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Rhodium complexes containing bidentate imidazolyl ligands: synthesis and structure

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Abstract

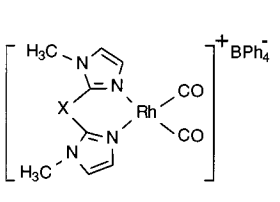
The preparation and characterisation of square planar cationic rhodium(I) dicarbonyl complexes $\{[Rh((mim)_2C{=}O)(CO)_2]^+BPh_4^-\}$ (**1**), $\{[Rh((mim)_2CH_2)(CO)_2]^+BPh_4^-\}$ (**2**) and $\{[Rh((mBnzim)_2CH_2)(CO)_2]^+BPh_4^-\}$ (**3**) [mim = *N*-methylimidazol-2-yl, mBnzim = *N*-methylbenzimidazol-2-yl] is reported. The carbonyl ligands in **2** and **3** are readily exchanged for triphenylphosphine to form $\{[Rh((mim)_2CH_2)(PPh_3)_2]^+BPh_4^-\}$ (**7**) and $\{[Rh((mBnzim)_2CH_2)(PPh_3)_2]^+BPh_4^-\}$ (**8**). Complexes **2** and **3** were characterised by multinuclear NMR spectroscopy as well as by X-ray crystallography. Structural characterisation by X-ray analysis confirmed that complexes **2** and **3** are essentially square planar.

Keywords: Bisimidazolylmethane; Carbonyl; Ligand exchange; NMR; Rhodium

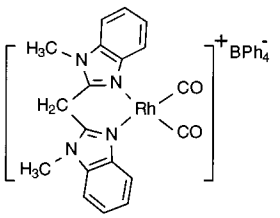
1. Introduction

Bidentate nitrogen-based ligands containing sp^2 hybridized nitrogen donors have been used in a variety of transition metal complexes [1–8], however, few Rh(I) complexes are known. Some of the earliest work using bidentate nitrogen donor ligands on rhodium involved the aromatic compound 1,10-phenanthroline (PHEN) as a ligand and Rh(I) complexes of PHEN have been tested for their biological activity in interfering with cell division in bacteria [1]. In the late 1970s and early 1980s rhodium and iridium complexes of 2,2′-bipyridyl (BIPY) and PHEN were prepared [2,3] and emerged as promising catalysts for a number of homogeneous reactions such as transfer hydrogenation [4]. The success of simple nitrogen donor ligands in rhodium and iridium complexes has meant that complexes containing BIPY and PHEN ligands and their chiral variants [5] have been explored in some depth. In 1984 Brunner et al. [6]. reported the synthesis of an extensive range of bidentate ligands derived from optically active primary amines, amino acids and amino acid derivatives and it was shown that rhodium and platinum complexes containing these ligands catalysed the enantioselective hydrosilation of ketones [7]. More recently, rhodium complexes containing a range of polypyridine ligands have been prepared and the catalytic activity of these complexes in the water gas shift reaction has been explored [8].

To date, there have been few reports of the synthesis of rhodium complexes containing imidazolyl ligands and, in general, details of catalytic activity have not been reported. One neutral complex containing an *N*-methylimidazolyl ligand [9] {Rh(*N*-methylimidazolyl)$(CO)_2Cl$} and analogues containing a variety of *N*-donor heterocyclic ligands $[RhL(CO)_2Cl]$, L = phenazine, quinoxaline and 1,2,4-triazole) have been patented [9]. These complexes are active catalysts for hydrosilation reactions in the formation of siloxane polymer gels.



1 X = CO
2 X = CH_2



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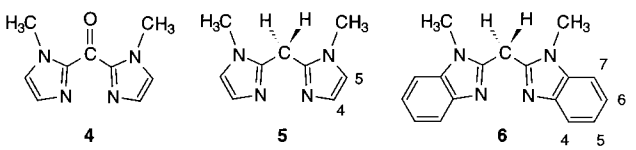
In this paper we report the synthesis and characterisation of the square planar cationic rhodium(I) dicarbonyl complexes $\{[Rh((mim)_2C{=}O)(CO)_2]^+BPh_4^-\}$ (**1**), $\{[Rh((mim)_2CH_2)(CO)_2]^+BPh_4^-\}$ (**2**) and $\{[Rh((mBnzim)_2CH_2)(CO)_2]^+BPh_4^-\}$ (**3**) [mim = *N*-methylimidazol-2-yl, mBnzim = *N*-methylbenzimidazol-2-yl]. The complexes were prepared by the reaction of the bidentate imidazolyl ligands $(mim)_2C{=}O$ (**4**), $(mim)_2CH_2$ (**5**) and $(mBnzim)_2CH_2$ (**6**) with $[Rh_2(CO)_4(Cl)_2]$. The square planar dicarbonyl complexes **2** and **3** were characterised by X-ray crystallography, and all complexes **1**–**3** were fully characterised by high-field NMR spectroscopy.

2. Discussion

2.1. Preparation of $(mim)_2C{=}O$ (4), $(mim)_2CH_2$ (5) and $(mBnzim)_2CH_2$ (6)

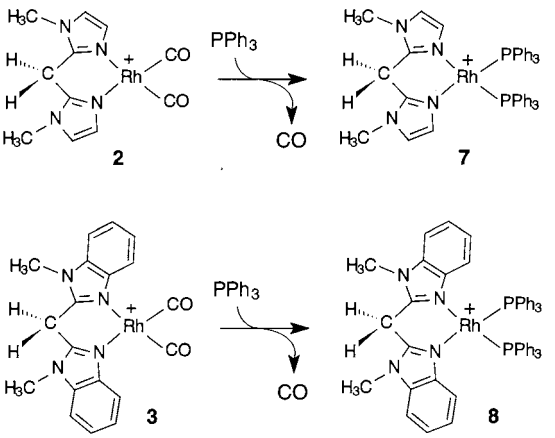
The bidentate ligands $(mim)_2C{=}O$ (**4**) and $(mim)_2CH_2$ (**5**), used in the preparation of $\{[Rh((mim)_2C{=}O)(CO)_2]^+BPh_4^-\}$ (**1**) and $\{[Rh((mim)_2CH_2)(CO)_2]^+BPh_4^-\}$ (**2**), were prepared by a previously reported method [10]. The ligand $(mBnzim)_2CH_2$ (**6**) used in the preparation of $\{[Rh((mBnzim)_2CH_2)(CO)_2]^+BPh_4^-\}$ (**3**) was prepared by two independent methods: (i) by reduction of bis(*N*-methylbenzimidazol-2-yl)ketone, $(mBnzim)_2C{=}O$ (**9**) with hydrazine under basic conditions; (ii) by the condensation of diethylmalonate with *N*-methyl-1,2-phenylenediamine.



2.2. Preparation of rhodium complexes containing the bidentate ligands $(mim)_2C{=}O$ (4), $(mim)_2CH_2$ (5) and $(mBnzim)_2CH_2$ (6)

The rhodium(I) dicarbonyl complexes $\{[RhL(CO)_2]^+BPh_4^-\}$ (where $L = (mim)_2C{=}O$, $(mim)_2CH_2$ and $(mBnzim)_2CH_2$) were readily prepared by the addition of the bidentate ligands $(mim)_2C{=}O$, $(mim)_2CH_2$ and $(mBnzim)_2CH_2$, respectively to methanol solutions of $[Rh_2(CO)_4(Cl)_2]$. Addition of $NaBPh_4$ precipitated the complexes $\{[Rh((mim)_2C{=}O)(CO)_2]^+BPh_4^-\}$ (**1**), $\{[Rh((mim)_2CH_2)(CO)_2]^+BPh_4^-\}$ (**2**) and $\{[Rh((mBnzim)_2CH_2)(CO)_2]^+BPh_4^-\}$ (**3**) in high yield.

When triphenylphosphine was added to a solution of **2** or **3** in acetone, bubbles of CO were immediately observed. The carbonyl ligands in complexes **2** and **3** are labile and undergo facile exchange with PPh_3 to form $\{[Rh((mim)_2CH_2)(PPh_3)_2]^+BPh_4^-\}$ (**7**) and $\{[Rh((mBnzim)_2CH_2)(PPh_3)_2]^+BPh_4^-\}$ (**8**), respectively (Scheme 1).



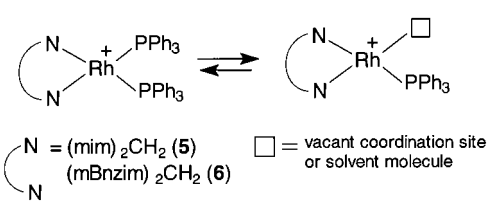
Scheme 1.

The ^1H- and $^{31}P\{^1H\}$-NMR spectra of $\{[Rh(mim)_2CH_2(PPh_3)_2]^+BPh_4^-\}$ (**7**) and $\{[Rh((mBnzim)_2CH_2)(PPh_3)_2]^+BPh_4^-\}$ (**8**) contain broad resonances at room temperature (r.t.).

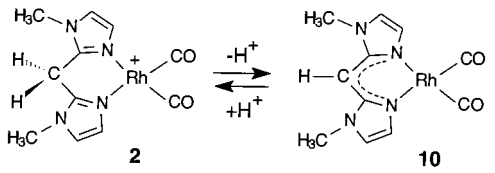
The $^{31}P\{^1H\}$-NMR spectrum (acetone-d_6, 300K) of **7** contains a broad singlet ($W_{1/2} = 880$ Hz). At low temperature (233 K), the single ^{31}P resonance appears as a broad doublet with a phosphorus–rhodium coupling constant $^1J_{Rh-P} = 116$ Hz. The $^{31}P\{^1H\}$-NMR spectrum (acetone-d_6) of **8** contains a broad singlet at 32.2 ppm ($W_{1/2} = 430$ Hz). At low temperature (243 K) the ^{31}P signal of **8** appears as a doublet at 32.2 ppm with a phosphorus–rhodium coupling constant $^1J_{Rh-P} = 125$ Hz.

The broadness of the resonances in the NMR spectra of **7** and **8** at r.t. is probably due to an equilibrium involving reversible dissociation of one of the triphenylphosphine ligands from the metal centre. This would form a three-coordinate species or a four-coordinate species where a solvent molecule is coordinated in place of a triphenylphosphine ligand (Scheme 2). This type of equilibrium has been reported previously for a number of related metal complexes [11].

The protons of the methylene group joining the imidazolyl rings in **2**, **3**, **7** and **8** are readily exchanged for deuterium in acetone-d_6 or methanol-d_4 once coordinated to the metal centre. The exchange is probably



Scheme 2.



Scheme 3.

due to the facile, reversible, deprotonation of the methylene bridge to give the neutral complex **10** (Scheme 3).

2.3. X-ray structure of $\{[Rh((mim)_2CH_2)(CO)_2]^+BPh_4^-\}$ (2)

The solvated complex $\{[Rh(mim)_2CH_2(CO)_2]^+BPh_4^-\}$ (0.5 acetone) crystallised from acetone as yellow plates that were suitable for X-ray crystallographic analysis. Two crystallographically independent molecules were located in the asymmetric unit and ORTEP [12] plots of the cations $\{[Rh((mim)_2CH_2)(CO)_2]^+\}$ are shown in Fig. 1 and selected bond lengths and angles for the inner coordination sphere are listed in Tables 1 and 2, respectively.

The two independent complexes are in close contact, with a Rh1(a)–Rh(1b) separation of 3.5197(4) Å. The rhodium centre of complex B is 3.41 Å above the coordination plane of complex A, and Rh(1a) is 3.50 Å away from the coordination plane of complex B. The N(1a)–N(2a)–C(1a)–C(2a) and N(1b)–N(2b)–C(1b)–C(2b) least-squares coordination planes are almost parallel, with an interplane dihedral angle of 7°. The coordination planes of the two complexes are slightly offset by approximately 0.7 Å (assuming parallel planes and an interplanar separation of 3.45 Å). The two complexes have a relative rotation about the Rh(1a)–Rh(1b) axis of 71.5(2), such that the carbonyl carbon of complex A (C(2a)) is 3.530(6) Å from the carbonyl carbon of complex B (C(1b)), and the carbonyl C(2b) is 3.635(5) Å away from the imidazolyl nitrogen of complex A (N(1a)). Both complexes have square planar coordination. Deviations from the least squares plane defined by N(1a)–N(2a)–C(1a)–C(2a) range between 0.044(3) and 0.115(4) Å, and the deviations from the least squares plane defined by N(1b)–N(2b)–C(1b)–C(2b) range between 0.041(3) and 0.103(4) Å. The rhodium metal centres are contained within their respective coordination planes. The Rh1a deviation from the N(1a)–N(2a)–C(1a)–C(2a) plane is 0.04 Å, and the Rh(1b) deviation from the N(1b)–N(2b)–C(1b)–C(2b) plane is 0.05 Å.

There may be a stacking interaction between the imidazolyl residues of the two molecules in the asymmetric unit and also between imidazolyl residues of the complexes and the phenyl residues of the associated tetraphenylborate counter ions. In particular, the N(2a)–C(9a) imidazolyl residue of complex A appears to have an offset stacking interaction with the N(1b)–C(5b) residue of complex B. The dihedral angle between the least squares planes of the imidazolyl residues of complexes A and B is 7°. Atom N(2b) is only 3.319(4) Å from C(9a) and C(3b) is 3.572(5) Å from C(5a), whereas C(6a) is 3.777(6) Å from C(3b). Presumably, the stacking interaction is responsible for the pairing of the complexes in the solid state. There appears to be weak hydrogen bonding between the acetone solvate and the two independent complexes. The O(3)–C(8a) distance is 3.350(5) Å and the O(3)–C(11b) distance is 3.447(6) Å.

2.4. X-ray structure of $\{[Rh((mBnzim)_2CH_2)(CO)_2]^+BPh_4^-\}$ (3)

The complex $\{[Rh((mBnzim)_2CH_2)(CO)_2]^+BPh_4^-\}$ (**3**) was readily recrystallised from acetone to give clear

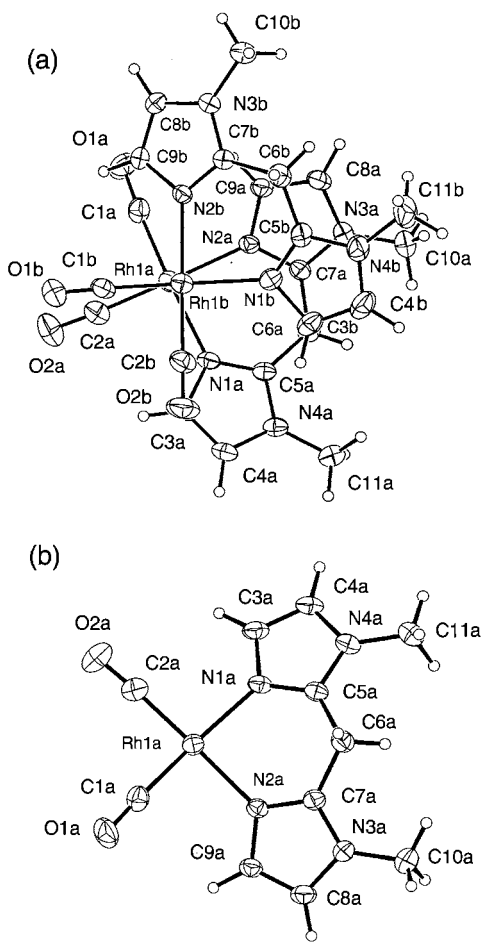


Fig. 1. ORTEP plot and crystal structure numbering of $\{[Rh(mim)_2CH_2(CO)_2]^+$, 25% thermal ellipsoids are shown for the non-hydrogen atoms; hydrogen atoms have an arbitrary radius 0.1 Å. (a) Stacking of the two independent complexes viewed from above. (b) A single cation with crystal structure numbering.

Table 1
Selected bond distances (Å) for {[Rh((mim)$_2$CH$_2$)(CO)$_2$]$^+$BPh$_4^-$} (**2**) and {[Rh((mBnzim)$_2$CH$_2$)(CO)$_2$]$^+$BPh$_4^-$} (**3**) [a]

Atoms	Bond distances (Å)
*{[Rh((mim)$_2$CH$_2$)(CO)$_2$]$^+$BPh$_4^-$} (**2**)*	
Rh(1a)–N(1a)	2.071(3)
Rh(1b)–N(1b)	2.055(3)
Rh(1a)–N(2a)	2.048(3)
Rh(1b)–N(2b)	2.063(3)
Rh(1a)–C(1a)	1.847(4)
Rh(1b)–C(1b)	1.840(4)
Rh(1a)–C(2a)	1.840(4)
Rh(1b)–C(2b)	1.854(4)
*{[Rh((mBnzim)$_2$CH$_2$)(CO)$_2$]$^+$BPh$_4^-$} (**3**)*	
Rh(1)–N(1)	2.069(6)
Rh(1)–N(2)	2.066(5)
Rh(1)–C(1)	1.79(1)
Rh(1)–C(2)	1.846(8)

[a] Estimated S.D.s in the least significant figure are given in parentheses.

colourless plates of the solvated complex {[Rh((mBnzim)$_2$CH$_2$)(CO)$_2$]$^+$BPh$_4^-$} (1.0 acetone). An ORTEP plot of the cation [Rh((mBnzim)$_2$CH$_2$)(CO)$_2$]$^+$ is shown in Fig. 2 and the bond lengths and angles for the inner coordination sphere are listed in Tables 1 and 2, respectively.

Complex **3** has square planar coordination. Deviations from the least squares plane defined by N(1)–N(2)–C(1)–C(2) range between 0.35(5) and 0.097(8) Å. The rhodium metal centre is contained within its coordination plane, with a deviation of only 0.04 Å from the plane N(1)–N(2)–C(1)–C(2). In contrast to the structure of {[Rh((mim)$_2$CH$_2$)(CO)$_2$]$^+$BPh$_4^-$} (**2**), there appears to be no interaction

Table 2
Selected bond angles (°) for {[Rh((mim)$_2$CH$_2$)(CO)$_2$]$^+$BPh$_4^-$} (**2**) and {[Rh((mBnzim)$_2$CH$_2$)(CO)$_2$]$^+$BPh$_4^-$} (**3**) [a]

Atoms	Bond angles (°)
*{[Rh((mim)$_2$CH$_2$)(CO)$_2$]$^+$BPh$_4^-$} (**2**)*	
N(1a)–Rh(1a)–N(2a)	87.6(1)
N(1b)–Rh(1b)–N(2b)	87.1(1)
N(1a)–Rh(1a)–C(2a)	93.5(1)
N(1b)–Rh(1b)–C(2b)	91.7(2)
N(2a)–Rh(1a)–C(1a)	90.1(1)
N(2b)–Rh(1b)–C(1b)	93.6(1)
C(1a)–Rh(1a)–C(2a)	89.1(2)
C(1b)–Rh(1b)–C(2b)	87.8(2)
*{[Rh((mBnzim)$_2$CH$_2$)(CO)$_2$]$^+$BPh$_4^-$} (**3**)*	
N(1)–Rh(1)–N(2)	85.8(2)
N(1)–Rh(1)–C(2)	95.3(3)
N(2)–Rh(1)–C(1)	92.9(3)
C(2)–Rh(1)–C(1)	86.2(4)

[a] Estimated S.D.s in the least significant figure are given in parentheses.

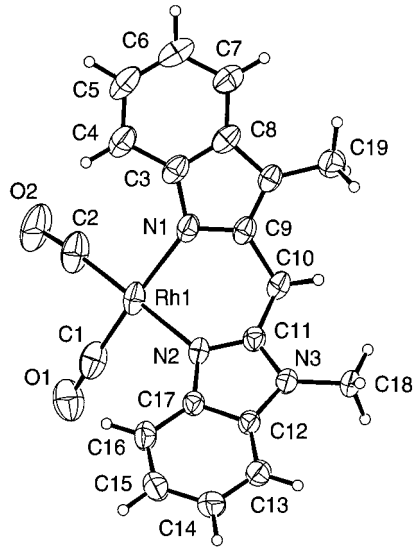


Fig. 2. ORTEP plot and crystal structure numbering of [Rh((mBnzim)$_2$CH$_2$)(CO)$_2$]$^+$, 25% thermal ellipsoids are shown for the non-hydrogen atoms; hydrogen atoms have an arbitrary radius 0.1 Å. The complex is viewed from above.

between the metal complex **3** and the solvent of crystallisation (acetone) or between the imidazolyl residues of the complexes and the phenyl residues of the associated tetraphenylborate counterion.

The solid state structures of complexes {[Rh((mim)$_2$CH$_2$)(CO)$_2$]$^+$BPh$_4^-$} (**2**) and {[Rh((mBnzim)$_2$CH$_2$)(CO)$_2$]$^+$BPh$_4^-$} (**3**) are very similar — both complexes are essentially square planar about the metal centre. In each molecule, there is a plane of symmetry that bisects the ligand N–Rh–N bite angle and the metal centre. The bite angles of the bidentate imidazolyl ligands are small, with the angle between the N–Rh–N bonds of 87.6(1) Å and 87.1(1) Å in complex **2** and 85.8(2) Å in complex **3**.

Only a small number of rhodium complexes containing bidentate nitrogen-based ligands with sp^2 hybridized donor atoms have been studied crystallographically [13]. The rhodium–nitrogen bond lengths of complexes directly comparable to **2** and **3** range between 2.033(5) and 2.111(8) Å. The Rh–N bond lengths are between 2.048(3) and 2.071(3) Å in complex **2** and 2.066(6) and 2.069(6) Å in complex **3** (Table 3). The rhodium carbonyl bond lengths for complexes comparable to **2** and **3** that appear in the literature [13] range between 1.848(5) Å and 1.868(7) Å (Table 3). The Rh–CO bond lengths in **2** are similar at 1.840(4) and 1.854(4) Å, however, in complex **3**, the carbonyl bond lengths differ slightly with Rh(1)–(C1) and Rh(1)–C(2) being 1.78(1) and 1.846(8) Å, respectively and C(1)–O(1) and C(2)–O(2) are 1.17(1) and 1.130(8) Å, respectively. The Rh–N distances in **3** are equivalent and there are no unusual contacts with C(1) that might otherwise explain the slightly shorter Rh–C(1) bond

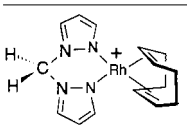
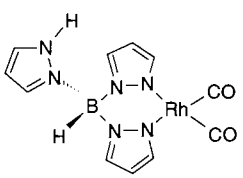
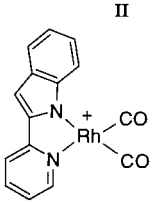
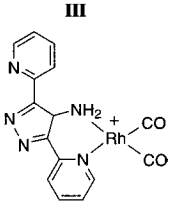
and the slightly longer Rh–C(2) bond. The angle between the two carbonyl ligands is only slightly smaller than 90° for both **2** and **3**, being 89.1(2) and 87.8(2)° in complex **2** and 86.2(4)° in complex **3**. The smaller angle in **3** is the result of carbonyl contact with the bulkier benzimidazolyl ligand. The C(1) to C(16) distance is 3.24(1) Å and the C(2) to C(4) distance is 3.22(1) Å. The coordination of the bidentate ligand to the metal is not symmetrical with respect to the carbonyl ligands. The N(2)–Rh(1)–C(1) angle is 92.9(3)° and the N(1)–Rh(1)–C(2) angle is 95.3(3)°. C(1) and C(2) are on opposite sides of the least squares coordination plane, with C(1) being displaced 0.087(8) Å from the plane away from the ligand and C(2) being displaced 0.096(8) Å towards the bidentate ligand.

3. Conclusions

The cationic rhodium complexes $\{[Rh(mim)_2C{=}O(CO)_2]^+BPh_4^-\}$ (**1**), $\{[Rh(mim)_2CH_2(CO)_2]^+BPh_4^-\}$ (**2**) and $\{[Rh((mBnzim)_2CH_2)(CO)_2]^+BPh_4^-\}$ (**3**) have been synthesised in good yield. Complexes **2** and **3** have been structurally characterised by X-ray analysis, confirming that the complexes are essentially square planar. The protons of the methylene group joining the imidazolyl rings in **2**, **3**, **7** and **8** readily undergo exchange in deuterated solvents once coordinated to the metal centre. The methylene protons exchange readily for deuterium in methanol-d_4 and acetone-d_6.

The carbonyl ligands in $[RhL(CO)_2]^+$ are labile and can be exchanged for triphenylphosphine to form $[RhL(PPh_3)_2]^+$ **7** and **8**. These complexes have broad resonances in the ^{31}P- and ^1H-NMR spectra at r.t., which is probably due to reversible dissociation of one of the triphenylphosphine ligands from the metal centre.

Table 3
Comparison of Rh–N and Rh–C (C of CO) bond lengths of previously reported Rh complexes with dinitrogen ligands [a]

	Rh–N bond lengths (Å)	Rh–C bond lengths (Å)
 I	2.111(8) 2.097(7)	
 II	2.070(4) 2.093(4)	1.848(5) 1.867(6)
 III	2.103(5) 2.040(5)	1.866(7) 1.868(7)
 IV	2.094(5) 2.033(5)	1.848(6) 1.864(9)

[a] Ligands used: $\{[Rh(COD)(CH_2(Pz)_2)]ClO_4{\cdot}1/2C_2H_4Cl_2$ (**I**) [13a]; $\{[Rh\{\eta^2\text{-}HBPz^*_2(Pz^*H)](CO)_2\}{\cdot}\{BF_4\}$ (**II**) [13b]; $[Rh(CO)_2(indolato)]$ (**III**) [13c]; $[Rh(CO)_2(NH_2bpt)][ClO_4]$ (**IV**) [13d].

4. Experimental

All manipulations of metal complexes and air-sensitive reagents were carried out using standard Schlenk or vacuum techniques [14], or in a Vacuum Atmospheres argon-filled drybox. Rhodium(III) trichloride hydrate was obtained from Aldrich or Johnson Matthey and was used without further purification. *n*-Butyllithium was used as a solution in hexane (approximately 2.4 M) as supplied by Aldrich and was titrated immediately prior to use against 2,5-dimethoxybenzyl alcohol [15]. Tetrahydrofuran and toluene were stored over sodium wire and were distilled under nitrogen immediately prior to use from sodium benzophenone ketyl. Acetone was dried over and distilled from anhydrous calcium sulfate.

All bulk compressed gases were obtained from British Oxygen Company (BOC Gases). Argon (> 99.99%), nitrogen (> 99.5%) were used as supplied without further purification. Mass spectra of organic compounds were recorded on a KRATOS MS9/MS50 double focussing mass spectrometer with an acceleration voltage of 8000 V and using electron impact ionisation (EI) with a source temperature of 150–350°C and an electron energy of 70 eV. Mass spectra of organometallic complexes were recorded on a VG Quattro mass spectrometer (VG Biotech, Altricham, UK). Data are quoted in the form $x(y)$, where x is the mass/charge ratio and y is the percentage abundance relative to the base peak. In the case of organometallic complexes in which the overall mass spectrum was dominated by that of the ligands, mass spectra were recorded scanning mass ranges greater than that of the free ligand, typically $m/z = 250$. Peaks with low intensity are not quoted unless deemed significant. Micro analyses were carried out at the Micro Analysis Facility at the University of New South Wales, Sydney. IR

Table 4
Crystallographic data for $\{[Rh((mim)_2CH_2)(CO)_2]^+BPh_4^-\}$ (**2**) and $\{[Rh((mBnzim)_2CH_2)(CO)_2]^+BPh_4^-\}$ (**3**)

	$\{[Rh((mim)_2CH_2)(CO)_2]^+BPh_4^-\}\cdot 0.5$ acetone (**2**)	$\{[Rh((mBnzim)_2CH_2)(CO)_2]^+BPh_4^-\}\cdot$acetone (**3**)
Empirical formula	$C_{36.50}H_{35.0}BN_{4.0}O_{2.50}Rh$	$C_{46.0}H_{42.0}BN_{4.0}O_{3.0}Rh$
Formula weight (g mol^{-1})	683.42	812.58
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (# 14)	$P2_1/n$ (# 14)
Unit cell dimensions		
a (Å)	22.182(3)	13.104(3)
b (Å)	11.362(2)	17.935(4)
c (Å)	28.051(6)	17.365(4)
β (°)	112.04(2)	96.32(2)
V (Å^3)	6553(2)	4056(2)
Z	8	4
D_{calc} (g cm^{-3})	1.385	1.330
$F(000)$	2816.00	1680.0
$2\theta_{max}$ (°)	49.9	44.9
hkl range	$-26\rightarrow 24$, $0\rightarrow 13$, $0\rightarrow 33$	$-14\rightarrow 14$, $-1\rightarrow 19$, $-1\rightarrow 18$
Number of reflections measured (N)	12091	6578
Unique number of reflections (N_0)	11827 ($R_{merge}=0.018$)	5843 ($R_{merge}=0.028$)
No. observations ($I>2.50\sigma>(I)$)	7938	3245
Wavelength Mo–K$_\alpha$ (cm^{-1})	5.60	4.65
R [a]	0.036	0.049
wR [a]	0.022	0.044
Max. transmission	0.95	0.89
Min. transmission	0.99	0.97
Residual extrema (e Å^{-3})	−0.34, 0.38	−0.57, 0.54

[a] $R=\Sigma(|F_o|-|F_c|)^2/\Sigma|F_o|$; $wR=(\Sigma\, w(|F_o|-|F_c|)^2/\Sigma\, w|F_o|^2)^{1/2}$; $w=1/\sigma^2(F_o)$.

spectra were recorded on a Perkin–Elmer 1600 series FTIR spectrophotometer. Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected.

$CDCl_3$ was used as supplied, acetone-d_6 was dried over and distilled from P_2O_5. All NMR solvents used on air sensitive compounds were degassed by at least three freeze–pump–thaw cycles before being distilled under high vacuum prior to use. ^{1}H-, ^{31}P- and ^{13}C-NMR, spectra were obtained on a Bruker AMX400 at 300K unless otherwise stated. ^{1}H and ^{13}C-NMR spectra are referenced to residual solvent resonances. ^{31}P-NMR spectra are referenced to external neat trimethyl phosphite taken as 140.85 ppm at the temperature quoted. $(mim)_2CH_2$ (**5**) was prepared by a method described previously [10]. Tetracarbonyldichlorodirhodium ($Rh_2(CO)_4Cl_2$) was synthesised by the procedure described by Cleverty and Wilkinson [16].

4.1. X-ray data collection

All measurements were made at 21 ± 1°C on an Enraf–Nonius CAD4 diffractometer with graphite monochromated Mo–K$_\alpha$ radiation. The crystallographic data are given in Table 4. All calculations were performed using the TEXSAN [17] crystallographic software package of Molecular Structure Corporation. Neutral atom scattering factors were taken from Cromer and Waber [18]. Anomalous dispersion effects were included in F_{calc} [19], the values for f' and f'' were those of Creagh and McAuley [20]. The values for the mass attenuation coefficients are those of Creagh and Hubbell [21].

4.2. Synthesis of bis(N-methylbenzimidazol-2-yl)ketone, (mBnzim)C=O, (9)

n-Butyllithium (54.0 mmol) was added to a stirred solution of *N*-methylbenzimidazole (8.25 g, 62.5 mmol) in THF (100 ml) at −78°C under nitrogen. The colour of the solution became bright red on addition of the base and the mixture was stirred at −78°C for 2 h. Diethyl carbonate (3 ml, 25 mmol) was added and the colour of the solution changed to yellow. The solution was allowed to warm to −40°C over several hours, quenched by addition of solid carbon dioxide and then allowed to warm to r.t. Water (100 ml) was added and the solution was extracted into ethyl acetate (600 ml) in a continuous liquid–liquid extractor for 16 h. The solvent was removed under vacuum to give a cream coloured residue which was extracted into chloroform. The solvent was removed under vacuum to give a brown oil which crystallised on addition of acetone (ca. 10 ml). The ketone $(mBnzim)_2C{=}O$ (**9**) was obtained as cream coloured needles (1.07 g, 26%). M.p. 167–169°C (see Ref. [22]. 190–191°C). ^{1}H-NMR (400 MHz,

$CDCl_3$): δ 7.99–7.97 (m, 1H, **H6**), 7.48–7.44 (m, 2H, **H4** and **H7**), 7.39–7.35 (m, 1H, **H5**), 4.14 (s, 3H, N–C**H**$_3$). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$): δ 179.6 (C=O), 147.5, 143.1, 137.5 (**C2**, **C3a** and **C7a**), 126.9, 124.4, 123.6, 110.9 (**C4**, **C5**, **C6** and **C7**), 32. 7 (N–**C**H$_3$). MS *m/z* (%): 291 (20, ($M+1^+$), 290 (77, M^+), 275 (11), 173 (10), 160 (10), 159 (30), 149 (14), 148 (13), 147 (14), 146 (100), 145 (25), 133 (14), 132 (40), 133 (33), 104 (11), 77 (24), 57 (19), 51 (11), 45 (23), 43 (30), 41 (16).

4.3. Synthesis of bis(N-methylbenzimidazol-2-yl)methane, $(mBnzim)_2CH_2$ (6)

4.3.1. Method I

The compound (mBnzim)CH_2 (**6**) was prepared using a method analogous to that of Byers and Canty for the synthesis of (mim)CH_2 [23]. The ketone $(mBnzim)_2C$=O **9** (2.0 g, 15 mmol) was placed in a glass-sleeved reaction bomb with hydrazine hydrate [24] (4.0 ml, 77 mmol) and sodium hydroxide (0.60 g, 15 mmol). The vessel was sealed and heated to 140°C for 4 h, after which time the vessel was cooled to r.t. and opened carefully. The product was extracted into acetone and the solvent removed to yield (mBnzim)CH_2 (**6**) as a cream solid (0.37 g, 19%). M.p. 206.5–208.5°C.

4.3.2. Method II

(mBnzim)CH_2 (**6**) was synthesised using a modification of the method described by Arnold et al. [25]. A solution of *N*-methyl-1,2-phenylenediamine (11.3 g, 92.6 mmol) in 1,6-dichlorotoluene (50 ml) was heated to 170°C in a flask equipped with an azeotroping (Dean–Stark) head. Diethyl malonate (7.40 g, 46.3 mmol) was added drop-wise over 90 min. The temperature gradually increased to 185°C during the addition and was maintained at 185–190°C for 2 h, during which time volatile materials (ethanol and water) were collected. The mixture was allowed to cool to r.t., and the precipitated solid was isolated by filtration, washed with benzene (225 ml) and methanol (50 ml) and dried under vacuum. The product $(mBnzim)_2CH_2$ (**6**) was obtained as a beige solid (7.62 g, 60%). M.p. 206.5–208.5°C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.76–7.71 (m, 2H), 7.33–7.22 (m, 6H), 4.69 (s, 2H, C**H**$_2$), 3.90 (s, 6H, N–C**H**$_3$). $^{13}C\{^1H\}$-NMR (100MHz, $CDCl_3$): δ 149.8, 142.9, 136.7 (**C2**, **C3a** and **C7a**), 123.3, 122.7, 120.0, 109.9 (**C4**, **C5**, **C6** and **C7**), 31.0 (N–**C**H$_3$), 29.1 (**C**H$_2$). MS *m/z* (%): 277 (22, ($M+1^+$), 275 (19), 216 (12), 148 (14), 147 (11), 146 (56), 145 (76), 138 (10), 131 (10), 145 (76), 144 (17), 138 (10), 131 (31), 119 (15), 77 (15).

4.4. Synthesis of $\{[Rh((mim)_2C{=}O)(CO)_2]^+ BPh_4^-\}$ (1)

A solution of $(mim)_2C$=O (**4**) (0.18 g, 0.95 mmol) in methanol (10 ml) was added to a stirred solution of $Rh_2(CO)_4Cl_2$ (0.16 g, 0.42 mmol) in methanol (30 ml) at r.t. The solution darkened immediately on addition of **4**. The mixture was stirred for 2 h, after which time an excess of $NaBPh_4$ in methanol (5 ml) was added. The mixture was stirred for several minutes and the orange precipitate that formed was isolated by filtration and washed with methanol (20 ml). $\{[Rh((mim)_2C{=}O)(CO)_2]^+ BPh_4^-\}$ (**1**) was recrystallised from acetone as red prisms (0.51 g, 92%). M.p. 178°C (decomposed without melting). ^{1}H-NMR (400 MHz, acetone-d_6): δ 7.84 (s, 2H, **H5**), 7.70 (s, 2H, **H4**), 7.40 (m, 8H, B**Ph**$_4$), 6.97 (m, 8H, B**Ph**$_4$), 6.82 (m, 4H, B**Ph**$_4$), 4.24 (s, 6H, N–C**H**$_3$).$^{13}C\{^1H\}$-NMR (100MHz, acetone-d_6): δ 183.0 (d, $^1J_{Rh-CO} = 68.7$ Hz, Rh–**C**O), 166.6 (CO), 163.9 (m, B–**C**), 138.8 (**C**$_2$), 136.0 (B**Ph**$_4$), 133.4 (**C5** or **C4**), 130.0 (**C4** or **C5**), 125.0 (B**Ph**$_4$), 121.2 (B**Ph**$_4$), 37.8 (N–**C**H$_3$). IR (Nujol, cm^{-1}): 2097 (m, Rh–**CO**), 2024 (m, Rh–**CO**), 1478(s, ligand **CO**). Anal. Calc. for $C_{35}H_{30}N_4O_2BRh$: C, 62.90; H, 4.52; N, 8.38. Found: C, 62.8; H,4.6; N, 8.4

4.5. Synthesis of $\{[Rh((mim)_2CH_2)(CO)_2]^+ BPh_4^-\}$ (2)

A solution of $(mim)_2CH_2$ (**5**) (0.22 g, 1.3 mmol) in methanol (5 ml) was added to a stirred solution of $Rh_2(CO)_4Cl_2$ (0.20 g, 0.52 mmol) in methanol (30 ml) at r.t. A yellow precipitate formed initially, and disappeared as the reaction proceeded giving a clear yellow solution which was stirred for 1.5 h. An excess of $NaBPh_4$ in methanol (5 ml) was added, the mixture was stirred for several minutes and the pale yellow precipitate that formed was isolated by filtration and washed with methanol (20 ml). $\{[Rh((mim)_2CH_2)(CO)_2]^+ BPh_4^-\}$ (**2**) was recrystallised from acetone as bright yellow prisms (0.62 g, 91%). M.p. 175°C (decomposed without melting, darkens from 146°C). ^{1}H-NMR (400 MHz, acetone-d_6, 233 K): δ 7.50 (d, 2H, $^3J_{H5-H4} = 1.7$ Hz, **H5**), 7.42 (dd, 2H, $^3J_{H4-H5} = 1.7$ Hz, $^3J_{H4-Rh} = 0.8$ Hz, **H4**), 7.37–7.32 (m, 8H, B**Ph**$_4$), 6.96 (t, 8H, $^3J_{H-H} =$ 7.4 Hz, B**Ph**$_4$), 6.84 – 6.79 (m, 4H, B**Ph**$_4$), 4.43 (s, 2H, C**H**$_2$), 3.85 (s, 6H, N–C**H**$_3$).$^{13}C\{^1H\}$-NMR (100MHz, acetone-d_6): δ 186.0 (d, $^1J_{Rh-CO} = 67.6$ Hz, Rh–**C**O), 166.2–164.8 (m, B–**C**), 144.3 (**C**$_2$), 137.6 (B**Ph**$_4$), 131.5 (**C5** or **C4**), 126.6 (B**Ph**$_4$), 124.9 (**C4** or **C5**), 122.9 (B**Ph**$_4$), 35.3 (N–**C**H$_3$), 24.9(**C**H$_2$). Electrospray MS *m/z*: (ES+) 335.3 (100, M^+), 307.2 (47, $[Rh((mim)_2CH_2)(CO)]^+$). (ES−) 318.7 (77, BPh_4). IR (nujol, cm^{-1}): 2076 (m, Rh–**CO**), 2004 (m, Rh–**CO**). Anal. Calc. for $C_{35}H_{32}N_{4.0}O_2BRh$·acetone: C, 64.15; H, 5.16; N, 8.20. Found: C, 64.3; H,5.4; N, 8.0.

Crystals of **2** that were suitable for X-ray crystal structure analysis were obtained by slow evaporation of solvent from an acetone solution. The atom numbering scheme is given in Fig. 1. Selected bond lengths and angles are given in Tables 1 and 2.

4.6. Synthesis of {[Rh((mBnzim)$_2$CH$_2$)(CO)$_2$]$^+$ BPh$_4^-$} (3)

A solution of (mBnzim)$_2$CH$_2$ (**6**) (0.40 g, 1.4 mmol) in methanol (5 ml) was added to a stirred solution of $Rh_2(CO)_4Cl_2$ (0.22 g, 0.57 mmol) in methanol (30 ml) at r.t. A cream precipitate formed initially and disappeared as the reaction progressed, giving eventually a clear pale orange solution. The mixture was stirred for 1.5 h, after which time an excess of $NaBPh_4$ in methanol (5 ml) was added. The mixture was stirred for several minutes and the cream precipitate that formed was isolated by filtration and washed with methanol (20 ml). {[Rh((mBnzim)$_2$CH$_2$)(CO)$_2$]$^+$ BPh$_4^-$} (**3**) was recrystallised from acetone to yield pale yellow prisms (0.83 g, 97%). M.p. 202°C (decomposed without melting). ^{1}H-NMR (400MHz, acetone-d_6): δ 8.08–8.01 (m, 1H, **H5** or **H4**), 7.87–7.81 (m, 1H, **H7**), 7.65–7.58 (m, 2H, **H6** and **H4** or **H5**), 7.41–7.36 (m, 4H, B**Ph**$_4$), 6.97–6.91 (m, 4H, B**Ph**$_4$), 6.82–6.76 (m, 2H, B**Ph**$_4$), 5.11 (s, 1H, C**H**$_2$), 4.22 (s, 3H, N–C**H**$_3$). ^{13}C{^{1}H}-NMR (100MHz, acetone-d_6): δ 189.8 (d, $^1J_{Rh-C} = 68.1$ Hz, Rh–**C**O), 169.8 (m, B–**C**), 149.7, 139.9, 13 4.4 (**C2**, **C3a**, **C7a**), 136.1 (B**Ph**$_4$), 125.0 (B**Ph**$_4$), 121.2 (B**Ph**$_4$), 125.1, 124.8, 117.0 (**C4**, **C5**, **C6**), 111.8 (**C7**), 31.0 (N–**C**H$_3$), 30.9 (**C**H$_2$). Electrospray MS m/z: (ES+) 435.1(62, M$^+$), 407.3 (100, [Rh((mBnzim)$_2$CH$_2$)(CO)]$^+$). (ES−) 319.5 (47, BPh$_4$). IR (Nujol, cm^{-1}): 2080 (s, Rh–**CO**), 2012 (s, Rh–**CO**).

Crystals of **3** that were suitable for X-ray crystal structure analysis were obtained by slow evaporation of solvent from an acetone solution. The atom numbering scheme is given in Fig. 2. Selected bond lengths and angles are given in Tables 1 and 2.

4.7. Synthesis of {[Rh((mim)$_2$CH$_2$)(PPh$_3$)$_2$]$^+$ BPh$_4^-$} (7)

A solution of triphenylphosphine (0.10 g, 0.38 mmol) in acetone (5 ml) was added to a stirred solution of {[Rh((mim)$_2$CH$_2$)(CO)$_2$]$^+$ BPh$_4^-$} (**2**) (90 mg, 0.14 mmol) in acetone (20 ml) at r.t. The solution began to effervesce immediately and the colour lightened to a golden–yellow. The solution was stirred for 4 h at r.t., followed by addition of hexane to cause precipitation of the crude product. The solid was isolated by filtration and washed with hexane (310 ml). The residue was recrystallised from acetone to give {[Rh((mim)$_2$CH$_2$)-(PPh$_3$)$_2$]$^+$ BPh$_4^-$} (**7**) as a yellow crystalline solid (0.15 g, 97%). M.p.165.9–169°C. ^{1}H-NMR (400 MHz, acetone-d_6, 233K): δ 7.71–7.47 (broad multiplet, 30H, P**Ph**$_3$), 7.38–7.34 (m, 8H, B**Ph**$_4$), 7.23 (broad s, 2H, **H5** or **H4**), 7.00 (broad s, 2H, **H4** or **H5**), 6.97 (m, 8H, 7.7Hz, B**Ph**$_4$), 6.83–6.80 (m, 4H, B**Ph**$_4$), 3.36 (broad s, 6H, N–C**H**$_3$[2]). ^{13}C{^{1}H}-NMR (100MHz, acetone-d_6): 164.5 (m, B–**C**), 141.5 (**C2**), 136.7 (B**Ph**$_4$), 134.8 (P**Ph**$_3$), 133.1 (broad s, *ipso*-P**Ph**$_3$), 131.4 (**C5** or **C4**), 130.1 (**C4** or **C5**),129.2 (P**Ph**$_3$), 126.1 (m, B**Ph**$_4$),122.3 (B**Ph**$_4$), 33.2 (N–**C**H$_3$)[2]. ^{31}P{^{1}H}-NMR (162 MHz, acetone-d_6, 233 K): δ 45.2 (d, $^1J_{Rh-P} = 116$ Hz). Anal. Calc. for $C_{69}H_{62}N_4P_2BRh\cdot 2H_2O$: C, 71.51; H, 5.74; N, 4.83. Found: C, 71.2; H, 5.9; N, 4.6.

4.8. Synthesis of {[Rh((mBnzim)$_2$CH$_2$)(PPh$_3$)$_2$]$^+$ BPh$_4^-$} (8)

A solution of triphenylphosphine (0.10 g, 0.38 mmol) in acetone (5 ml) was added to a stirred solution of {[Rh((mBnzim)$_2$CH$_2$)(CO)$_2$]$^+$ BPh$_4^-$} (**3**) (0.10 g, 0.13 mmol) in acetone (20 ml) at r.t. The solution was stirred for 4 h at r.t., followed by addition of hexane to cause precipitation of the crude product. The solid was isolated by filtration and washed with hexane (20 ml). {[Rh((mBnzim)$_2$CH$_2$)(PPh$_3$)$_2$]$^+$ BPh$_4^-$} (**8**) was obtained as a pale yellow solid (0.14 g, 83%). M.p. 196–198.5°C. ^{1}H-NMR (400 MHz, acetone-d_6, 243 K): δ 7.65–7.21 (m, 46H, P**Ph**$_3$, B**Ph**$_4$, **mBnzim**), 6.99 (m, 8H, B**Ph**$_4$), 6.83 (m, 4H, B**Ph**$_4$), 4.52 (C**H**$_2$(C**H**D)), 3.77 (s, 6H, N–C**H**$_3$). ^{13}C{^{1}H}-NMR (100 MHz, acetone-d_6): δ 167.7 (m, B–**C**), 150.9, 142.9 (**C2** and **C3a** or **C7a**), 139.1 (B**Ph**$_4$), 138.4 (**C3a** or **C7a**), 136.8 (P**Ph**$_3$), 134.0 (br s, *ipso*-P**Ph**$_3$), 133.8 (P**Ph**$_3$), 131.4 (P**Ph**$_3$), 128.0 (m, B**Ph**$_4$), 125.9 (**C**H(**mBnzim**)), 125.2 (**C**H(**mBnzim**)), 124.3 (B**Ph**$_4$), 121.3 (**C**H(**mBnzim**)), 113.1 (**C**H(**mBnzim**)), 33.3 (N–**C**H$_3$)[3]. ^{31}P{^{1}H}-NMR (162 MHz, acetone-d_6, 243 K): 32.2 (d, $^1J_{Rh-P} = 125$Hz, **P**Ph$_3$). Anal. Calc. for $C_{77}H_{66}N_4P_2BRh\cdot 2H_2O$ C, 73.45; H, 5.60; N, 4.45. Found: C, 73.4; H, 5.7; N, 4.4.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 114536 for **2** and 114537 for **3**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Listings of atom coordinates, anisotropic thermal parameters, torsion angles, details of least squares planes calculations (34 pages) for **2** and **3** attached.

[2] The CH$_2$ resonance of this complex was not observed in either the ^{1}H or ^{13}C{^{1}H}-NMR spectra due to exchange of the CH$_2$ to CD$_2$ in acetone-d_6 solvent.

[3] The CH$_2$ of this complex was not observed in the ^{13}C{^{1}H}-NMR spectrum due to exchange of the CH$_2$ to CD$_2$ in acetone-d_6 solvent.

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