2′)–Ir(2)	123.1(6)
C(2)–N(3)–C(4)	110.2(8)	C(2′)–N(3′)–C(4′)	107.8(7)
C(2)–N(3)–Ir(1)	123.8(6)	C(2′)–N(3′)–Ir(1)	122.5(6)
C(4)–N(3)–Ir(1)	125.7(6)	C(4′)–N(3′)–Ir(1)	129.7(6)
N(3)–C(4)–C(5)	107.1(9)	N(3′)–C(4′)–C(5′)	107.9(8)
C(4)–C(5)–N(1)	106.5(8)	C(4′)–C(5′)–N(1′)	107.3(8)
N(1)–C(10)–C(11)	112.4(8)	N(1′)–C(10′)–C(11′)	114.0(8)
C(10)–C(11)–C(12)	118.0(9)	C(10′)–C(11′)–C(12′)	120.8(9)
C(10)–C(11)–C(16)	123(1)	C(10′)–C(11′)–C(16′)	120.6(9)
In the phenyl rings: weighted average of bond distances and endocyclic angles			
C(C(10))–C(*ortho*)	1.377(8)	C(*ipso*)	118.8(7)
C(*ortho*)–C(*meta*)	1.392(9)	C(*ortho*)	120.1(6)
C(*meta*)–C(*para*)	1.36(1)	C(*meta*)	121.0(6)
		C(*para*)	118.9(9)

The interatomic distances and bond angles are listed in Table 3, and their averages in Table 4 [15]. An ORTEP [16] view of the molecule with the numbering scheme is shown in Fig. 2.

The molecule has a virtual C_s symmetry with the mirror plane passing through the Ir atoms and C(2)–C(2′) and N(3)–N(3′) midpoints, but it exhibits no real crystallographic symmetry and all atoms lie in general positions. Both coordination planes depart from regular square planar coordination.

The least-squares planes passing through the atoms involved in coordination and the displacements of atoms from them are as follows.

Plane I: $-0.8063X' + 0.5823Y' - 0.1042Z' + 3.2081 = 0$. Ir(1) 0.0000(3), N(3) 0.012(8), N(3′) −0.011(7), C(6) −0.025(11), C(7) 0.026(12) Å;

Plane II: $0.5169X' + 0.8075Y' - 0.2841Z' + 3.2986 = 0$ Ir(2) 0.0002(4), C(2) −0.046(9), C(2′) −0.013(9), C(8) −0.076(11), C(9) −0.033(13) Å.

The least-squares planes of the five-membered rings are as shown.

Plane III: $-0.2875X' + 0.5730Y' - 0.7675Z' + 4.3542 = 0$. N(1) +0.002(7), C(2) −0.001(9), N(3) 0.003(7), C(4) −0.007(9), C(5) 0.06(9) Å.

Plane IV: $0.1782X' - 0.9193Y' - 0.3508Z' + 1.0035 = 0$. N(1′) 0.000(8), C(2′) 0.000(9), N(3′) 0.000(7), C(4′) 0.000(10), C(5′) 0.000(10) Å (X', Y', Z': orthogonal coordinates).

The imidazolato-ligands are planar, and the probability that the N(1)–C(2)–N(3)–C(4)–C(5) ring (plane III) is planar is $p = 58.0\%$. The corresponding value for the N(1′)–C(2′)–N(3′)–C(4′)–C(5′) ring (plane IV) is $p > 99\%$. The biggest displacement from the best planes is −0.007(9) Å for C(4).

The planes of the imidazolato-ligands lie in a position intermediate between normal and parallel to the coordination planes, because the dihedral angles between the imidazolato-planes III and IV and the coordination plane I are 49.8° and 130.0°, respectively, and those between the imidazolato-planes III and IV and the coordination plane II are 57.8° and 123.4°, respectively.

As for the *N*-benzylimidazolate ligand, we have compared its structure with that of other related complexes as shown in Table 5 [17,18]. In the ring of these compounds, N(1)–C(5) and N(3)–C(4) have the longest distances and C(4)–C(5) exhibits consequently a remarkable double bond character except in the case of d. The smallest endocyclic angle is N(1)–C(2)–N(3) and the largest ones are consequently C(2)–N(1)–C(5) and C(2)–N(3)–C(4). The structure of this C^2-metallated imidazolate differs from those of N^3-metallated imidazoles or of free imidazoles [7].

The six-membered $Ir_2(CN)_2$ ring adopts the inverted boat conformation with puckering parameters

TABLE 4. Average bond distances (Å) and angles (deg) with their standard errors *

	N	x_m	σ_m	σ'_m
Ir(1)–N	2	2.071	0.001	0.005
Ir(1)–CO	2	1.854	0.007	0.007
Ir(2)–C	2	2.072	0.015	0.006
Ir(2)–CO	2	1.886	0.006	0.008
C–O[Ir(1)]	2	1.129	0.004	0.010
C–O[Ir(2)]	2	1.125	0.002	0.011
N(1)–C(2)	2	1.359	0.006	0.008
C(2)–N(3)	2	1.341	0.001	0.008
N(3)–C(4)	2	1.402	0.008	0.008
C(4)–C(5)	2	1.342	0.003	0.010
C(5)–N(1)	2	1.380	0.018	0.009
N(1)–C(10)	2	1.470	0.007	0.010
C(10)–C(11)	2	1.513	0.005	0.011
N–Ir(1)–CO[*trans*]	2	176.9	0.1	0.3
N–Ir(1)–CO[*cis*]	2	90.0	0.1	0.3
C–Ir(2)–CO[*trans*]	2	175.5	0.4	0.3
C–Ir(2)–CO[*cis*]	2	92.1	0.2	0.3
Ir(1)–C–O	2	178.2	0.2	0.7
Ir(2)–C–O	2	178.1	0.6	0.8
Ir(1)–N(3)–C(2)	2	123.1	0.7	0.4
Ir(1)–N(3)–C(4)	2	127.9	2.0	0.4
Ir(2)–C(2)–N(3)	2	122.5	0.6	0.4
Ir(2)–C(2)–N(1)	2	130.8	1.5	0.5
C(2)–N(1)–C(5)	2	110.0	0.5	0.5
N(1)–C(2)–N(3)	2	106.6	1.0	0.5
C(2)–N(3)–C(4)	2	108.9	1.2	0.5
N(3)–C(4)–C(5)	2	107.5	0.4	0.6
C(4)–C(5)–N(1)	2	106.9	0.4	0.6
C(2)–N(1)–C(10)	2	125.2	1.8	0.5
C(5)–N(1)–C(10)	2	124.4	0.9	0.6
N(1)–C(10)–C(11)	2	113.2	0.8	0.6
C(10)–C(11)–C[*ortho*]	4	120.5	0.9	0.5

* All values were calculated according to ref. [15].

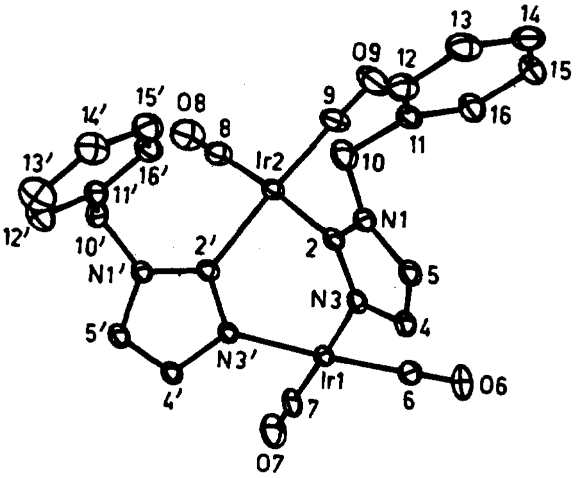
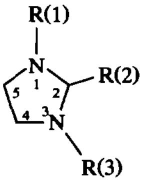


Fig. 2. ORTEP plot of complex 5 with the atom numbering scheme. Thermal ellipsoids enclose 25% of the electron density. Hydrogen atoms are omitted for clarity.

TABLE 5. Comparison of structural features (Å and deg) in some C^2-metallated 1-benzylimidazoles



Compound	a*	b (Ref. 18)	c (Ref. 17)	d (Ref. 1)
R(1)	$CH_2C_6H_5$	$CH_2C_6H_5$	$CH_2C_6H_5$	$CH_2C_6H_5$
R(2)	Ir(2)	Au	Au	Au
R(3)	Ir(1)	COC_6H_5	$COOC_2H_5$	H
N(1)–C(2)	1.359(8)	1.33(2)	1.34(1)	1.34(2)
C(2)–N(3)	1.341(8)	1.38(1)	1.38(1)	1.36(2)
N(3)–C(4)	1.402(8)	1.42(1)	1.39(1)	1.36(2)
C(4)–C(5)	1.342(10)	1.33(1)	1.31(1)	1.36(1)
C(5)–N(1)	1.380(18)	1.40(1)	1.40(1)	1.35(1)
N(1)–R(1)	1.470(10)	1.48(1)	1.46(1)	1.48(1)
C(2)–N(1)–C(5)	110.0(5)	112.1(8)	110.6(8)	111.1(5)
N(1)–C(2)–N(3)	106.6(1.0)	104.4(1.2)	104.5(7)	104.5(4)
C(2)–N(3)–C(4)	108.9(1.2)	109.8(9)	110.0(7)	111.3(8)
N(3)–C(4)–C(5)	107.5(6)	106.3(6)	107.1(8)	106.0(6)
C(4)–C(5)–N(1)	106.9(6)	107.2(6)	107.9(9)	107.0(7)
C(2)–N(1)–R(1)	125.2(1.8)	124.6(8)	126.3(8)	123.2(7)
C(5)–N(1)–R(1)	124.4(9)	123.2(7)	123.1(8)	125.4(1.0)
N(1)–C(2)–R(2)	130.8(1.5)	126.5(9)	127.5(6)	129.5(2.0)
N(3)–C(2)–R(2)	122.5(6)	129.1(1.1)	128.1(6)	125.2(2.0)
C(2)–N(3)–R(3)	123.1(7)	125.0(9)	123.8(7)	
C(4)–N(3)–R(3)	127.9(2.0)	125.2(6)	126.2(8)	

* Weighted average values.

[a] This work.

[b] ClAu$\overline{\text{CN(CH}_2\text{Ph)CH=CHN}}$COPh.

[c] ClAu$\overline{\text{CN(CH}_2\text{Ph)CH=CHN}}$COOEt.

[d] Cl[Au($\overline{\text{CN(CH}_2\text{Ph)CH=CHN}}H)_2$].

[19] $Q = 1.176$, $\theta = 92.7°$, $\phi = 181.8°$ to be compared with $\theta = 90°$ and $\phi = 180°$ for an ideal inverted boat.

The shortest intermolecular approaches between the molecule (x, y, z) and the equivalent ones, $1-x, 1-y, 1-z$ and $1-x, -y, 1-z$, are normal Van der Waals contacts.

3. Experimental section

3.1. Measurements

Elemental analyses were carried out with a Perkin-Elmer 240B microanalyzer. Infrared spectra (range 4000–200 cm^{-1}) were recorded on a Perkin-Elmer 783 spectrophotometer using Nujol mulls between polyethylene sheets or cyclohexane solutions in cells with sodium chloride windows. Abscissa expansion was used in the carbonyl region. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded with benzene or chloroform solutions on Varian XL 200 or Varian UNYT 300 spectrophotometers, using $SiMe_4$ as internal standard. Fast atom bombardment (FAB) mass spectra were recorded on an AUTOSPEC VG spectrometer.

3.2. Syntheses

All preparations were carried out at room temperature under dinitrogen on a vacuum line using Schlenk techniques. Prior to use, solvents were dried, distilled, and stored under dinitrogen. The complexes $[M_2(\mu\text{-}Cl)_2(\text{diolefin})_2]$ were prepared according to literature methods [20–22].

3.2.1. $[M_2(\mu\text{-}Bzim\text{-}N^3,C^2)_2(\text{diolefin})_2]$

[M = Rh, diolefin = cod (**1**), nbd (**2**); M = Ir, diolefin = cod (**3**)] To a solution of *N*-benzylimidazole (235.5 mg, 1.48 mmol) in diethyl ether (25 cm^3) was added dropwise butyllithium (1.6 M in hexane) (1 cm^3, 1.6 mmol). After stirring for 1 h, solid $[M_2(\mu\text{-}Cl)_2(\text{diolefin})_2]$ (0.74 mmol) was added. Stirring was continued for 1 h and then the suspension was evaporated to dryness under vacuum. Addition of methanol (25 cm^3) yielded the expected complexes as microcrystalline orange **1**, **2** or dark-red **3**, which were filtered off, washed with cold methanol (5 cm^3), and vacuum dried.

3.2.2. $[Rh_2(\mu\text{-}Bzim\text{-}N^3,C^2)_2(cod)_2]$

(**1**) Yield 75%. Found: C, 58.5; H, 5.9; N, 7.2. Calc. for $C_{36}H_{42}N_4Rh_2$: C, 58.7; H, 5.7; N, 7.6%.

3.2.3. $[Rh_2(\mu\text{-}Bzim\text{-}N^3,C^2)_2(nbd)_2]$

(**2**) Yield 80%. Found: C 56.7; H, 4.8; N, 7.8. Calc. for $C_{34}H_{34}N_4Rh_2$: C, 57.9; H, 4.9; N, 7.9%.

3.2.4. $[Ir_2(\mu\text{-}Bzim\text{-}N^3,C^2)_2(cod)_2]$

(**3**) Yield 90%. Found: C, 46.8; H, 4.6; N, 6.1. Calc. for $C_{36}H_{42}N_4Ir_2$: C, 47.2; H, 4.6; N, 6.1%.

3.2.5. $[M_2(\mu\text{-}Bzim\text{-}N^3,C^2)_2(CO)_4]$

M = Rh (**4**) and M = Ir (**5**). Dry carbon monoxide was slowly bubbled through a concentrated suspension of $[M_2(\mu\text{-}Bzim\text{-}N^3,C^2)_2(\text{diolefin})_2]$ (0.4 mmol) in deoxygenated diethyl ether (*ca.* 10 cm^3). After 30 min the initially orange (**1**, **2**) or dark-red (**3**) suspensions had become yellow, and hexane (5 cm^3) was added. Bubbling was continued for 2 h and small amounts of hexane were added to complete the crystallization of the yellow tetracarbonyl compounds, which were filtered off, washed with cold hexane (5 cm^3), and vacuum dried.

3.2.6. $[Rh_2(\mu\text{-}Bzim\text{-}N^3,C^2)_2(CO)_4]$

(**4**) Yield 75%. Found: C, 45.1; H, 2.9; N, 8.4. Calc. for $C_{24}H_{18}N_4Rh_2$: C, 45.6; H, 2.9; N, 8.9%. IR (cyclohexane): 1995, 2002, 2050, 2072 cm^{-1} [ν(CO)].

3.2.7. $[Ir_2(\mu\text{-}Bzim\text{-}N^3,C^2)_2(CO)_4]$

(**5**) Yield 90%. Found: C, 35.4; H, 2.3; N, 6.8. Calc. for $C_{24}H_{18}N_4Ir_2$: C, 35.5; H, 2.2; N, 6.9%. IR (cyclohexane): 1982, 1992, 2040, 2060 cm^{-1} [ν(CO)].

3.3. X-Ray analysis, structure determination and refinement

A suitable crystal was used for data collection. Accurate unit-cell dimensions were obtained by a least-squares fit of 2θ values for 25 reflections and the triclinic nature of the unit-cell was confirmed by the TRACER program [23].

The intensities of three standard reflections monitored every 180 min showed only random variations. The intensities were corrected for Lorentz and polarization effects and for absorption [24] with minimum and maximum absorption factors of 0.9902 and 4.0464 respectively.

An approximate absolute scale and a mean thermal factor of 4.08 Å^2 were determined by Wilson's method [25]. Table 6 summarizes crystal data and details of the structure analysis.

The reflections having $I \geqslant 3\sigma\ (I)$ were considered as observed and employed in the calculations.

The structure was solved by standard Patterson and Fourier methods. The positions of the two iridium

TABLE 6. Crystal data. Data collection, and refinement of the structure

Formula	$C_{24}H_{18}N_4O_4Ir_2$
Formula weight	810.9
space group	*P*-1
colour	yellow
a, Å	10.973(5)
b, Å	11.280(4)
c, Å	10.697(5)
α, deg	111.04(2)
β, deg	104.29(2)
γ, deg	87.38(2)
V_c, Å^3	1196.2(9)
Z	2
Dcalcd, gcm^{-3}	2.25
cryst. size, mm	0.13×0.16×0.32
μ(Mo Kα), cm^{-1}	117.9
data collcn instrument	Philips PW 1100
radiation (monochromated)	MoKα (λ = 0.7107 Å)
scan mode	$\theta/2\theta$
scan speed, deg s^{-1}	0.02
scan width, deg	1.2
data collcn range	$2 < \theta < 28$
no. of unique reflcns measd	57765 ($\pm h$, $\pm k$, l)
no. of data with $F_o^2 > 3\sigma(F_o^2)$	4611
no. of param refined	307
R^a and R_w^b	0.037, 0.047

[a] $R = (\Sigma \| F_o | - k | F_c \|)/\Sigma | F_o |$.

[b] $R_w = [\Sigma w(| F_o | - k | F_c |)^2 / \Sigma_w | F_o |^2]^{1/2}$.

TABLE 7. Final coordinates and equivalent isotropic thermal parameters (with e.s.d.'s in parentheses)

Atom	x	y	z	B (Å^2)
Non-hydrogen atoms				
Ir(1)	0.42526(3)	0.14903(3)	0.44067(3)	2.70(1)
Ir(2)	0.73610(3)	0.18689(3)	0.40321(4)	2.88(1)
N(1)	0.6849(7)	0.4575(7)	0.6002(7)	3.1(2)
C(2)	0.6481(8)	0.3334(8)	0.5220(8)	2.9(2)
N(3)	0.5364(7)	0.3153(7)	0.5443(7)	3.1(2)
C(4)	0.5026(9)	0.4282(9)	0.6381(9)	3.5(2)
C(5)	0.5948(9)	0.5170(8)	0.6714(9)	3.3(2)
C(6)	0.4043(9)	0.1497(9)	0.6071(10)	3.7(3)
O(6)	0.3931(8)	0.1529(8)	0.7107(7)	5.5(3)
C(7)	0.3237(10)	0.0015(10)	0.3392(9)	4.1(3)
O(7)	0.2597(10)	−0.0854(9)	0.2768(9)	7.0(3)
C(8)	0.8032(10)	0.0446(10)	0.2891(11)	3.9(3)
O(8)	0.8395(9)	−0.0427(8)	0.2201(11)	6.8(4)
C(9)	0.8771(10)	0.2070(11)	0.5538(12)	4.7(4)
O(9)	0.9597(9)	0.2192(11)	0.6449(10)	7.9(4)
C(10)	0.7935(11)	0.5228(10)	0.5895(11)	4.6(3)
C(11)	0.8641(8)	0.6167(9)	0.7283(9)	3.4(3)
C(12)	0.9041(10)	0.7331(10)	0.7333(12)	4.3(3)
C(13)	0.9734(11)	0.8205(11)	0.8585(15)	5.5(4)
C(14)	1.0024(11)	0.7936(15)	0.9741(15)	6.9(5)
C(15)	0.9628(12)	0.6762(16)	0.9704(13)	6.5(5)
C(16)	0.8940(11)	0.5888(11)	0.8458(11)	4.6(4)
N(1′)	0.5614(7)	0.1741(7)	0.1191(7)	2.9(2)
C(2′)	0.5733(8)	0.1720(8)	0.2474(9)	2.9(2)
N(3′)	0.4576(6)	0.1550(6)	0.2602(7)	2.6(2)
C(4′)	0.3722(9)	0.1463(9)	0.1364(9)	3.3(3)
C(5′)	0.4374(9)	0.1583(9)	0.0507(9)	3.4(3)
C(10′)	0.6623(10)	0.1948(9)	0.0607(9)	3.8(3)
C(11′)	0.6955(9)	0.3331(9)	0.0951(9)	3.2(3)
C(12′)	0.6467(12)	0.3927(12)	0.0020(12)	5.1(4)
C(13′)	0.6789(14)	0.5186(13)	0.0332(15)	6.1(5)
C(14′)	0.7615(12)	0.5873(11)	0.1564(13)	4.9(4)
C(15′)	0.8094(11)	0.5286(11)	0.2464(12)	4.9(4)
C(16′)	0.7797(10)	0.4014(10)	0.2176(10)	3.9(3)

atoms were determined from a three-dimensional Patterson map. A difference electron density synthesis phased on the Ir atoms revealed the positions of all the non-hydrogen atoms. The structure was refined by full-matrix least-squares methods, using first isotropic and later anisotropic thermal parameters. Hydrogen atoms were located from a difference synthesis and checked through the geometry of the compound. The least-squares refinement continued, including the hydrogen atoms in fixed positions with the same isotropic thermal factors of their parent atoms. In the early stages of analysis the observed reflections were given unit weights, in the last three cycles weights $w = \sigma^{-2}$ ($[F_o]$) was applied.

The atomic scattering factors for non-hydrogen atoms were taken from ref. [26] and those for hydrogen atoms from ref. [27]. Anomalous dispersion effects were included in the scattering factors.

Final atomic coordinates and isotropic equivalent thermal parameters for non-hydrogen atoms are given in Table 7.

Tables of thermal parameters, hydrogen atom positions, bond lengths and angles for H atoms are available from the Cambridge Crystallographic Data Centre and a list of structure factors can be obtained from B. Bovio on request.

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