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Ferrocenyl-nitrogen donor ligands. Synthesis and characterization of rhodium(I) complexes of ferrocenylpyridine and related ligands

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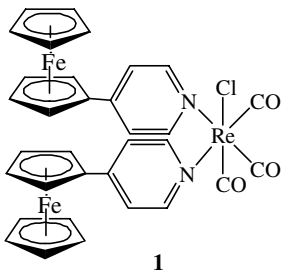
Abstract

The preparation of a series of complexes of the types $[RhCl(CO)_2(L)]$, $[RhCl(cod)(L)]$ and $[Rh(cod)(L)_2]ClO_4$, where L is a ligand incorporating a ferrocenyl group and a pyridine ring is described. Complexes were characterized using NMR, IR and electronic spectroscopy. The electrochemical behaviour of the complexes was examined using cyclic voltammetry. The X-ray structures of three of the complexes, $[RhCl(CO)_2\{NC_5H_4C{=}NC_6H_4(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)\}]$, [RhCl(cod)(3-Fcpy)] and $[RhCl(cod)\{3\text{-}Fc(C_6H_4)py\}]$, were determined.

Keywords: Ferrocenyl-nitrogen donor ligands; Ferrocenylpyridines; Rhodium(I); Electrochemistry

1. Introduction

Despite the extensive work on the symmetrical ferrocenylphosphine [1] and unsymmetrical ferrocenyl ligands [2], it was apparent from reviewing the literature that the chemistry and application of symmetrical and unsymmetrical ferrocenyl-nitrogen donor ligands has not been very well developed. Miller et al. [3] described the use of 4-ferrocenylpyridine as a ligand. It was coordinated to rhenium to provide complex **1**. The electrochemical properties of the complex were compared to a series of rhenium-ferrocenyl complexes containing ferrocenylphosphine coordination complexes. The complexes were investigated to determine whether changes in the oxidation state of the redox ferrocenyl ligand could result in changes in the reactivity of the rhenium centre, essentially without changing the coordination sphere of rhenium. The preparation of a platinum complex (**2**) of 3-ferrocenylpyridine has also been described [4].



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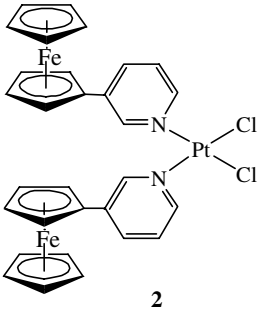

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Of particular interest was the specific role of platinum as a linker between the ferrocenyl groups. A single redox wave was observed for **2** corresponding to a two-electron oxidation at the platinum electrode indicating little or no communication between the respective ferrocenyl groups. It would appear that the platinum metal centre in **2** inhibits electronic communication between the ferrocenyl groups. Complexes **1** and **2** contain systems in which the metals are connected through conjugated pathways and this provides an avenue for through-bond electronic communication. The significance of a conjugated system has been illustrated by Carr and co-workers with a comparison of the electrochemical behaviour of complexes **3** and **4** [5].

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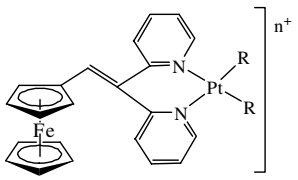

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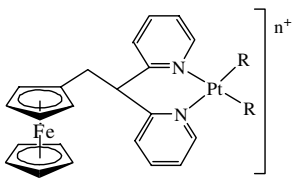

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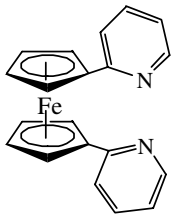
a: R = Cl^-, n = 0

b: R = py, n = 2

The redox behaviour of the uncomplexed ferrocenyl ligands in **3** and **4** were similar but on complexation there was a shift of approximately +150 mV in the case of the conjugated system of complex **3b** compared to only +30 mV in the unconjugated system of complex **4b**. Although the synthesis of the disubstituted ferrocenyl ligand, 1,1′-bis(2-pyridyl)ferrocene (**5**), was reported many years ago [6], it was only in more recent times that the coordination chemistry of **5** has been investigated. Tani et al. [7] described the preparation and characterization of rhodium(I) and silver(I) complexes of **5**. Subsequently, the platinum and palladium complexes of **5** have been prepared (**6** and **7**) and their catalytic reactivity with regard to carbonyl insertion reactions has been studied [8]. Insertion of carbon monoxide into the palladium–methyl bond of **6** occurred rapidly but detailed kinetic studies on the reaction were not possible due to weak ligand–metal binding. The ligand **5** has also been shown to act as an efficient electrochemical sensor for magnesium, calcium, zinc and cadmium ions in acetonitrile solution [9].



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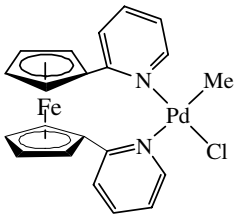

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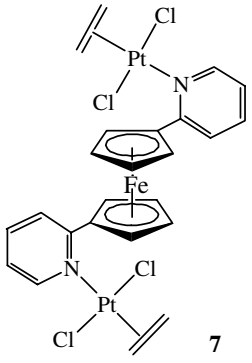

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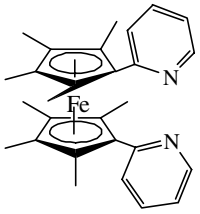
Neumann et al. have described the synthesis and coordination chemistry of octamethyl-1′,1′-bis(2-pyridyl)ferrocene (**8**) [10]. The reactivity of **8** with two equivalents of $K[PtCl_3(C_2H_4)]$ provided the analogous complex to **7**. Work has also been reported on the coordination chemistry of ferrocenyl-4-pyridylacetylene. Nunes et al. reported on the preparation of some ruthenium(II) complexes containing this ligand [11], whilst Santos et al. reported on the preparation of a complex between this ligand and methyltrioxorhenium(VII) [12]. Ferrocenyl-nitrogen donor ligands have also received some attention by materials chemists. Examples include ligands incorporated into dendrimer architectures [13], redox-active sensors [14], non-linear optical materials [15] and organometallic oligomers [16]. In a previous publication, we reported on the synthesis and medicinal properties of a series of ferrocenyl-nitrogen donor coordination complexes of palladium, platinum, iridium and rhodium [17]. In that paper, the emphasis was placed on the synthesis and characterization of the palladium and platinum complexes. The current paper describes in full the chemistry and properties of the rhodium(I) complexes of ferrocenylpyridine and related ligands.



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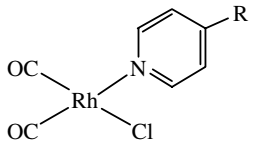
2. Results and discussion

2.1. Preparation of rhodium carbonyl complexes

The rhodium(I) carbonyl monosubstituted pyridyl coordination complexes **9a**–**e** in this study were prepared through a bridge-splitting reaction of the rhodium carbonyl dimer, dichlorotetracarbonyldirhodium. Replacement of this dimer by the related cyclooctadiene dimer, chloro(1,5-cyclooctadiene)rhodium(I), leads to the formation of the analogous cyclooctadiene complexes. The carbonyl complexes may also be obtained by bubbling carbon monoxide through a solution of the cyclooctadiene complex. The labile cyclooctadiene group is displaced by the carbonyl ligands.



9a: R = H

9b: R = NH_2

9c: R = Fc

9d: R = (C=N)-Ph

9e: R = $(C=N)(C_6H_4)Fc$

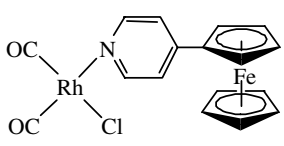
Complexes **9a**–**e** were obtained in good yield. The effect of derivatising the pyridyl ligand as well as the effect of the

substituent on the electron density at the rhodium metal centre was reflected in shifts in the carbonyl stretching frequencies in the infrared spectra. The spectra were recorded as potassium bromide pellets. Strong bands were obtained at 2091 and 2016 cm^{-1} for complex **9a** and are assigned to the carbonyl stretching frequencies of the *cis*-isomer. The introduction of the amine group in **9b** results in a shift in the bands to 2076 and 2012 cm^{-1} whilst substitution of a ferrocenyl group in complex **9c** moves the bands to 2086 and 2011 cm^{-1}. Comparison of shifts in the carbonyl stretching frequency of **9a** with **9b**–**9e** showed a shift to lower energy. This corresponded to an increased electron density at the rhodium centre. A further comparison can be made between the free ligand and complex in both **9d** and **9e** by evaluating the imine stretching frequency. A stretching frequency of 1595 cm^{-1} was obtained for the free ligand in **9d**. This shifted to 1605 cm^{-1} on complexation to the rhodium centre. Similarly, a shift from 1623 to 1643 cm^{-1} was observed on complexation in **9e**. This was attributed to a lowering in energy on coordination of the ligand to the rhodium metal. Minor differences in the chemical shifts of the ^1H NMR between the free ligand and coordinated complex were observed mainly on the α-proton adjacent to the nitrogen-donor atom on the pyridyl ring. Shifts in the position of the imine bond proton in **9d** and **9e** were also observed on comparison of the free ligand with complex, with downfield shifts of 8.44 to 8.81 and 8.54 to 8.57 ppm, respectively. Comparing the cyclopentadienyl ^1H NMR chemical shifts of the ferrocenyl groups of **9c** and **9e** as well as relative to the free respective ligands, assisted in the evaluation of the effect of the spacer group. Furthermore, the effect of coordinating the rhodium metal could be determined on comparison of the NMR spectra of the free ligand and complex (Fig. 1).

On comparing the shifts due to the complex with that of the free ligand, no significant differences could be established between these specific chemical shifts in **9e**. It would appear that the long-range conjugative effect between the rhodium centre and the ferrocenyl group was reduced by the presence of the spacer, despite a conjugated system of bonds between the two. This proposal is lent some validity when comparing the differences between the free ligand and complex for **9c**.

2.2. Preparation of rhodium cyclooctadiene complexes

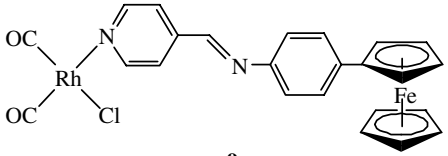
The rhodium cyclooctadiene dimer, chloro(1,5-cyclooctadiene)rhodium(I), can be readily prepared by the reaction of excess cyclooctadiene and rhodium trichloride trihydrate. This dimer is known to readily undergo a bridge-splitting reaction on addition of an uncharged monodentate ligand. The presence of the labile cyclooctadiene ligand appears to promote catalytic activity by readily dissociating as part of the catalytic cycle. Several nitrogen donor ligands were coordinated to the rhodium metal centre in a bridge splitting reaction of the rhodium dimer followed by addition of the ligand (see **10a**–**g**, **11a**–**b**, **12a**–**b**, **13**). Changes in the proton chemical shift values for the pyridyl groups were observed on variation of the substituent on the pyridyl ring. For example, complex **10d** showed chemical shifts at 8.76 and 7.32 ppm whilst introduction of the phenyl substituent in **10e** showed a shift of these peaks to 8.75 and 7.57 ppm for H_a and H_b, respectively. Complex **10f** showed a more pronounced shift of 8.88 and 7.46 ppm for H_a and H_b. A slight shift in the imine proton peak position from 8.44 to 8.47 ppm was observed on complexation for complex **10f**. This can also be compared to the related carbonyl complex **9d** where an imine peak was observed at 8.81 ppm. Complex **10g** showed shifts in both sets of pyridyl ring protons to 8.60 and 7.30 ppm, respectively. The direction of shifts in peak positions on comparison of free ligand and complex are similar for both the carbonyl and cyclooctadiene complexes. The positional shifts were overall more pronounced in the carbonyl complexes. This may be accounted for by considering the synergistic effect of the carbonyl groups on the metal through significant π back-bonding interaction. Complexes **10a**–**c**, **11a**–**b**, **12a**–**b** and **13** include ferrocenyl substituents on the pyridyl ring. Several structural comparisons can be made between these complexes and the effect considered in terms of their impact on the rhodium centre. Complex **13** is unique with the nitrogen donor atom occurring on the cyclopentadienyl ring of the 1′,2′,3′,4′,5′-pentamethylazaferrocene compound. The cyclopentadienyl protons for complexes **10a**–**c** showed similar chemical shift values, while only **10a** showed significant differences on comparison of the free ligand and complex. The α-H and β-H in **10a** showed upfield shifts relative to



9c

α-H: 4.76; β-H: 4.56; Cp: 4.08 **[9c]**

α-H: 4.82; β-H: 4.61; Cp: 4.08 **(ligand)**



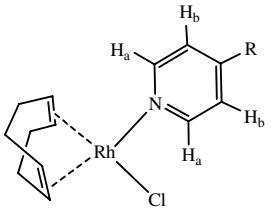
9e

α-H: 4.68; β-H: 4.36; Cp: 4.06 **[9e]**

α-H: 4.68; β-H: 4.36; Cp: 4.06 **(ligand)**

Fig. 1. Comparison of ^1H NMR chemical shifts (ppm) for the ferrocenyl substituents in **9c** and **9e**.

the free ligand, indicating shielding of these protons on coordination of the rhodium metal, similar to the related carbonyl complex, **9c**. The comparable chemical shifts for the free ligand and complex for both **10b** and **10c** indicated a reduced conjugative effect between the ferrocenyl group and rhodium metal due to the presence of the spacer groups. The protons in complex **13**, contrary to those in complex **10a**, showed significant downfield shifts on complexation of the rhodium metal centre. This indicated deshielding of these protons. The complex was paramagnetic and broad signals were obtained for it in the ^{1}H NMR.



10a: R = Fc

10b: R = (C_6H_4)Fc

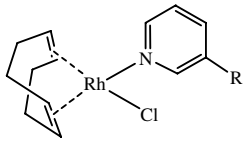
10c: R = (C=N)(C_6H_4)Fc

10d: R = H

10e: R = Ph

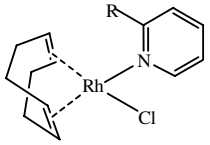
10f: R = (C=N)-Ph

10g: R = (C=C)(C_6H_4)-OC_8H_{17}



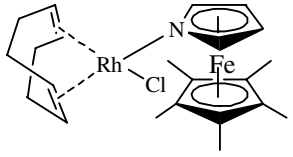
11a: R = Fc

11b: R = (C_6H_4)Fc



12a: R = Fc

12b: R = (C_6H_4)Fc



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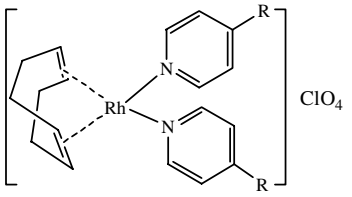
2.3. Preparation of cationic rhodium complexes $[Rh(cod)L_2]ClO_4$

The cationic rhodium complexes examined in this study contain two pyridyl ligands and in the case of ferrocenyl ligands, constitute the preparation of a trimetallic complex. The cationic rhodium(I) complexes **14a**–**f** were prepared using the general synthetic route described in Scheme 1. Silver perchlorate was added to a solution of the rhodium dimer in acetone, yielding a solvated complex of general formula $[Rh(cod)(Me_2CO)_x]ClO_4$. The addition of a nitrogen-donor ligand to this complex produced a cationic complex by displacement of the solvent from the rhodium coordination sphere.



14a: R = H

14b: R = Ph

14c: R = (C=N)-Ph

14d: R = Fc

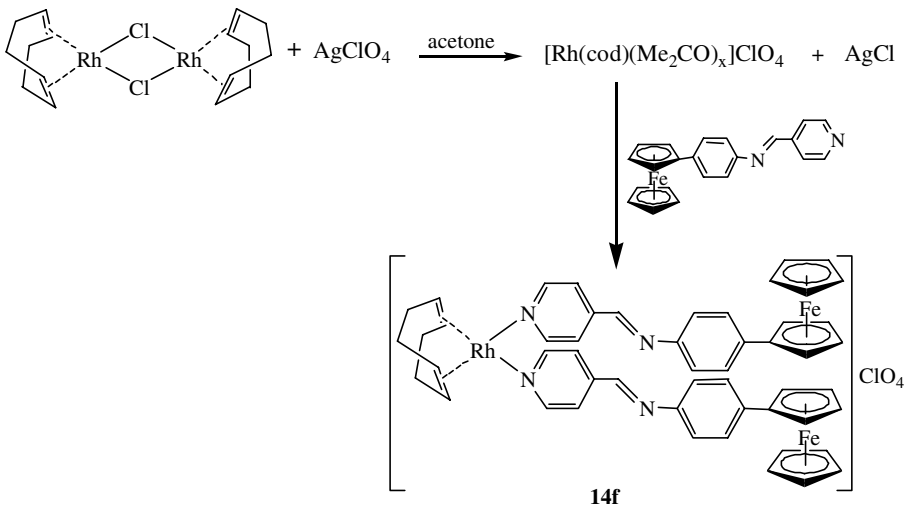
14e: R = (C_6H_4)Fc

14f: R = (C=N)(C_6H_4)Fc

A variation on the preparation of complex **14a** included preparation of the complex with a hexafluorophosphate counter-ion. The synthesis of the complex $[Rh(cod)L_2]PF_6$ involved the addition of excess pyridine to the rhodium dimer in ethanol, followed by addition of a concentrated aqueous solution of ammonium hexafluorophosphate. The product was obtained as a precipitate that was collected by vacuum filtration. The preparation of further complexes with this counter-ion was not carried out as the complex $[Rh(cod)L_2]PF_6$ showed similar properties to that of complex **14a**. The cationic complexes were obtained in good yield through concentration of the reaction mixture followed by addition of solvents such as diethyl ether or pentane to precipitate the product.

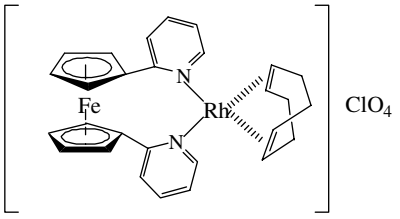
2.4. Preparation of 1,1′-bis(pyridyl)ferrocene ligand complexes

The rhodium complexes described so far have been prepared using monosubstituted ferrocenyl nitrogen donor ligands. For comparative purposes, a selection of 1,1′-disubstituted ferrocenylpyridines were prepared and complexed to rhodium using similar synthetic routes to those already described. The preparation of complexes **15a**–**b** has been reported using this synthetic route. Complex **15b** was prepared using the same synthetic route as described in the literature except that ethanol was used as solvent since some decomposition was observed in acetone. A downfield shift was observed for the ferrocenyl protons of complex **15b** on complexation to the rhodium, in contrast to complex **15a**, where no difference was observed. The negligible change in chemical shifts for the ferrocenyl group for complex **15a** was in line with those observed with the monosubstituted complex **12a**. The downfield shifts observed in the ferrocenyl protons for complex **15b** were contrary to the upfield shifts observed for the monosubstituted neutral complex **10a** and cationic complex **14d**. Assuming that the effect of coordination to rhodium is felt through the conjugative system of bonds, it would appear that the effect differs in the disubstituted complexes.

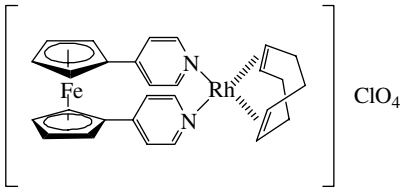


14f

Scheme 1. Preparation of cationic rhodium complexes.



15a



15b

2.5. X-ray crystal structure analysis

The molecular structure for complex **9e** with atom numbering scheme is shown in Fig. 2. Complex **9e** crystallized with two molecules in an asymmetric unit (see Table 2 for details of crystal and refinement data). The molecules have no obvious intermolecular coordination between them. Selected bond lengths and angles for **9e** are listed in Table 1 and were found to compare favourably with literature-cited bond lengths and angles for similar complexes. The coordination geometry around the rhodium is square planar. The dihedral angle between the plane of the pyridyl ring and the rhodium square plane was obtained as 136.3°(3) and 140.1°(2) for each of the molecules, similar to the observed angle of 141° in complex **9a**. The *trans* geometry of the imine bond and its double bond character were confirmed by X-ray crystallography. A torsion angle of 178.0°(3) and 177.3°(3) along the imine bond axis was obtained for each of the molecules. The pyridyl and phenyl rings were confirmed as delocalized.

The spectroscopic data and crystal structure analysis of the complex **9e** suggests that despite the existence of a conjugated network between the respective metals, the extended spacer group between the metals results in a diminished interaction. In both molecules the cyclopentadienyl ferrocene rings are planar. The rings show a marginal tilt towards each other with angles of 0.73° (0.27) and 1.93° (0.29) for the molecules. The cyclopentadienyl rings are not completely eclipsed in the ferrocenyl group but are rotated away from each other by an angle of 7.8° and 3.0° in each of the molecules. This degree of rotation has been related to monosubstitution of the ferrocenyl group and to the nature of the substituent. The phenyl ring showed a 26.7° rotation relative to the plane of the adjacent cyclopentadienyl ring of the ferrocenyl group. The molecules are packed in a tail-to-tail arrangement in the unit cell.

The crystal structure of complex **11a** was obtained from single crystals grown from a mixture of dichloromethane and pentane (Fig. 3). The complex was observed to crystallize in the triclinic space group $P\bar{1}$. Details of crystal and structure refinement data are summarized in Table 3. The coordination geometry around the rhodium metal in complex **11a** is square planar. A torsion angle of 129° was obtained between the pyridyl ring and the adjacent cyclopentadienyl ring. The cyclopentadienyl rings are planar with a tilt angle of 1.6°. The rings are not completely eclipsed, having a rotation angle of 5.6°. The Rh–N bond length is 2.109 Å, which is in accordance with observed bond lengths of similar complexes reported in the literature. The crystal structure of **11b** was also obtained using single crystals grown in a mixture of dichloromethane and pentane (Fig. 4). The complex was observed to crystallize in the triclinic space group $P\bar{1}$. Least squares refinement of the structure gave a final R factor of 0.0289. Details of crystal and structure refinement data are summarized in

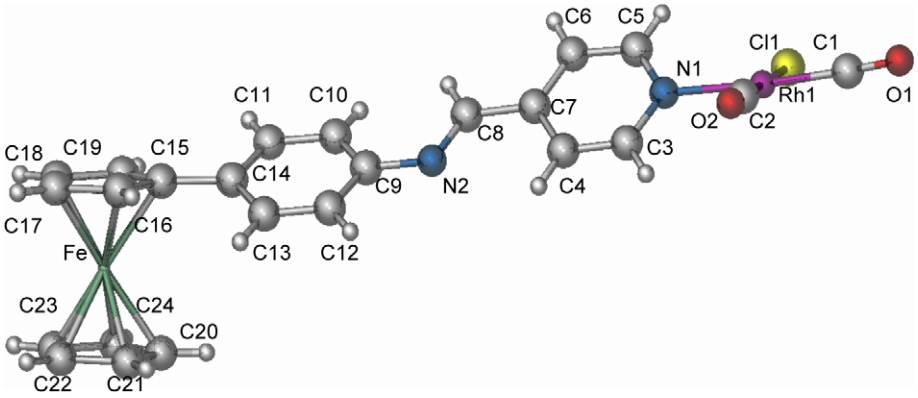


Fig. 2. Molecular structure of complex **9e** showing the atom numbering scheme.

Table 1
Selected bond lengths (Å) and angles (°) for the two molecules in the asymmetric unit of **9e**

Molecule 1		Molecule 2	
Rh(1)–Cl(1)	2.357(1)	Rh(2)–Cl(2)	2.353(1)
Rh(1)–N(1)	2.108(4)	Rh(2)–N(5)	2.115(4)
Rh(1)–C(1)	1.852(5)	Rh(2)–C(28)	1.862(6)
Rh(1)–C(2)	1.857(6)	Rh(2)–C(29)	1.850(5)
O(1)–C(1)	1.133(6)	O(3)–C(28)	1.098(6)
O(2)–C(2)	1.111(6)	O(4)–C(29)	1.128(6)
N(2)–C(9)	1.415(6)	N(38)–C(39)	1.416(6)
N(2)–C(8)	1.265(6)	C(37)–N(38)	1.271(6)
C(7)–C(8)	1.467(6)	C(34)–C(37)	1.478(6)
N(1)–C(5)	1.333(4)	N(5)–C(32)	1.345(4)
C(5)–C(6)	1.374(5)	C(32)–C(33)	1.367(5)
C(6)–C(7)	1.388(5)	C(33)–C(34)	1.387(5)
C(9)–C(12)	1.386(5)	C(39)–C(42)	1.395(5)
C(12)–C(13)	1.377(5)	C(42)–C(43)	1.371(5)
C(13)–C(14)	1.395(5)	C(43)–C(44)	1.387(5)
C(14)–C(15)	1.478(5)	C(44)–C(45)	1.474(5)
Cl(1)–Rh(1)–N(1)	90.20(8)	Cl(2)–Rh(2)–N(5)	91.22(8)
N(1)–Rh(1)–C(1)	176.22(14)	N(5)–Rh(2)–C(29)	177.96(15)
C(1)–Rh(1)–C(2)	89.09(16)	C(28)–Rh(2)–C(29)	88.67(16)
Cl(1)–Rh(1)–C(2)	179.14(13)	Cl(2)–Rh(2)–C(29)	90.20(11)
Cl(1)–Rh(1)–C(1)	90.62(11)	Cl(2)–Rh(2)–C(28)	176.53(13)

Table 2
Crystal and structure refinement data for complex **9e**

Compound	**9e**
Empirical formula	$C_{24}H_{18}ClFeN_2O_2Rh$
Formula weight	560.61
Crystal size (mm)	$0.25 \times 0.09 \times 0.07$
Temperature (K)	173(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	14.480(1)
b (Å)	18.790(1)
c (Å)	17.116(1)
α (°)	90
β (°)	111.507(1)
γ (°)	90
Volume (Å^3)	4332.7(5)
μ (Mo Kα) (mm^{-1})	1.579
Z	8
Reflections collected/unique	23441/9672 [$R_{int} = 0.0513$]
Goodness-of-fit on F^2	1.008
Final R indices [$I > 2$sigma(I)]	$R_1 = 0.0430$, $wR_2 = 0.0725$
R indices (all data)	$R_1 = 0.1013$, $wR_2 = 0.0857$

Table 3 with selected bond lengths and angles for **11a** and **11b** listed in Table 4.

2.6. Electrochemical study of rhodium complexes

We have investigated the electrochemical behaviour of selected complexes and our results are summarized in Table 5. Cyclic voltammetry of the complexes in acetonitrile (containing 0.1 M tetra-*n*-butylammonium perchlorate) at a platinum disk electrode shows, for all the ferrocenyl-containing compounds, the typical reversible redox waves expected for the Fc/Fc$^+$ couple. In Table 5 the half-wave potential, $E_{1/2}$(Fc), and the corresponding anodic E_{pa}(Fc) and cathodic E_{pc}(Fc) peak potentials are listed, while Fig. 5 displays the reversible redox waves for the ferrocenyl groups in complexes **11b** and **10b** compared with ferrocene itself. Shifts in the half-wave potential of this wave can be related to the substituents on the ferrocenyl group and to the presence of coordinated rhodium(I). In some of the

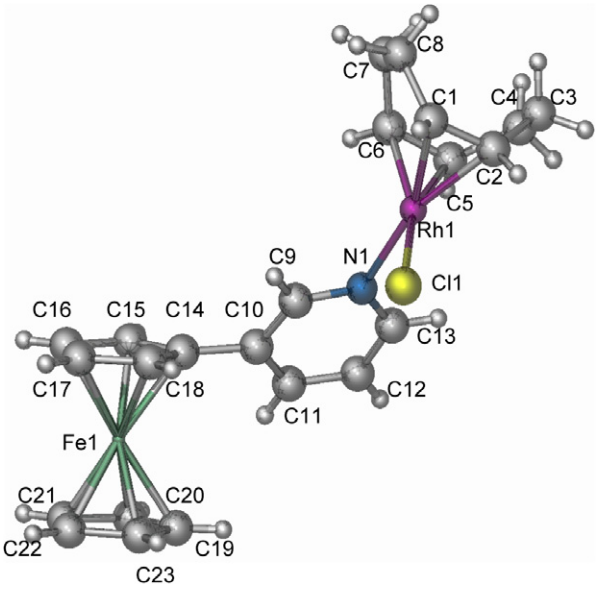


Fig. 3. Molecular structure of complex **11a** showing the atom numbering scheme.

Table 3
Crystal and structure refinement data for compounds **11a** and **11b**

	11a	**11b**
Empirical formula	$C_{23}H_{25}ClFeNRh$	$C_{29}H_{29}ClFeNRh$
Formula weight	509.65	585.74
Crystal size (mm)	$0.30 \times 0.07 \times 0.04$	$0.12 \times 0.10 \times 0.03$
Temperature (K)	298(2)	298(2)
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions		
a (Å)	6.946(1)	7.003(1)
b (Å)	9.999(2)	10.026(2)
b (Å)	14.789(3)	17.609(4)
α (°)	91.38(3)	78.60(3)
β (°)	99.30(3)	80.79(3)
γ (°)	97.11(3)	85.92(3)
Volume (Å^3)	1004.8(4)	1195.5(4)
μ (Mo Kα) (mm^{-1})	1.683	1.427
Z	2	2
Reflections collected/unique	8208/4397 [$R_{int} = 0.0315$]	34055/5459 [$R_{int} = 0.0465$]
Goodness-of-fit on F^2	1.019	1.025
Final R indices [$I > 2$sigma(I)]	$R_1 = 0.0308$, $wR_2 = 0.0568$	$R_1 = 0.0289$, $wR_2 = 0.0657$
R indices (all data)	$R_1 = 0.0586$, $wR_2 = 0.0627$	$R_1 = 0.0405$, $wR_2 = 0.0698$

Table 4
Selected bond lengths (Å) and angles (°) for complexes **11a** and **11b**

11a		**11b**	
Rh(1)–Cl(1)	2.3585(10)	Rh(1)–Cl(1)	2.3719(11)
Rh(1)–N(1)	2.109(2)	Rh(1)–N(1)	2.1031(9)
Rh(1)–C(1)	2.130(3)	Rh(1)–C(1)	2.118(3)
Rh(1)–C(2)	2.124(3)	Rh(1)–C(2)	2.109(3)
Rh(1)–C(5)	2.104(3)	Rh(1)–C(5)	2.131(2)
Rh(1)–C(6)	2.104(3)	Rh(1)–C(6)	2.138(2)
N(1)–C(9)	1.340(3)	N(1)–C(13)	1.340(3)
C(9)–C(10)	1.380(3)	C(13)–C(12)	1.389(3)
N(1)–C(13)	1.343(3)	N(1)–C(9)	1.343(3)
C(13)–C(12)	1.366(4)	C(9)–C(10)	1.376(3)
C(12)–C(11)	1.373(4)	C(11)–C(10)	1.371(4)
C(11)–C(10)	1.387(4)	C(12)–C(11)	1.397(3)
C(10)–C(14)	1.481(4)	C(12)–C(14)	1.482(3)
C(2)–Rh(1)–C(1)	37.84(12)	C(14)–C(19)	1.390(3)
N(1)–Rh(1)–Cl(1)	88.26(6)	C(14)–C(15)	1.385(3)
C(2)–Rh(1)–Cl(1)	90.19(9)	C(19)–C(18)	1.381(3)
C(9)–N(1)–Rh(1)	119.70(17)	C(15)–C(16)	1.375(4)
		C(18)–C(17)	1.389(3)
		C(16)–C(17)	1.384(4)
		C(17)–C(20)	1.474(3)
		C(2)–Rh(1)–C(1)	38.48(11)
		N(1)–Rh(1)–Cl(1)	86.88(6)
		C(2)–Rh(1)–Cl(1)	158.17(8)
		C(9)–N(1)–Rh(1)	122.98(16)

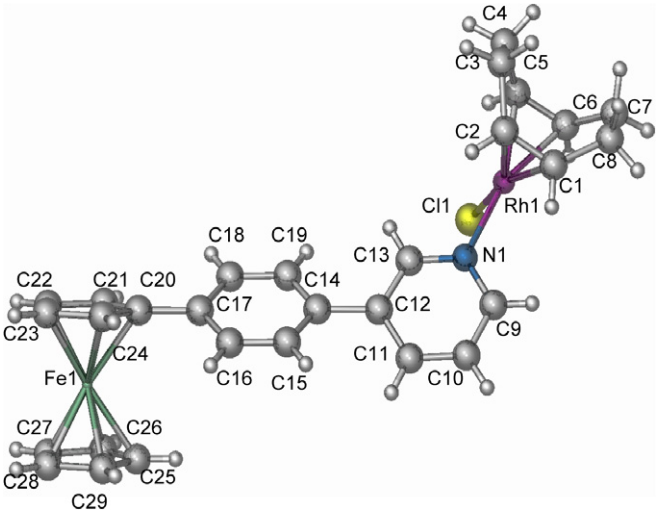


Fig. 4. Molecular structure of complex **11b** showing the atom numbering scheme.

complexes an irreversible anodic peak was observed at more positive potential than the ferrocenyl peak, and this often broad peak was ascribed to the irreversible oxidation of the rhodium(I) metal centre, E_{pa}(Rh). No reduction of the rhodium(I) metal centre was observed, even scanning cathodically down to −1.5 V.

Comparing the half-wave potentials of the free ligands with those of the Fc/Fc^+ couples in the corresponding binuclear complexes, it is apparent that only in the case of **10a**, where L = 4-Fcpy, is there evidence of significant electronic interaction between the Rh and Fc centres, the effect falling off rapidly in going from the 4- to the 3- and 2-substituted ligands. Interspersing a phenylene group between the Fc and py moieties decreases the interaction markedly. The inductive effect of the rhodium metal centre on the ease of oxidation of the ferrocenyl group was demonstrated by the decreasing half-wave potentials observed on comparison of complexes **10a**, **11a** and **12a**. This trend is further observed in the related complexes **10b**, **11b** and **12b** with phenylene spacer groups. The effect of the spacer groups is clearly demonstrated on comparison of complexes **10a**, **10b** and **10c**, where a gradual decrease in $E_{1/2}$ value is observed. Changes in the spectator ligands do not appear to play a significant role in electronic interactions as complexes **9e** and **10c** displayed similar $E_{1/2}$ values. The single reversible peak obtained for the cyclic voltammogram of complex **14d** indicated that no electronic communication occurs between the two ferrocenyl groups in this complex, though there is evidence of very limited electronic coupling between the rhodium metal centre and ferrocenyl groups.

2.7. Electronic spectroscopy of rhodium complexes

A comparison of the wavelengths of the major bands together with extinction coefficients for a selection of the rhodium complexes in dichloromethane is given in Table 6. Bands due to transitions in the ferrocenyl and pyridyl groups were observed, as well as a rhodium → ligand π^* metal-to-ligand charge transfer band in the range 350–550 nm (depending on the specific ligand). The lowest energy Fe d–d transitions of the free ferrocenyl-pyridine ligands (around 450 nm) are not significantly shifted in wavelength upon coordination to a rhodium centre, and

Table 5
Electrochemical data for selected rhodium(I) complexes in acetonitrile[a]

Complex number	Complex type	Ligand	E_{pa}(Rh) (mV)	E_{pa}(Fc) (mV)	E_{pc}(Fc) (mV)	$E_{1/2}$(Fc) (mV)	$E_{1/2}$(L) (mV)
	Ferrocene	–	–	+120	+31	+76	–
	$[RhCl(cod)]_2$	–	+446	–	–	–	–
10d	RhCl(cod)L	py	+529	–	–	–	–
10a		4-Fcpy	–	+377	+240	+309	+206
11a		3-Fcpy	–	+223	+148	+186	+168
12a		2-Fcpy	–	+192	+118	+155	+154
10b		4-Fc(C_6H_4)py	+612	+194	+125	+160	+134
11b		3-Fc(C_6H_4)py	–	+165	+96	+130	+132
12b		2-Fc(C_6H_4)py	–	+165	+89	+127	+126
10f		Ph(NC)py	+632	–	–	–	–
10c		Fc(C_6H_4)NCpy	+616	+161	+91	+126	+113
9e	$RhCl(CO)_2L$	Fc(C_6H_4)NCpy	–	+145	+82	+114	+113
14d	$[Rh(cod)L_2]ClO_4$	4-Fcpy	–	+270	+179	+224	+206

[a] Measured in CH_3CN containing 0.1 M [$^nBu_4N$][ClO_4] at a scan rate of 100 mV s^{-1} and referenced to Ag/Ag^+.

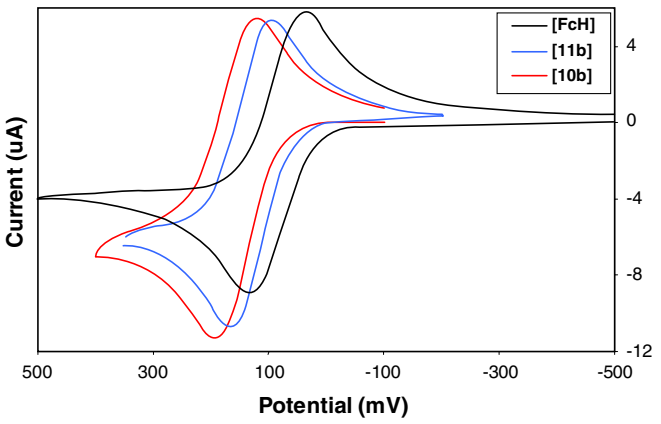


Fig. 5. Overlay of cyclic voltammograms for ferrocene and complexes **10b** and **11b**.

from this point of view the influence of the Rh^I centre on ferrocene is weak or non-existent, the largest effect (a bathochromic shift of 12 and 28 nm upon complexation) being noted for **10a** and **14d**, respectively. This is in accordance with the results obtained by cyclic voltammetry. Interesting comparisons can be made between the mono- and bis-ligand complexes **10a** or **10b** and **14d**. In each of these cases, a shift in the transitions to a longer wavelength and larger extinction coefficient was found on incorporation of an additional ligand.

The highly conjugated complexes **10f**, **10c**, **14f** and **9e** in Table 6 all show relatively large extinction coefficients for each of the transitions. A comparison of complexes **10c** and **9e** showed a variation in the middle band, with complex **9e** exhibiting a more intense transition and increased extinction coefficient with a bathochromic shift relative to complex **10c**. This band also became more intense for complex **14f**.

3. Conclusion

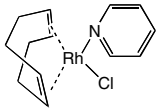
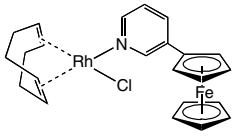
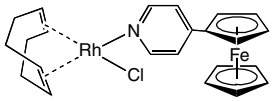
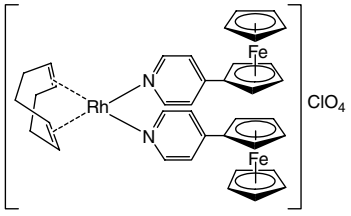
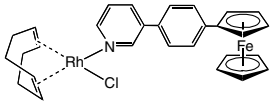
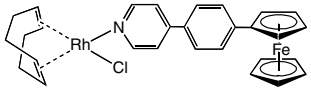
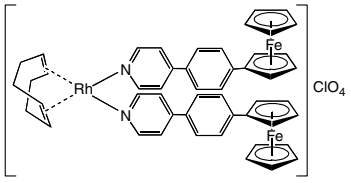
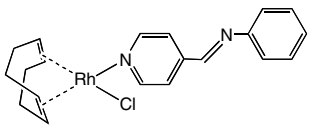
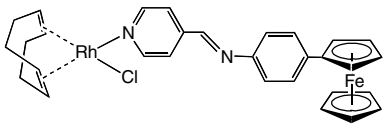
In this paper, a series of new multinuclear complexes consisting of ferrocenyl-nitrogen donor ligands coordinated to rhodium were successfully prepared and characterized using an array of analytical techniques. Three of the complexes were analysed successfully by X-ray crystallography. Selected compounds were also analysed by cyclic voltammetry and electronic spectroscopy; results from these methods provided information on electronic communication between the metals or lack of it in the complexes. Compounds described here should offer potential catalytic activity and studies in this regard are currently in progress.

4. Experimental

4.1. Purification and characterization of the materials

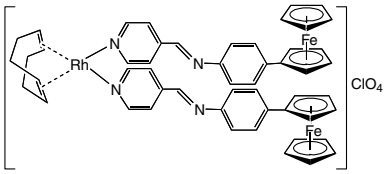
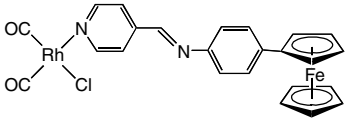
All manipulations, unless otherwise stated were carried out under an inert atmosphere of nitrogen using standard Schlenk techniques. Glass syringes were stored at 60 °C and all other glassware thoroughly dried at 210 °C for at least four hours prior to use. Melting points were determined on a Kofler hotstage microscope (Reichart Thermovar). Microanalyses were obtained on a Carlo Erba EA 1108 elemental analyser. Fast atomic bombardment (FAB) and high resolution (EI) mass spectra were recorded on a VG-70SEQ mass spectrometer at the mass spectrometry unit, Cape Technikon. In all cases the isotopic distribution was checked against the theoretical distribution. Infrared spectra were recorded on a Perkin Elmer Paragon 1000 FT-IR spectrometer, with solid samples prepared as potassium bromide disks and solution samples in sodium chloride solution cells. NMR spectra were recorded on either a Varian Unity-400 (^1H: 400 MHz; ^{13}C: 100.6 MHz) or Varian Mercury-300 (^1H: 300 MHz; ^{13}C: 75.5 MHz) spectrometer at ambient temperatures. ^1H NMR spectra were referenced internally using residual protons in the deuterated solvent ($CDCl_3$: δ 7.27; C_6D_6: δ 7.24, CD_3OD: δ 5.84, CD_3COCD_3: δ 2.09) and values reported relative to tetramethylsilane (δ 0.00). ^{13}C NMR spectra were similarly referenced internally to the solvent resonance ($CDCl_3$: δ 77.0; C_6D_6: δ 128.1, CD_3OD: δ 49.1, CD_3COCD_3: δ 30.60 and 205.87) with values reported relative to tetramethylsilane (δ 0.0). UV–Vis spectra were recorded on a Hewlett Packard 8452A diode array spectrophotometer in dichloromethane. Cyclic voltammograms

Table 6
Electronic spectral bands and extinction coefficients for selected rhodium complexes

Complex number		Wavelength/nm [Extinction coefficient/mol^{-1} dm^3 cm^{-1}]		
10d		–	366 [1634]	298 [4210]
11a		450 [593]	358 [2474]	308 [4344]
10a		466 [1811]	360 [5670]	308 [14712]
14d		482 [2760]	370 [4880]	314 [17249]
11b		452 [1050]	362 [4333]	322 [5076]
10b		460 [1755]	376 [6095]	318 [8122]
14e		472 [4887]	384 [10080]	314 [16192]
10f		–	354 [11644]	336 [12405]
10c		488 [1998]	358 [9459]	298 [9701]

(*continued on next page*)

Table 6 (*continued*)

Complex number		Wavelength/nm [Extinction coefficient/mol^{-1} dm^3 cm^{-1}]		
14f		504 [7895]	364 [14296]	302 [13328]
9e		500 [3621]	374 [13318]	300 [9518]

were obtained on a BAS 100W electrochemical analyser with a one compartment three-electrode system consisting of a $Ag/AgNO_3$ (0.01 M) reference electrode, platinum wire auxiliary electrode and platinum disc working electrode. Samples (1–2 mM) were prepared and run under argon at ambient temperature, in anhydrous acetonitrile with tetrabutylammonium perchlorate (0.1 M) as background electrolyte. The scan rate used was 100 mV s^{-1} and the system gave ferrocene $E_{1/2} = +76$ mV. The platinum disc working electrode was polished between runs. X-ray diffraction data were collected at 173 K or 298 K using Nonius Kappa CCD with 1.5 kW graphite-monochromated Mo radiation. The strategy for data collection was evaluated using COLLECT [18]. Several sets of data were collected with both a 199° phi scan and omega scans to collect cusp data. The data were scaled and reduced as well as treated for absorption by a semi-empirical method using DENZO-SMN [19]. Unit cell dimensions were refined on all data. The structure was solved and refined using SHELX97 [20,21]. Molecular graphics were generated using ORTEP-III [22], PLATON [23] and X-SEED [24], a graphical interface for the SHELX program. For the most part, reaction solvents were purified, dried and distilled prior to use according to the literature methods. Less commonly used reagents and solvents such as *N*,*N*-dimethylformamide, pyridine and triethylamine were purified and dried, followed by storage under nitrogen in dry glass storage vessels equipped with Teflon valve stopcocks. Chromatography solvents were of analytical grade and used without purification, with the exception of dichloromethane and hexane which were of chemically pure grade and distilled in air prior to use. *n*-Butyllithium (1.6 M in hexanes), Superhydride® (1.0 M in tetrahydrofuran) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine was purchased from Sigma–Aldrich and transferred under nitrogen into a glass storage vessel with Teflon stopcock. All other commercial reagents were used as obtained without further purification. The following known compounds were prepared and fully characterized by us as part of this work. 4-Pyridylimine-4′-phenylferrocene [15c], 4-pyridylvinyl-4′-phenylferrocene [14c], 4-ferrocenylpyridine [3], 3-ferrocenylpyridine [4], 2-ferrocenylpyridine [25], 4-ferrocenylphenyl-3′-pyridine [17], 4-ferrocenylphenyl-2′-pyridine [17], 1,1′-bis(2-pyridyl)ferrocene [6b,8], 1,1′-bis-(4-pyridyl)ferrocene [17], ferrocenyldiphenylphosphine [26], dichlorotetracarbonyldirhodium [27], dicarbonylchloro(pyridine)rhodium [28], bis(carbonyl)chloro(4-aminopyridine)dicarbonylchlororhodium [29], chloro(1,5-cyclooctadiene)rhodium(I) dimer [30], chloro(1,5-cyclooctadiene)(pyridine)rhodium [31], (1,5-cyclooctadiene)-bis(pyridine)rhodium hexafluorophosphate [32] and (1,5-cyclooctadiene)bis(pyridine)rhodium perchlorate [32]. 1′,2′,3′,4′,5′-Pentamethylazaferrocene was prepared according to the method of Fu [33] and obtained courtesy of Dr. P. Beagley, Organometallic Research Group, University of Cape Town. Rhodium was obtained as the chloride salt on loan from Johnson–Matthey and ferrocene was obtained commercially from Sigma–Aldrich. Thin-layer chromatography was performed on aluminium-backed silica gel or aluminium oxide $60F_{254}$ plates in a variety of solvent systems using the ascending technique. Plates were analysed under ultraviolet light. Column chromatography was conducted either on silica gel 60, particle size 0.063–0.200 mm (70–230 mesh ASTM) or neutral alumina, particle size 0.063–0.200 mm (70–230 mesh ASTM). Columns were generally prepared with 1:100 ratio product to chromatographic material.

4.2. Rhodium carbonyl complexes

4.2.1. Dicarbonylchloro(4-phenylimine-4′-pyridine)rhodium (**9d**)

4-Phenylimine-4′-pyridine (56.2 mg, 0.31 mmol) was added slowly to a solution of the rhodium dimer, dichlorotetracarbonyldirhodium (60.7 mg, 0.15 mmol) in dichloromethane (10 mL). The reaction mixture was stirred under nitrogen for 20 min and then concentrated in vacuo. Pentane was added to precipitate the product. The product was collected by vacuum filtration as a yellow crystalline solid (74.0 mg, 63%); IR (KBr, cm^{-1}): 3040, 2088 (CO), 2013 (CO), 1605 (C=N). ^{1}H NMR (300 MHz; CD_3COCD_3): δ 8.96 (2H, dd, $J = 6.8$ Hz, C_5H_4N), 8.81 (1H, s, N=CH), 8.16 (2H, dd, $J = 6.8$ Hz, C_5H_4N), 7.51–7.44 (2H, tt,

$J = 15.1$ Hz, C_6H_5), 7.41 (2H, d, $J = 1.5$ Hz, C_6H_5), 7.35 (1H, t, $J = 10.6$ Hz, C_6H_5). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.42 (N=C), 154.78 (C_5H_4N), 130.93 (C_6H_5), 129.20 (C_5H_4N), 125.57 (C_6H_5), 122.94 (C_6H_5).

4.2.2. Dicarbonylchloro(4-pyridylimine-4′-phenylferrocene)-rhodium (**9e**)

4-Pyridylimine-4′-phenylferrocene (120.1 mg, 0.33 mmol) was added to a solution of dichlorotetracarbonyldirhodium (79.9 mg, 0.16 mmol) in dichloromethane (20 mL) and further stirred for 25 min. The reaction mixture was concentrated in vacuo and hexane was added to precipitate the product. The product was collected by vacuum filtration as small maroon-red rod-shaped crystals (56.0 mg, 61%); m.p. 165–175 °C. Anal. Calc. for $C_{24}H_{18}ClFeN_2O_2Rh$: C, 51.4%; H, 3.2; N, 5.0; M^+ 560. Found: C, 51.2%; H, 3.1; N, 4.8; M^+ 560.0. IR (KBr, cm^{-1}): 3054, 2359, 2080, 2003, 1684, 1643, 1589, 1427, 1326, 1280, 1106, 1014, 846, 823, 759, 740, 704, 491, 414. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.81 (2H, d, $J = 6.6$ Hz, C_5H_4N), 8.57 (1H, s, N=CH), 7.93 (2H, d, $J = 6.5$ Hz, C_5H_4N), 7.54 (2H, d, $J = 8.5$ Hz, C_6H_4), 7.27 (2H, d, $J = 8.3$ Hz, C_6H_4), 4.68 (2H, t, $J = 1.8$ Hz, C_5H_4), 4.36 (2H, t, $J = 1.8$ Hz, C_5H_4), 4.06 (5H, s, C_5H_5). ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.18 (N=C), 152.89 (C_5H_4N), 147.13 (C_6H_4), 145.97 (C_6H_4), 140.34 (C_5H_4N), 126.78 (C_5H_4N), 123.75 (C_6H_4), 121.65 (C_6H_4), 84.01 (C_5H_4), 69.71 (C_5H_5), 69.44 (C_5H_4), 66.54 (C_5H_4). FABMS (*m*/*z*): 560 (M^+, 8%), 525 (M−Cl, 5), 496 (M−CO, 2), 469 (M−CO, 2), 367 (M−Rh, 50), 366 (M−ligand, 90), 287 (M−py, 10).

4.2.3. Dicarbonylchloro(4-ferrocenylpyridine)rhodium (**9c**)

4-Ferrocenylpyridine (94.9 mg, 0.36 mmol) was added to a light yellow solution of dichlorotetracarbonyldirhodium (70.6 mg, 0.18 mmol) in anhydrous pentane (10 mL). A red suspension was observed almost immediately with the supernatant turning to a much lighter, almost clear colour. The product was isolated via vacuum filtration as red micro-crystals (113.8 mg, 69%); m.p. 128–130 °C. Anal. Calc. for $C_{17}H_{13}ClFeNO_2Rh$: C, 44.6%; H, 2.7; N, 3.1; M 458.9. Found: C, 44.4%; H, 2.6; N, 3.0; M^+ 458.7. IR (KBr, cm^{-1}): 3020, 2086 (CO), 2011 (CO), 1615, 1522, 1435, 1382, 1107, 1034, 833, 482. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.49 (2H, dd, $J = 6.7$ Hz, C_5H_4N), 7.39 (2H, dd, $J = 6.7$ Hz, C_5H_4N), 4.76 (2H, t, C_5H_4), 4.56 (2H, t, C_5H_4), 4.08 (5H, s, C_5H_5). ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.65 (C_5H_4N), 121.66 (C_5H_4N), 71.68 (C_5H_4), 70.36 (C_5H_5), 67.45 (C_5H_4); FABMS (*m*/*z*): 459 (M^+, 8%), 424 (M−Cl, 8), 389 (4), 367 (M−2CO, 3), 312 (34), 265 (ligand, 100), 235 (1), 200 (1).

4.3. Rhodium cyclooctadiene complexes

4.3.1. Chloro(1,5-cyclooctadiene)(4-phenylpyridine)-rhodium (**10e**)

4-Phenylpyridine (100.8 mg, 0.64 mmol) was added to a solution of chloro(1,5-cyclooctadiene)rhodium(I) dimer (159.0 mg, 0.32 mmol) in dichloromethane (10 mL). The reaction mixture was stirred for a further 31 min. The reaction mixture was then concentrated in vacuo and diethyl ether added to precipitate the product. The product was collected via vacuum filtration as bright yellow crystals (206.7 mg, 80%). Anal. Calc. for $C_{19}H_{21}ClNRh$: C, 56.8%; H, 5.3; N, 3.5; M^+ 401.74272. Found: C, 56.73%; H, 5.15; N, 3.46; M^+ 401.04176. IR (KBr, cm^{-1}): 2990, 2931, 2880, 2825, 2367, 2324, 1772, 1674, 1607, 1541, 1471, 1429, 1413, 1333, 1215, 1068, 993, 961, 848, 765, 733, 690, 626, 565, 486, 480. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.75 (2H, dd, $J = 6.6$ Hz, C_5H_4N), 7.57 (2H, d, $J = 5.6$ Hz, C_5H_4N), 7.48 (5H, m, C_6H_5), 4.19 (4H, br s, cod-CH), 2.51 (4H, m, cod-CH_2), 1.84 (4H, d, $J = 8.0$ Hz, cod-CH_2). ^{13}C NMR (75 MHz; solvent $CDCl_3$): δ 151.03 (C_5H_5N), 149.63 (C_5H_5N), 136.59 (C_6H_5), 129.86 (C_6H_5), 129.29 (C_6H_5), 126.97 (C_6H_5), 122.46 (C_5H_5N), 80.05 (cod), 30.88 (cod); FABMS (*m*/*z*): 401 (M^+, 13%), 366 (M−Cl, 100), 346 (3), 310 (4), 258 (M−cod, 9), 211 (42), 181 (11), 156 (38), 136 (8), 103 (Rh, 5) and 77 (5).

4.3.2. (1,5-Cyclooctadiene)bis(4-phenylpyridine)rhodium perchlorate (**14b**)

A white precipitate was observed to form immediately on addition of silver perchlorate (66.8 mg, 0.32 mmol) to a solution of chloro(1,5-cyclooctadiene)rhodium(I) dimer (79.7 mg, 0.16 mmol) in acetone (20 mL). 4-Phenylpyridine (100.1 mg, 0.64 mmol) was then added slowly to the supernatant, which was stirred at room temperature for a further 20 min. The reaction mixture was then concentrated and diethyl ether added to precipitate the product. The product was collected by vacuum filtration as a light yellow powder (117.2 mg, 59%); Anal. Calc. for $C_{30}H_{30}ClN_2O_4Rh$: C, 58.0%; H, 4.9; N, 4.5; M^+ 521.5. Found: C, 57.85%; H, 4.92; N, 4.12; M^+ 521.2. IR (KBr, cm^{-1}): 3056, 2872, 2818, 2370, 2324, 1616, 1575, 1544, 1516, 1483, 1418, 1398, 1221, 1095, 841, 766, 733, 696, 623, 565, 481, 437. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.88 (4H, d, $J = 5.9$ Hz, C_5H_4N), 7.62–7.53 (10H, m, C_6H_5), 7.46 (4H, d, $J = 5.8$ Hz, C_5H_4N), 4.14 (4H, br s, cod-CH), 2.69 (4H, m, cod-CH_2), 1.99 (4H, d, $J = 10.3$ Hz, cod-CH_2). ^{13}C NMR (101 MHz, CD_3COCD_3): δ 153.85 (C_5H_5N), 136.02 (C_5H_5N), 130.43 (C_5H_5N), 129.77 (C_6H_5), 129.58 (C_6H_5), 127.58 (C_6H_5), 127.28 (C_6H_5), 123.54 (C_5H_5N), 85.15 (cod), 30.54 (cod). FABMS (*m*/*z*): 521 (M^+, 10%), 465 (3), 413 (M^+−cod, 11), 398 (6), 366 (90), 258 (29), 218 (7), 211 (37), 156 (100), 136 (17), 89 (19).

4.3.3. Chloro(1,5-cyclooctadiene)(4-phenylimine-4′-pyridine)rhodium (**10f**)

4-Phenylimine-4′-pyridine (52.4 mg, 0.29 mmol) was added to a solution of chloro(1,5-cyclooctadiene)rhodium(I) dimer (70.6 mg, 0.14 mmol) in dichloromethane (10 mL). The reaction mixture was stirred for a further 28 min. The reaction mixture was then concentrated in vacuo and diethyl ether added to precipitate the product. The product was collected via vacuum filtration as fine

yellow crystals (85.3 mg, 83%). Anal. Calc. for $C_{20}H_{22}ClN_2Rh$: C, 44.6%; H, 2.7; N, 7.4. Found: C, 44.56%; H, 2.69; N, 7.26. IR (KBr, cm^{-1}) 3049, 2948, 2873, 2359, 1651, 1608, 1574, 1485, 1191, 1166, 1075, 1055, 961, 818, 668, 481, 459, 406. ^1H NMR (300 MHz, $CDCl_3$): δ 8.89 (2H, dd, C_5H_4N), 8.47 (1H, s, N=CH), 7.88 (2H, d, $J = 6.2$ Hz, C_5H_4N), 7.44 (2H, t, C_6H_5), 7.34 (2H, d, $J = 7.2$ Hz, C_6H_5), 7.26 (1H, t, C_6H_5), 4.21 (4H, br s, cod-CH), 2.54–2.48 (4H, m, cod-CH_2), 1.82 (4H, d, $J = 8.3$ Hz, cod-CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.85 (N=C), 154.28 (C_5H_4N), 151.89 (C_5H_4N), 144.51 (C_6H_5), 129.38 (C_5H_4N), 127.65 (C_6H_5), 124.24 (C_6H_5), 122.06 (C_6H_5), 85.42 (cod), 30.55 (cod).

4.3.4. (1,5-Cyclooctadiene)bis(4-phenylimine-4′-pyridine)-rhodium perchlorate (**14c**)

A white precipitate was observed to form immediately on addition of silver perchlorate (58.9 mg, 0.28 mmol) to a solution of chloro(1,5-cyclooctadiene)rhodium(I) dimer (70.6 mg, 0.14 mmol) in acetone (15 mL). 4-Phenylimine-4′-pyridine (103.5 mg, 0.57 mmol) was then added slowly to the supernatant, which was stirred at room temperature for a further 20 min. The reaction mixture was then concentrated and diethyl ether added to precipitate the product. The product was collected by vacuum filtration as a yellow powder (110.9 mg, 59%); m.p. 199 °C dec. Anal. Calc. for $C_{32}H_{32}ClN_4O_4Rh$: C, 56.5%; H, 4.8; N, 8.3; M^+ 575.53486. Found: C, 55.98%; H, 4.63; N, 8.06; M^+ 575.1682. IR (KBr, cm^{-1}) 3583, 2339, 1770, 1738, 1622, 1610, 1109, 1086, 833, 552, 445. ^1H NMR (300 MHz, $CDCl_3$): δ 9.01 (4H, d, $J = 5.6$ Hz, C_5H_4N), 8.39 (2H, s, N=CH), 7.86 (4H, d, $J = 5.5$ Hz, C_5H_4N), 7.40 (4H, t, $J = 7.3$ Hz, C_6H_5), 7.28 (2H, t, $J = 7.3$ Hz, C_6H_5), 7.19 (4H, d, $J = 8.0$ Hz, C_6H_5), 4.15 (4H, br s, cod-CH), 2.71 (4H, m, cod-CH_2), 2.00 (4H, d, $J = 8.8$ Hz, cod-CH_2). ^{13}C NMR (75 MHz; $CDCl_3$): δ 158.21 (N=C), 151.12 (C_5H_4N), 150.89 (C_5H_4N), 143.15 (C_6H_5), 129.35 (C_5H_4N), 127.74 (C_6H_5), 124.24 (C_6H_5), 121.06 (C_6H_5), 85.42 (cod), 30.55 (cod). FABMS (*m/z*): 575 (M^+, 10%), 546 (4), 532 (2), 492 (2), 471 (4), 439 (4), 409 (5), 393 (100), 364 (4), 350 (8), 284 (8), 211 (47), 183 (37), 136 (12), 89 (17), 80 (17).

4.3.5. Chloro(1,5-cyclooctadiene)(4-pyridylimine-4′-phenylferrocene)rhodium (**10c**)

4-Pyridylimine-4′-phenylferrocene (109.0 mg, 0.29 mmol) was added to a solution of chloro(1,5-cyclooctadiene)rhodium(I) dimer (73.4 mg, 0.15 mmol) in dichloromethane (10 mL). The reaction mixture was stirred for a further 34 min. The reaction mixture was then concentrated in vacuo and hexane added to precipitate the product. The product was collected via vacuum filtration as red crystalline flakes (134.1 mg, 75%); m.p. 200–202 °C. Anal. Calc. for $C_{30}H_{30}ClFeN_2Rh$: C, 58.8%; H, 4.9; N, 4.6; M^+ 612.79361. Found: C, 58.29%; H, 4.59; N, 4.40; M^+ 612.05019. IR (KBr, cm^{-1}): 3056, 2954, 2879, 2356, 2329, 2295, 1745, 1731, 1684, 1616, 1609, 1575, 1541, 1514, 1480, 1426, 1392, 1371, 1106, 1004, 977, 950, 841, 814, 807, 672, 638, 543, 495, 481, 434. ^1H NMR (300 MHz, $CDCl_3$): δ 8.84 (2H, d, $J = 5.9$ Hz, C_5H_4N), 8.48 (1H, s, N=CH), 7.77 (2H, dd, $J = 5.9$ Hz, C_5H_4N), 7.51 (2H, dd, $J = 6.7$ Hz, C_6H_4), 7.22 (2H, d, $J = 8.5$ Hz, C_6H_4), 4.66 (2H, t, $J = 1.8$ Hz, C_5H_4), 4.35 (2H, t, $J = 1.8$ Hz, C_5H_4), 4.19 (4H, br s, cod-CH), 4.03 (5H, s, C_5H_5), 2.52–2.48 (4H, m, cod-CH_2), 1.85 (4H, d, $J = 8.6$ Hz, cod-CH_2). ^{13}C NMR (300 MHz, $CDCl_3$): δ 156.02 (N=C), 151.10 (C_5H_4N), 126.83 (C_5H_4N), 124.13 (C_6H_4), 121.55 (C_6H_4), 69.75 (C_5H_5), 69.40 (C_5H_4), 66.58 (C_5H_4), 30.62 (cod). FABMS (*m/z*): 612 (M^+, 1%), 532 (2), 519 (3), 382 (5), 366 (ligand, 100), 305 (26), 289 (41), 277 (41), 229 (9), 176 (27), 89 (22).

4.3.6. (1,5-Cyclooctadiene)bis(4-pyridylimine-4′-phenylferrocene)rhodium perchlorate (**14f**)

A white precipitate was observed to form immediately on addition of silver perchlorate (22.6 mg, 0.11 mmol) to a solution of chloro(1,5-cyclooctadiene)rhodium(I) dimer (26.9 mg, 0.05 mmol) in acetone (10 mL). 4-Pyridylimine-4′-phenylferrocene (80.0 mg, 0.22 mmol) was then added slowly to the supernatant, which was stirred at room temperature for a further 30 min. The reaction mixture was then concentrated and diethyl ether added to precipitate the product. The product was collected by vacuum filtration as a fine dark maroon-red powder (92.8 mg, 81%); m.p. 265–268 °C dec. Anal. Calc. for $C_{52}H_{48}Fe_2N_4RhClO_4$: C, 66.2%; H, 5.1; N, 5.9; M^+ 943.2. Found: C, 65.97%; H, 5.12; N, 5.78; M^+ 943.2. IR (KBr, cm^{-1}): 3076, 3063, 2363, 2322, 2295, 1738, 1684, 1616, 1575, 1541, 1514, 1487, 1432, 1398, 1120, 1100, 1086, 1065, 998, 963, 889, 841, 821, 760, 726, 678, 617, 549, 501, 481, 434. ^1H NMR (400 MHz, $CDCl_3$): δ 8.99 (4H, br s, C_5H_4N), 8.47 (2H, s, N=CH), 7.87 (4H, d, $J = 4.4$ Hz, C_5H_4N), 7.49 (4H, d, $J = 8.4$ Hz, C_6H_4), 7.19 (4H, d, $J = 8.1$ Hz, C_6H_4), 4.67 (4H, br s, C_5H_4), 4.36 (4H, br s, C_5H_4), 4.16 (4H, br s, cod-CH), 4.05 (10H, s, C_5H_5), 2.81–2.66 (4H, m, cod-CH_2), 2.02 (4H, d, $J = 8.8$ Hz, cod-CH_2). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.95 (N=C), 129.84 (C_5H_4N), 126.94 (C_5H_4N), 124.25 (C_6H_4), 121.66 (C_6H_4), 80.24 (cod), 69.95 (C_5H_5), 69.58 (C_5H_4), 66.75 (C_5H_4), 30.71 (cod). FABMS (*m/z*): 943 (M^+, 4%), 577 (M−ligand, 93), 366 (ligand, 100).

4.3.7. Chloro(1,5-cyclooctadiene)(4-ferrocenylpyridine)-rhodium (**10a**)

4-Ferrocenylpyridine (74.6 mg, 0.28 mmol) was added to a solution of chloro(1,5-cyclooctadiene)rhodium(I) dimer (69.8 mg, 0.14 mmol) in dichloromethane (10 mL). The reaction mixture was stirred for a further 15 min. The reaction mixture was then concentrated in vacuo and pentane added to precipitate the product. The product was collected via vacuum filtration as an orange solid (111.7 mg, 78%); m.p. 167–169 °C. Anal. Calc. for $C_{23}H_{25}ClFeNRh$: C, 54.2%; H, 4.0; N, 2.7; M^+ 509.0. Found: C, 54.2%; H, 4.6; N, 2.7; M^+ 509.0. IR (KBr,

cm^{-1}): 3069, 2872, 2832, 2358, 2331, 1739, 1670, 1615, 1568, 1544, 1516, 1475, 1436, 1398, 1338, 1286, 1106, 1031, 963, 825, 809, 674, 503. ^1H NMR (300 MHz; $CDCl_3$): δ 8.51 (2H, dd, $J = 6.7$ Hz, C_5H_4N), 7.27 (2H, dd, $J = 7.3$ Hz, C_5H_4N), 4.69 (2H, t, C_5H_4), 4.47 (2H, t, C_5H_4), 4.19 (4H, br s, cod-CH), 4.04 (5H, s, C_5H_5), 2.53–2.49 (4H, m, cod-CH_2), 1.84 (4H, d, $J = 8.1$ Hz, cod-CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.28 (C_5H_4N), 121.19 (C_5H_4N), 79.28 (cod-CH), 70.98 (C_5H_4), 70.14 (C_5H_5), 67.15 (C_5H_4), 30.90 (cod-CH_2). FABMS (*m*/*z*): 509 (M^+, 3%), 312 (32), 265 (58), 167 (17), 89 (44).

4.3.8. (1,5-Cyclooctadiene)bis(4-ferrocenylpyridine)-rhodium perchlorate (**14d**)

A white precipitate was observed to form immediately on addition of silver perchlorate (43.8 mg, 0.20 mmol) to a solution of chloro(1,5-cyclooctadiene)rhodium(I) dimer (50.4 mg, 0.10 mmol) in acetone (15 mL). 4-Ferrocenylpyridine (106.1 mg, 0.40 mmol) was then added slowly to the supernatant, which was stirred at room temperature for a further 21 min. The reaction mixture was then concentrated and diethyl ether added to precipitate the product. The product was collected by vacuum filtration as small red-brown crystalline flakes (162.2 mg, 96%); m.p. 225 °C dec. Anal. Calc. for $C_{38}H_{38}Fe_2N_2RhClO_4$: C, 54.5%; H, 4.6; N, 3.3; M^+ 737.0. Found: C, 54.2%; H, 4.6; N, 3.1; M^+ 737.1. IR (KBr, cm^{-1}): 3069, 2349, 2322, 1684, 1616, 1608, 1575, 1544, 1516, 1429, 1397, 1340, 1217, 1122, 832, 686, 677, 622, 538, 481, 472, 418. ^1H NMR (300 MHz, $CDCl_3$): δ 8.60 (4H, d, $J = 6.2$ Hz, C_5H_4N), 7.36 (4H, d, $J = 6.4$ Hz, C_5H_4N), 4.68 (4H, br s, C_5H_4), 4.45 (4H, br s, C_5H_4), 4.12 (4H, br s, cod-CH), 3.98 (10H, s, C_5H_5), 2.75–2.68 (4H, m, cod-CH_2), 1.98 (4H, d, $J = 8.8$ Hz, cod-CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.78 (C_5H_4N), 122.55 (C_5H_4N), 77.82 (cod-CH), 70.52 (C_5H_5), 70.04 (C_5H_4), 67.36 (C_5H_4), 30.62 (cod-CH_2). FABMS (*m*/*z*): 737 (M^+, 10%), 476 (30), 312 (19), 265 (97), 155 (67), 137 (56), 89 (20).

4.3.9. Chloro(1,5-cyclooctadiene)(3-ferrocenylpyridine)-rhodium (**11a**)

3-Ferrocenylpyridine (78.3 mg, 0.30 mmol) was added to a solution of chloro(1,5-cyclooctadiene)rhodium(I) dimer (73.4 mg, 0.15 mmol) in dichloromethane (15 mL). The reaction mixture was stirred for a further 35 min. The reaction mixture was then concentrated in vacuo and pentane added to precipitate the product. The product was collected via vacuum filtration as golden yellow microcrystals (134.5 mg, 88%); m.p. 162–164 °C. Anal. Calc. for $C_{23}H_{25}ClFeNRh$: C, 54.2%; H, 4.9; N, 2.7; M^+ 509.65806. Found: C, 54.20%; H, 4.76; N, 2.68; M^+ 509.00799. IR (KBr, cm^{-1}) 3616, 3584, 2830, 2349, 1798, 1703, 1634, 1615, 1422, 1105, 814, 667, 439, 408. ^1H NMR (400 MHz, $CDCl_3$): δ 8.80 (1H, br s, C_5H_4N), 8.52 (1H, dd, $J = 6.6$ Hz, C_5H_4N), 7.70 (1H, dt, $J = 8.1$ Hz, C_5H_4N), 7.18 (1H, dd, $J = 5.5$ Hz, C_5H_4N), 4.66 (2H, t, $J = 1.8$ Hz, C_5H_4), 4.40 (2H, t, $J = 1.8$ Hz, C_5H_4), 4.22 (4H, br s, cod-CH), 4.08 (5H, s, C_5H_5), 2.51 (4H, m, cod-CH_2), 1.85 (4H, d, $J = 8.0$ Hz, cod-CH_2). ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.41 (C_5H_4N), 147.52 (C_5H_4N), 133.89 (C_5H_4N), 124.01 (C_5H_4N), 80.00 (cod), 69.91 (C_5H_4), 69.81 (C_5H_5), 66.70 (C_5H_4), 30.82 (cod). FABMS (*m*/*z*): 509 (M^+, 3%), 474 (M−Cl, 41), 365 (M-cod, 4), 350 (6), 310 (18), 263 (ligand, 100), 211 (M−ligand, 18), 154 (6), 136 (6).

4.3.10. Chloro(1,5-cyclooctadiene)(2-ferrocenylpyridine)-rhodium (**12a**)

2-Ferrocenylpyridine (45.0 mg, 0.17 mmol) was added to a solution of chloro(1,5-cyclooctadiene)rhodium(I) dimer (42.2 mg, 0.08 mmol) in dichloromethane (10 mL). The reaction mixture was stirred for a further 25 min. The reaction mixture was then concentrated in vacuo and pentane added to precipitate the product. The product was collected via vacuum filtration as an orange-brown powder (26.6 mg, 31%); m.p. 123–125 °C. Anal. Calc. for $C_{23}H_{25}ClFeNRh$: C, 54.2%; H, 4.9; N, 2.7; M^+ 509. Found: C, 54.48%; H, 4.72; N, 2.48; M^+ 509. IR (KBr, cm^{-1}) 3616, 3584, 2830, 2349, 1798, 1703, 1634, 1615, 1598, 1495, 1422, 1386, 1105, 817, 457, 408. ^1H NMR (400 MHz, $CDCl_3$): δ 8.50 (1H, d, $J = 4.8$ Hz, C_5H_4N), 7.57 (1H, t, $J = 7.7$ Hz, C_5H_4N), 7.41 (1H, d, $J = 8.1$ Hz, C_5H_4N), 7.06 (1H, t, $J = 4.8$ Hz, C_5H_4N), 4.92 (2H, t, $J = 1.8$ Hz, C_5H_4), 4.39 (2H, t, $J = 1.8$ Hz, C_5H_4), 4.23 (4H, s, cod-CH), 4.05 (5H, s, C_5H_5), 2.49 (4H, m, cod-CH_2), 1.74 (4H, d, $J = 8.4$ Hz, cod-CH_2). ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.25 (C_5H_4N), 145.18 (C_5H_4N), 136.51 (C_5H_4N), 120.36 (C_5H_4N), 120.04 (C_5H_4N), 78.66 (cod), 69.78 (C_5H_4), 68.48 (C_5H_5), 67.16 (C_5H_4), 30.79 (cod). FABMS (*m*/*z*): 510 (M, 9%), 509 (M^+, 1), 473 (M^+-Cl), 365 (M−cod, 13), 303 (7), 263 (2-Fcpy, 2), 185 (100), 115 (20).

4.3.11. Chloro(1,5-cyclooctadiene)(4-ferrocenylphenyl-4′-pyridine)rhodium (**10b**)

4-Ferrocenylphenyl-4′-pyridine (50.0 mg, 0.15 mmol) was added to a solution of chloro(1,5-cyclooctadiene)rhodium(I) dimer (36.3 mg, 0.07 mmol) in dichloromethane (7 mL). The reaction mixture was stirred for a further 20 min. The reaction mixture was then concentrated in vacuo and diethyl ether added to precipitate the product. The product was collected via vacuum filtration as a dark red powder (59.9 mg, 70%); m.p. 213 °C dec. Anal. Calc. for $C_{29}H_{29}ClFeNRh$: C, 59.4%, H, 5.0, N, 2.4; M^+ 585. Found: C, 59.62%; H, 5.12; N, 2.48; M^+ 585. IR (KBr, cm^{-1}): 3069, 2356, 2322, 2295, 1682, 1616, 1593, 1569, 1544, 1516, 1489, 1432, 1398, 1338, 1283, 1222, 1106, 1079, 1032, 998, 964, 814, 719, 698, 644, 597, 502, 475, 441. ^1H NMR (300 MHz, $CDCl_3$): δ 8.72 (2H, dd, $J = 6.6$ Hz, C_5H_4N), 7.59–7.50 (6H, m, C_6H_4 and C_5H_4N), 4.68 (2H, t, $J = 1.8$ Hz, C_5H_4), 4.37 (2H, t, $J = 1.8$ Hz, C_5H_4), 4.18 (4H, br s, cod-CH), 4.05 (5H, s, C_5H_5), 2.54–2.49 (4H, m, cod-CH_2), 1.84 (4H, d, $J = 7.9$ Hz, cod-CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.97 (C_5H_4N), 149.25 (C_5H_4N), 142.02 (C_6H_4), 133.56

(C_6H_4), 126.92 (C_6H_4), 126.73 (C_6H_4), 121.89 (C_5H_4N), 83.65 (cod-CH), 69.73 (C_5H_5), 69.55 (C_5H_4), 66.66 (C_5H_4), 30.90 (cod-CH_2). FABMS (*m*/*z*): 585 (M^+, 1%), 574 (23), 387 (4-Fc(C_6H_4)py, 3), 339 (3), 273 (2), 241 (24), 185 (100), 115 (10).

4.3.12. (1,5-Cyclooctadiene)bis(4-ferrocenylphenyl-4′-pyridine)rhodium perchlorate (**14e**)

A white precipitate was observed to form immediately on addition of silver perchlorate (42.0 mg, 0.20 mmol) to a solution of chloro(1,5-cyclooctadiene)rhodium(I) dimer (50.0 mg, 0.10 mmol) in acetone (15 mL). 4-Ferrocenylphenyl-4′-pyridine (106.1 mg, 0.40 mmol) was then added slowly to the supernatant, which was stirred at room temperature for a further 46 min. The reaction mixture was then concentrated and diethyl ether added to precipitate the product. The product was collected by vacuum filtration as small dark red crystals (164.6 mg, 83%); m.p. 110–112 °C. Anal. Calc. for $C_{50}H_{46}ClFe_2N_2O_4Rh$: C, 60.7%; H, 4.7; N, 2.8; M^+ 988. Found: C, 60.32%; H, 4.72; N, 2.59; M^+ 988. IR (KBr, cm^{-1}): 3069, 2879, 2832, 2356, 2322, 2023, 1772, 1616, 1602, 1589, 1541, 1487, 1432, 1405, 1283, 1215, 1120, 1100, 1004, 889, 814, 760, 726, 624, 509, 481, 475, 447. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.85 (4H, d, $J = 5.0$ Hz, C_5H_4N), 7.87–7.34 (12H, m, C_6H_4 and C_5H_4N), 4.80 (4H, br s, C_5H_4), 4.50 (4H, br s, C_5H_4), 4.31 (4H, br s, cod-CH), 4.14 (10H, s, C_5H_5), 2.89–2.56 (4H, m, cod-CH_2), 2.00 (4H, d, $J = 8.4$ Hz, cod-CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.50 (C_5H_4N), 142.47 (C_5H_4N), 126.87 (C_6H_4), 126.68 (C_6H_4), 122.88 (C_5H_4N), 84.89 (cod-CH), 70.83 (C_5H_5), 70.56 (C_5H_4), 67.40 (C_5H_4), 30.62 (cod-CH_2). FABMS (*m*/*z*): 988 (M^+, 10%), 851 (3), 639 (7), 559 (11), 474 (9), 375 (58), 338 (4-Fc(C_6H_4)py, 7), 277 (100), 258 (20), 186 (100), 115 (33).

4.3.13. Chloro(1,5-cyclooctadiene)(4-ferrocenylphenyl-3′-pyridine)rhodium (**11b**)

4-Ferrocenylphenyl-3′-pyridine (70.0 mg, 0.21 mmol) was added to a solution of chloro(1,5-cyclooctadiene)rhodium(I) dimer (50.9 mg, 0.10 mmol) in dichloromethane (10 mL). The reaction mixture was stirred for a further 31 min. The reaction mixture was then concentrated in vacuo and diethyl ether added to precipitate the product. The product was collected via vacuum filtration as an orange-mustard powder (84.6 mg, 69%); m.p. 215–217 °C. Anal. Calc. for $C_{29}H_{29}ClFeNRh$: C, 59.5%; H, 5.0; N, 2.4; M^+ 585. Found: C, 59.59%; H, 5.00; N, 2.32; M^+ 585.0. IR (KBr, cm^{-1}) 3689, 3671, 2832, 1612, 1395, 1104, 803, 700, 531, 442, 430, 406, 404. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.98 (1H, br s, C_5H_4N), 8.68 (1H, dd, $J = 6.6$ Hz, C_5H_4N), 7.88 (1H, dt, $J = 7.3$ Hz, C_5H_4N), 7.58 (2H, d, $J = 8.4$ Hz, C_6H_4), 7.49 (2H, d, $J = 8.4$ Hz, C_6H_4), 7.37 (1H, dd, $J = 5.9$ Hz, C_5H_4N), 4.69 (2H, t, $J = 1.8$ Hz, C_5H_4), 4.37 (2H, t, $J = 1.8$ Hz, C_5H_4), 4.22 (4H, br s, cod-CH), 4.07 (5H, s, C_5H_5), 2.52 (4H, m, cod-CH_2), 1.86 (4H, d, $J = 8.1$ Hz, cod-CH_2). ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.45 (C_5H_4N), 147.26 (C_5H_4N), 133.25 (C_5H_4N), 125.50 (C_6H_4), 125.15 (C_6H_4), 122.77 (C_5H_4N), 82.26 (cod), 68.11 (C_5H_5), 67.74 (C_5H_4), 65.00 (C_5H_4), 29.25 (cod). FABMS (*m*/*z*): 585 (M^+, 1%), 550 (M−Cl, 28), 386 (21), 339 (3-Fc(C_6H_4)py, 100), 274 (6), 238 (50), 211 (17).

4.3.14. Chloro(1,5-cyclooctadiene)(4-ferrocenylphenyl-2′-pyridine)rhodium (**12b**)

4-Ferrocenylphenyl-2′-pyridine (60.0 mg, 0.18 mmol) was added to a solution of chloro(1,5-cyclooctadiene)rhodium(I) dimer (43.6 mg, 0.09 mmol) in dichloromethane (10 mL). The reaction mixture was stirred for a further 31 min. The reaction mixture was then concentrated in vacuo and diethyl ether added to precipitate the product. The product was collected via vacuum filtration as an orange powder (42.6 mg, 40%); m.p. 90–92 °C. Anal. Calc. for $C_{29}H_{29}ClFeNRh$: C, 59.5%; H, 5.0; N, 2.4; M^+ 585. Found: C, 59.42%; H, 5.12; N, 2.32; M^+ 585. IR (KBr, cm^{-1}) 3629, 3568, 2323, 1740, 1700, 1646, 1336, 1607, 1474, 783, 500, 409. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (1H, dd, $J = 4.8$ Hz, C_5H_4N), 7.93 (2H, dd, $J = 8.4$ Hz, C_6H_4), 7.74 (2H, dd, $J = 6.2$ Hz, C_5H_4N), 7.57 (2H, dd, $J = 8.8$ Hz, C_6H_4), 7.21 (1H, dd, $J = 6.6$ Hz, C_5H_4N), 4.74 (2H, t, $J = 1.8$ Hz, C_5H_4), 4.23 (2H, t, $J = 2.2$ Hz, C_5H_4), 4.11 (4H, s, cod-CH), 4.05 (5H, s, C_5H_5), 2.51 (4H, m, cod-CH_2), 1.84 (4H, d, $J = 8.2$ Hz, cod-CH_2). ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.60 (C_5H_4N), 136.58 (C_5H_4N), 126.25 (C_6H_4), 126.77 (C_6H_4), 121.70 (C_5H_4N), 120.05 (C_5H_4N), 78.67 (cod), 69.63 (C_5H_5), 69.12 (C_5H_4), 66.49 (C_5H_4), 30.79 (cod). FABMS (*m*/*z*): 585 (M^+, 1%), 548 (M−Cl, 3), 388 (2-Fc(C_6H_4)py, 60), 340 (60), 274 (10), 238 (3), 115 (10).

4.3.15. [1,1′-Bis(2-pyridyl)ferrocene](1,5-cyclooctadiene)-rhodium perchlorate (**15a**)

A white precipitate was observed to form immediately on addition of silver perchlorate (48.7 mg, 0.24 mmol) to a solution of chloro(1,5-cyclooctadiene)rhodium(I) dimer (58.0 mg, 0.12 mmol) in acetone (15 mL). 1,1′-Bis(2-pyridyl)ferrocene (80.0 mg, 0.24 mmol) was added to the supernatant, which was stirred at room temperature for a further 35 min. The reaction mixture was then concentrated and pentane added to precipitate the product. The product was collected by vacuum filtration as small dark red crystals (92.6 mg, 70%); m.p. 148–150 °C. Anal. Calc. for $C_{28}H_{28}ClFeN_2O_4Rh$: C, 59.5%; H, 5.0; N, 2.4; M^+ 551.28874. Found: C, 59.62%; H, 4.89; N, 2.21; M^+ 551.06569. IR (KBr, cm^{-1}) 1596, 1555, 1494, 1419, 1283, 1120, 1086, 889, 814, 780, 746, 692, 624, 522, 447, 420; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (2H, d, $J = 5.3$ Hz, C_5H_4N), 7.67 (2H, t, $J = 7.8$ Hz, C_5H_4N), 7.50 (2H, dd, $J = 6.7$ Hz, C_5H_4N), 7.08 (2H, dd, $J = 11.6$ Hz, C_5H_4N), 4.91 (4H, t, $J = 1.8$ Hz, C_5H_4), 4.50 (4H, s, cod-CH), 4.36 (4H, t, $J = 1.8$ Hz, C_5H_4), 2.81 (cod-CH_2), 2.00 (4H, br s, cod-CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.97 (C_5H_4N), 136.51 (C_5H_4N), 131.90 (C_5H_4N), 128.39

(C_5H_4N), 120.30 (C_5H_4N), 75.21 (cod), 71.48 (C_5H_4), 68.73 (C_5H_4), 30.02 (cod). FABMS (*m*/*z*): 551 (M^+, 14%), 443 (M^+-cod, 17), 387 (7), 341 ($Fc(2\text{-py})_2$, 11), 258 (23), 189 (19), 154 (37), 115 (58), 89 (100).

4.3.16. [1,1′-Bis(4-pyridyl)ferrocene](1,5-cyclooctadiene)-rhodium perchlorate (**15b**)

A white precipitate was observed to form immediately on addition of silver perchlorate (60.9 mg, 0.29 mmol) to a solution of chloro(1,5-cyclooctadiene)rhodium(I) dimer (72.5 mg, 0.15 mmol) in ethanol (15 mL). 1,1′-Bis(4-pyridyl)ferrocene (100.0 mg, 0.29 mmol) was added to the supernatant, which was stirred at room temperature for a further 40 min. The reaction mixture was then concentrated and pentane added to precipitate the product. The product was collected by vacuum filtration as small dark red crystals (107.1 mg, 67%); m.p. 208–210 °C dec. Anal. Calc. for $C_{28}H_{28}ClFeN_2O_4Rh$: C, 59.5%; H, 5.0; N, 2.4; M^+ 551. Found: C, 59.32%; H, 4.86; N, 2.32; M^+ 551. IR (KBr, cm^{-1}) 3504, 3436, 3361, 2363, 1650, 1595, 1426, 1113, 1086, 841, 692, 617, 543. ^1H NMR (400 MHz, $CDCl_3$): δ 8.52 (4H, d, $J = 5.8$ Hz, C_5H_4N), 7.16 (4H, d, $J = 5.6$ Hz, C_5H_4N), 4.85 (4H, t, $J = 1.8$ Hz, C_5H_4), 4.52 (4H, t, $J = 1.8$ Hz, C_5H_4), 4.39 (4H, s, cod-CH), 2.89 (4H, m, cod-CH_2), 1.98 (4H, br s, cod-CH_2). ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.69 (C_5H_4N), 120.18 (C_5H_4N), 75.18 (cod), 72.24 (C_5H_4), 68.45 (C_5H_4), 30.21 (cod). FABMS (*m*/*z*): 551 (M^+, 7%), 442 (1), 387 (1), 342 ($Fc(4\text{-py})_2$, 3), 279 (100), 258 (3), 223 (3), 207 (5), 185 (100), 115 (10).

4.3.17. Chloro(1,5-cyclooctadiene)(1′,2′,3′,4′,5′-pentamethylazaferrocene)rhodium (**13**)

1′,2′,3′,4′,5′-Pentamethylazaferrocene (70.0 mg, 0.27 mmol) was added to a solution of chloro(1,5-cyclooctadiene)rhodium(I) dimer (67.1 mg, 0.14 mmol) in dichloromethane (10 mL). The reaction mixture was stirred for a further 37 min. The reaction mixture was then concentrated in vacuo and pentane added to precipitate the product. The product was collected via vacuum filtration as an orange powder (47.3 mg, 67%); m.p. 192–193 °C. Anal. Calc. for $C_{22}H_{31}ClFeNRh$: C, 52.4%; H, 6.2; N, 2.8; M^+ 504.75. Found: C, 52.12%; H, 5.98; N, 2.65; M^+ 505. IR (KBr, cm^{-1}) 2907, 2872, 2832, 1738, 1704, 1650, 1575, 1473, 1446, 1371, 1324, 1113, 1066, 1018, 943, 869, 814, 767, 468. ^1H NMR (400 MHz, $CDCl_3$): δ 5.33 (2H, s, C_4H_4N), 4.53 (2H, s, C_4H_4N), 4.16 (2H, s, cod-CH), 3.81 (2H, s, cod-CH), 2.41 (4H, s, cod-CH_2), 2.08 (15H, s, CH_3), 1.75 (4H, s, cod-CH_2). ^{13}C NMR (101 MHz, $CDCl_3$): δ 88.96 (C_5Me_5), 82.64 (C_4H_4N), 75.38 (cod), 74.21 (C_4H_4N), 31.04 (cod), 30.45 (cod), 11.50 (CH_3). FABMS (*m*/*z*): 505 (M^+, 10%), 466 (2), 402 (2), 341 (3), 290 (4), 258 (100), 244 (8). 226 (4), 207 (7).

4.3.18. Chloro(1,5-cyclooctadiene)(4-octyloxystilbene)-rhodium (**10g**)

4-Octyloxystilbene (70.0 mg, 0.23 mmol) was added to a solution of chloro(1,5-cyclooctadiene)rhodium(I) dimer (55.8 mg, 0.11 mmol) in dichloromethane (10 mL). The reaction mixture was stirred for a further 50 min. The reaction mixture was then concentrated in vacuo and pentane added to precipitate the product. The product was collected via vacuum filtration as a light yellow powder (86.3 mg, 67%); m.p. 89–128 °C (lit. 85–130 °C). ^1H NMR (400 MHz, $CDCl_3$): δ 8.60 (2H, d, $J = 6.6$ Hz, C_5H_4N), 7.45 (2H, d, $J = 8.4$ Hz, C_6H_4), 7.30 (2H, d, $J = 6.6$ Hz, C_5H_4N), 7.26 (1H, d, $J = 16.1$ Hz, CH=CH), 6.90 (2H, d, $J = 8.8$ Hz, C_6H_4), 6.78 (1H, d, $J = 16.1$ Hz, CH=CH), 4.22 (4H, br s, cod-CH), 3.98 (2H, t, $J = 6.6$ Hz, OCH_2), 2.50 (4H, m, cod-CH_2), 1.83 (4H, d, $J = 7.7$ Hz, cod-CH_2), 1.42 (2H, m, CH_2), 1.29 (10H, m, $CH_2 \times 5$), 0.89 (3H, m, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.10 (C_5H_4N), 133.41 (C=C), 127.12 (C_6H_4), 120.42 (C=C), 119.72 (C_6H_4), 113.34 (C_5H_4N), 66.59 (cod), 30.17 (cod), 29.28 (OCH_2), 27.70 ($CH_2 \times 5$), 21.01 (CH_2), 12.43 (CH_3).

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 296884 for compound **9e**, CCDC No. 296885 for compound **11a** and CCDC No. 296886 for compound **11b**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EC, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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