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Rhodium carbonyl complexes containing pyridine; crystal structure of an unusual octahedral rhodium(I) complex $[Rh_2(\mu\text{-}CO)_3Cl_2(py)_4]$

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The products resulting from the progressive addition of pyridine (py) to a solution of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ **1** have been found to depend both upon the solvent and the atmosphere (CO or N_2). In CH_2Cl_2 under N_2, *cis*-$[Rh(CO)_2Cl(py)]$ **2**, $[Rh(CO)_2Cl(py)_2]$ **3** and $[Rh_2(\mu\text{-}CO)_3Cl_2(py)_4]$ **4** were obtained successively; under CO, **4** was converted into **3** and under N_2 disproportionation of **4** slowly occurred to give **3** and *trans*-$[Rh(CO)Cl(py)_2]$ **5** which reacted with CO to give **3**. In more polar solvents (thf or MeOH), **1** reacted under N_2 to give the lightly solvent-stabilised complex $[Rh(CO)_2Cl(solv)]$ **6** (solv = thf **a** or MeOH **b**) and, in the presence of $AgClO_4$, *cis*-$[Rh(CO)_2(solv)_2]^+$ **7** (solv = thf **a** or MeOH **b**); additionally, when solv = MeOH there was spectroscopic evidence for the formation of $[Rh_2(\mu\text{-}CO)_x(MeOH)_y]^{2+}$ **8** ($x = 2$, $y = 4$ or $x = 3$, $y = 6$) which reacted with CO to give $[Rh(CO)_2(MeOH)_2]^+$. Complex **7** reacted with py to give successively *cis*-$[Rh(CO)_2(py)_2]^+$ **9** and $[Rh(CO)(py)_3]^+$ **10**; under CO **10** was converted into **9**. The stereochemistry of all the above complexes has been established through a combination of IR and multinuclear (^{13}C, ^{15}N, ^{103}Rh) NMR measurements and X-ray crystallography for **2** and **4**. Analogous reactions have been carried out using *trans*-$[Rh_2(\mu\text{-}Cl)_2(CO)_2(C_xH_y)_2]$ **11** ($C_xH_y = C_2H_4$ **a** or C_8H_{14} **b**) under a nitrogen atmosphere and spectroscopic measurements on the reaction of **11a** with pyridine were consistent with the successive formation of $[Rh_2(\mu\text{-}Cl)_2(CO)_2(C_2H_4)_2(py)_2]$ **12**, which lost ethylene and rearranged to give $[Rh_2(\mu\text{-}CO)_2Cl_2(py)_2]$ **13**. Reaction of **11b** with pyridine gave immediately *trans*-$[Rh_2(\mu\text{-}Cl)_2(CO)_2(py)_2]$ **14** and both **13** and **14** further reacted with pyridine to give **5**.

Compared to the plethora of data available on mono- and dinuclear rhodium complexes containing both CO and P-donor ligands which are catalytically active, there are few reports of analogous rhodium carbonyl complexes containing N-donor ligands.

A common cause of catalytic deactivation with Rh/PR_3 homogeneous catalysts is P–C bond cleavage and progressive replacement of phosphines by N-donor ligands should increasingly alleviate this problem. Successful examples using this approach are illustrated by the following. (a) The complex $[\overline{Rh_2\{(NH_2N}H)_2CH_2\}(PPh_3)_4]^{2+}$, which results from the reaction of $Rh(NO_3)_3$–PPh_3–N_2H_4 in MeOH, is used commercially as a more selective efficient hydrogenation catalyst than $[RhCl(PPh_3)_3]$.[1] (b) Dissolution of $[RhCl(PPh_3)_3]$ in pyridine selectively catalyses the dimerisation of enolisable C_n aldehydes into saturated dimers, C_{2n} monoaldehydes, which are useful in the perfumery industry.[2] (c) The water gas shift reaction is catalysed by an aqueous pyridine (or substituted pyridine) solution of $RhCl_3$[3] and rhodium carbonyl clusters in the presence of N-heterocyclic ligands exhibit high catalytic activity under mild conditions;[4] these are much more effective than other transition metal/cluster catalysts.[4] Fachinetti *et al.*[5] examined these reactions in much more detail; they were able to isolate and identify $[Rh(CO)_n(py)_{4-n}]$ $[Rh_5(CO)_{13}(py)_2]$ ($n = 2$ or 3) and proposed a mechanism for the catalytic cycle.

This paper concentrates on the preparation and characterisation of rhodium complexes containing CO and N-heterocyclic ligands. Previously reported complexes of this type have often been formulated only on the basis of IR, ^1H NMR and elemental analysis, with few reports of structural characterisation from ^{13}C NMR and/or X-ray crystallography, and the proposed formulations are sometimes contradictory.

The complex $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ **1** undergoes bridge cleavage on reaction with pyridine to give *cis*-$[Rh(CO)_2Cl(py)]$ **2**,[6] and consistent with this formulation has two equally intense bands due to ν(CO) in the IR spectrum[7] and two equally intense doublets in the ^{13}C NMR spectrum.[8] However, further addition of py to **1** has been claimed by Hieber *et al.*[6] to give $[Rh_2(\mu\text{-}Cl)_2(CO)_4(py)_4]$, on the basis of elemental analysis and diamagnetism, whereas later studies by Lawson and Wilkinson[9] reformulated this product as a neutral five-co-ordinate complex $[Rh(CO)_2Cl(py)_2]$. We show later that these structural formulations are both incorrect and this product is actually $[Rh_2(\mu\text{-}CO)_3Cl_2(py)_4]$. Similarly, we have reinvestigated the nature of the products formed on the progressive addition of py to *trans*-$[Rh_2(\mu\text{-}Cl)_2(CO)_2(C_xH_y)_2]$ ($C_xH_y = C_2H_4$ **a** or C_8H_{14} **b**).[10] In both this reaction and that of **1** with pyridine we have made extensive use of multinuclear NMR measurements [including ^{15}N NMR measurements using the insensitive nucleii enhanced by polarisation transfer (INEPT) pulse sequence,[11] which we have found to be most useful] structurally to characterise the products and we find that the nature of the product often varies on changing either the solvent or reaction atmosphere (N_2 or CO).

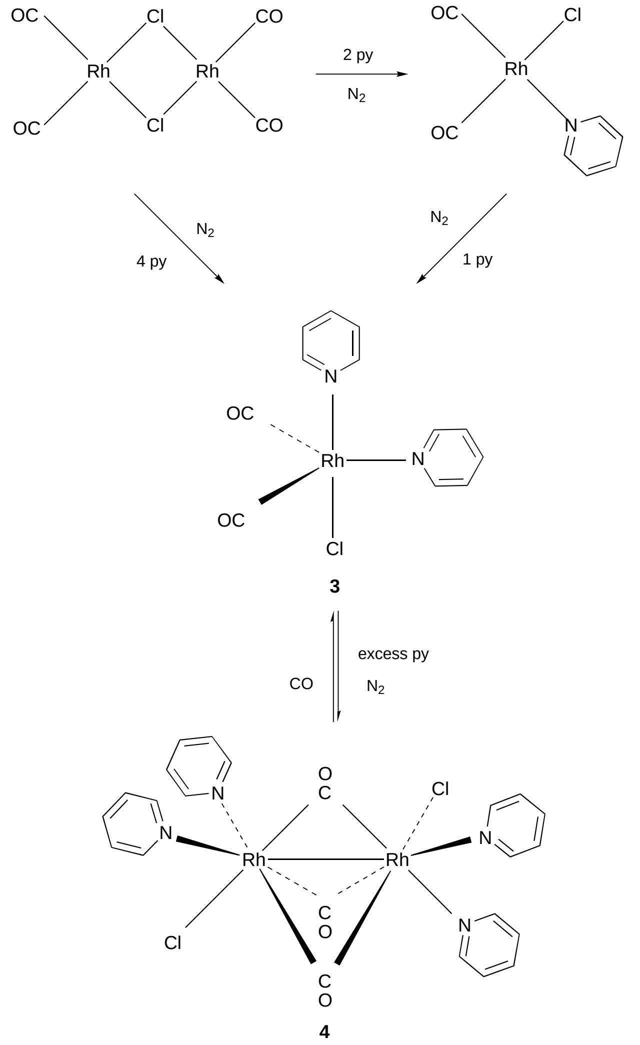
Results and Discussion

$[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ 1 + py

The nature of the products resulting from the incremental addition of py to complex **1** depends on the solvent and we now report on the nature of the products formed on reaction in low-polarity (*e.g.* CH_2Cl_2) *versus* polar solvents (*e.g.* thf, MeOH).

(a) Reaction in CH_2Cl_2. The products resulting from the incremental addition of py to complex **1** in CH_2Cl_2 under a nitrogen atmosphere are shown in Scheme 1. The first formed product **2** has been reported[6] and characterised by IR[7] and ^{13}C NMR spectroscopy.[8] In order to build up a spectroscopic and structural data base of Rh/CO/py complexes, we have measured the ^{15}N NMR spectrum (see Table 1) and also determined the crystal structure (see Fig. 1).

The complex *cis*-$[Rh(CO)_2Cl(py)]$ **2** crystallises with two molecules in the asymmetric unit; there is no intermolecular co-ordination between these two molecules which show only marginal differences in bond lengths/angles. Selected bond lengths/angles of the two molecules are given in Table 2. The geometry around rhodium is square planar and, consistent with the



Scheme 1 Products resulting from the progressive addition of py to $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ **1** in CH_2Cl_2

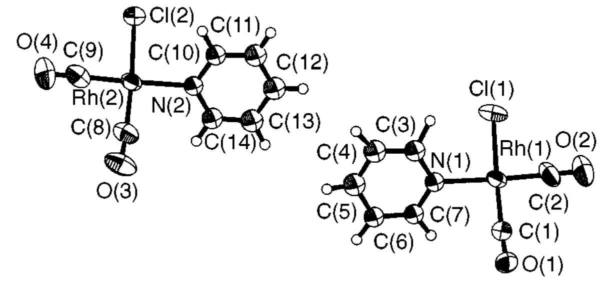
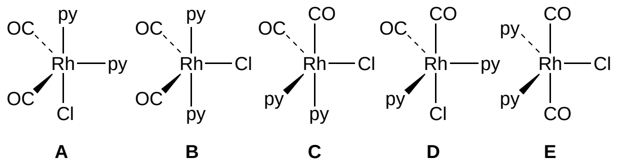


Fig. 1 Crystal structure of *cis*-$[Rh(CO)_2Cl(py)]$ **2**

solution spectroscopic data, there are two *cis*-carbonyls. The dihedral angle between the plane of the pyridine ring and the rhodium(I) square plane is 141° and is very similar to that found for *cis*-$[Ir(CO)_2Cl(py)]$ (143°).[13]

Further addition of py to complex **1** or **2** (Rh : py = 1 : 2) gives a new compound for which microanalytical data suggest the empirical formula $[Rh(CO)_2Cl(py)_2]$ **3** and, since it is a non-conductor in both CH_2Cl_2 and MeOH solution, can be formulated as a five-co-ordinate neutral complex. For this formulation there are five possible isomers (see Scheme 2) and a combination of IR and $^{13}C/^{15}N$ NMR measurements allows **3** to be assigned unambiguously to isomer **A**. Thus, there are two equally intense doublets in the $^{15}N\text{-}\{^1H\}$ spectrum at 223 K, a sharp doublet in the carbonyl region of the ^{13}C NMR spectrum which remains unchanged from 297 to 193 K and two strong ν(CO) bands in the IR spectrum (see Table 1).



Scheme 2 Possible isomers of $[Rh(CO)_2Cl(py)_2]$ **3**

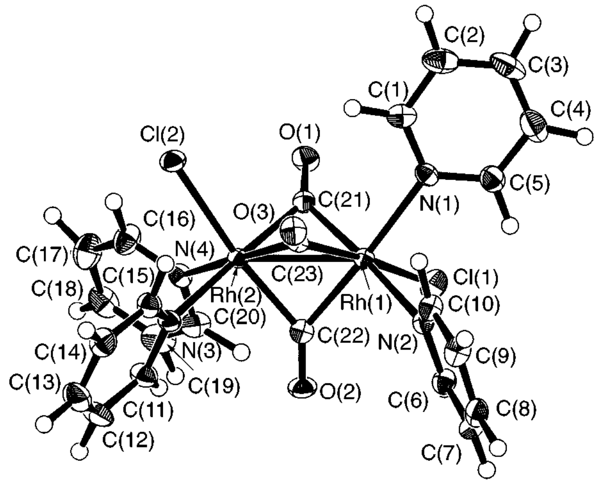


Fig. 2 Crystal structure of $[Rh_2(\mu\text{-}CO)_3Cl_2(py)_4]$ **4**

Attempts to obtain crystals of complex **3** suitable for X-ray analysis failed but further evidence for the formation of the five-co-ordination has been obtained by addition of 1 equivalent of NBu^n_4Cl to a solution of *cis*-$[Rh(CO)_2(py)_2]ClO_4$ which, on the basis of NMR measurements, gives exclusively **3** [equation (1)].

$$\textit{cis}\text{-}[Rh(CO)_2(py)_2]^+ \underset{AgClO_4}{\overset{NBu^n_4Cl}{\rightleftharpoons}} \underset{\textbf{3}}{[Rh(CO)_2Cl(py)_2]} \quad (1)$$

It should be noted that Fachinetti *et al.*[5] proposed, on the basis of IR evidence, that addition of 1 equivalent of $[N(PPh_3)_2]Cl$ to a pyridine solution of *cis*-$[Rh(CO)_2(py)_2][BPh_4]$ under a CO atmosphere gives *cis*-$[Rh(CO)_2Cl(py)]$ **2**. However, since the bands due to ν(CO) for **2** are almost identical to those of **3** we suspect that, on the basis of our NMR measurements, their product should have been formulated as **3** rather than **2** [see equation (1)].

Over *ca.* 12 h in CH_2Cl_2 solution complex **3** does not lose CO under a nitrogen atmosphere and does not lose pyridine under a CO atmosphere. However, in the presence of a trace of pyridine and under a nitrogen atmosphere it loses CO immediately to give the air-stable yellow solid $[Rh_2(\mu\text{-}CO)_3Cl_2(py)_4]$ **4** which has been prepared previously[6,9] but wrongly formulated. We have been able fully to characterise this compound both crystallographically and spectroscopically. The structure is shown in Fig. 2 and selected bond lengths and angles are given in Table 3. It has a pseudo-two-fold axis which is coincident with the unique bridging carbonyl vector, C(21)O(1). As a result there are two different types of bridging carbonyls in the ratio 1 : 2 and two different types of pyridines in the ratio 2 : 2 with two pyridines being *trans* to the unique carbonyl, C(21)O(1), and the other two equivalent pyridines *trans* to C(22)O(2) and C(23)O(3) respectively. This structure, which is retained in solution, see below, is very unusual and to our knowledge is the only example of a dinuclear rhodium(I) complex containing an octahedral array of ligands about the metal. Consistent with each rhodium having 17 electrons, a Rh–Rh bond is formed and because of the compact geometry the Rh–Rh distance is very short (2.566 Å), comparable to distances found for dinuclear rhodium(I) A-frame complexes, *e.g.* 2.612 Å in $[Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}$

Table 1 Spectroscopic data for mono- and di-nuclear rhodium(I) carbonyl complexes containing pyridine

		IR		^{13}C NMR				^{15}N NMR			
Complex		Solvent	ṽ(CO)/cm^{-1}	Solvent	*T*/K	δ(^{13}CO)^a	^{1}*J*(Rh–CO)/ Hz	Solvent	*T*/K	δ(^{15}N)^a	^{1}*J*(Rh–N)/ Hz
2	*cis*-[Rh(CO)$_2$Cl(py)]	CH$_2$Cl$_2$	2089s, 2015s,	CH$_2$Cl$_2$	223	183.9(1) 180.2(1)	66.2 74.9	CH$_2$Cl$_2$	223	−143.8	15.9
		CH$_2$Cl$_2$	2089s, 2014s^b	C$_6$H$_5$Me	213	185.6(1)^c 181.3(1)^c	67 73				
3	[Rh(CO)$_2$Cl(py)$_2$]	CH$_2$Cl$_2$	2089s, 2015s	CH$_2$Cl$_2$	297	182.6	69.6	CH$_2$Cl$_2$	223	−128.6(1) −128.3(1)	16.8 17.6
				CH$_2$Cl$_2$	223	182.1	70.6				
4	[Rh$_2$(μ-CO)$_3$Cl$_2$(py)$_4$]	CH$_2$Cl$_2$	1835s, 1814s	CH$_2$Cl$_2$	223	213.2 (t, 2) 211.7 (t, 1)	28.7 27.6				
5	*trans*-[Rh(CO)Cl(py)$_2$]	CH$_2$Cl$_2$	1962	CH$_2$Cl$_2$	297	184.5	83.9	CH$_2$Cl$_2$	297	−152.2	18.6
		CH$_2$Cl$_2$	1961^d	CH$_2$Cl$_2$	223	183.7	84.7	CH$_2$Cl$_2$	213	−153.3	18.6
6a	*cis*-[Rh(CO)$_2$Cl(thf)]	thf	2083s, 2011s	thf	297	181.5	74.3				
				thf	183	185.4(1) 181.4(1)	73.8 71.6				
6b	*cis*-[Rh(CO)$_2$Cl(MeOH)]	MeOH	2087s, 2014s	MeOH	297	182.2	74.6				
				MeOH	193	184.5(1) 180.6(1)	78.9 70.6				
7a	*cis*-[Rh(CO)$_2$(thf)$_2$]$^+$	thf	2102s, 2029s	thf	223	181.6	76.6				
7b	*cis*-[Rh(CO)$_2$(MeOH)$_2$]$^+$	MeOH	2105s, 2031s	MeOH	223	181.2	75.7				
8	[Rh$_2$(μ-CO)$_x$(MeOH)$_y$]$^{2+}$ ($x = 2$, $y = 4$ or $x = 3$, $y = 6$)	MeOH	1865	MeOH	223	198.4 (t)	30.1				
9	*cis*-[Rh(CO)$_2$(py)$_2$]$^{+\,e}$	CH$_2$Cl$_2$	2104s, 2043s	CH$_2$Cl$_2$	223	182.2	69.2	thf	297	−153.4	19
		thf	2098s, 2033s	thf	297	184.5	69.4				
		py	2100s, 2038s								
10	[Rh(CO)(py)$_3$]$^+$	thf	1991	thf	223	189.8	78.9				
		py	1993^f	MeOH	223	191.0	78.2				
11a	*trans*-[Rh$_2$(μ-Cl)$_2$(CO)$_2$-(C$_2$H$_4$)$_2$]	CH$_2$Cl$_2$	2022	CH$_2$Cl$_2$	223	178.8	77.6				
		C$_6$H$_6$	2010^d								
11b	*trans*-[Rh(μ-Cl)$_2$(CO)$_2$-(C$_8$H$_{14}$)$_2$]	CH$_2$Cl$_2$	2008	CH$_2$Cl$_2$	297	182.2	82.3				
12	[Rh$_2$(μ-Cl)$_2$(CO)$_2$(C$_2$H$_4$)$_2$-(py)$_2$]	CH$_2$Cl$_2$	2089s, 2006s	CH$_2$Cl$_2$	223	184.7	68.4				
13	[Rh$_2$(μ-CO)$_2$Cl$_2$(py)$_2$]	Nujol	1789								
14	*trans*-[Rh$_2$(μ-Cl)$_2$(CO)$_2$-(py)$_2$]	CH$_2$Cl$_2$	2015	CH$_2$Cl$_2$	213	187.4	72.7	CH$_2$Cl$_2$	213	−127.3	13.5

^{a} Figures in parentheses are relative intensities; all signals appear as doublets except as shown. ^{b} Ref. 7. ^{c} Ref. 8. ^{d} Ref. 10. ^{e} δ(Rh) 73. ^{f} Ref. 12.

Table 2 Selected bond lengths (Å) and angles (°) for the two molecules in the asymmetric unit of *cis*-[Rh(CO)$_2$Cl(py)] **2**

Rh(1)–Cl(1)	2.347(4)	N(1)–C(3)	1.35(1)
Rh(1)–N(1)	2.122(7)	N(1)–C(7)	1.34(1)
Rh(1)–C(1)	1.84(1)	N(2)–C(10)	1.35(1)
Rh(1)–C(2)	1.81(1)	N(2)–C(14)	1.35(1)
Rh(2)–Cl(2)	2.344(3)	C(3)–C(4)	1.37(1)
Rh(2)–N(2)	2.114(7)	C(4)–C(5)	1.38(2)
Rh(2)–C(8)	1.84(1)	C(5)–C(6)	1.38(1)
Rh(2)–C(9)	1.83(1)	C(6)–C(7)	1.37(1)
O(1)–C(1)	1.12(1)	C(10)–C(11)	1.35(1)
O(2)–C(2)	1.14(1)	C(11)–C(12)	1.38(1)
O(3)–C(8)	1.13(2)	C(12)–C(13)	1.39(2)
O(4)–C(9)	1.13(2)	C(13)–C(14)	1.36(1)
Cl(1)–Rh(1)–N(1)	91.3(2)	Cl(2)–Rh(2)–N(2)	90.6(2)
Cl(1)–Rh(1)–C(1)	177.5(3)	Cl(2)–Rh(2)–C(8)	176.6(3)
Cl(1)–Rh(1)–C(2)	87.4(4)	Cl(2)–Rh(2)–C(9)	87.2(5)
N(1)–Rh(1)–C(1)	91.2(4)	N(2)–Rh(2)–C(8)	92.8(4)
N(1)–Rh(1)–C(2)	175.7(5)	N(2)–Rh(2)–C(9)	177.7(5)
C(1)–Rh(1)–C(2)	90.1(5)	C(8)–Rh(2)–C(9)	89.4(6)

Table 3 Selected bond lengths (Å) and angles (°) for [Rh$_2$(μ-CO)$_3$-Cl$_2$(py)$_4$] **4**

Rh(1)–Rh(2)	2.566(5)	Rh(2)–N(3)	2.188(3)
Rh(1)–Cl(1)	2.462(8)	Rh(2)–N(4)	2.223(3)
Rh(1)–N(1)	2.185(3)	Rh(2)–C(21)	2.011(3)
Rh(1)–N(2)	2.198(3)	Rh(2)–C(22)	1.995(3)
Rh(1)–C(21)	2.021(3)	Rh(2)–C(23)	2.016(3)
Rh(1)–C(22)	2.002(3)	C(21)–O(21)	1.155(4)
Rh(1)–C(23)	1.997(3)	C(22)–O(22)	1.164(4)
Rh(2)–Cl(2)	2.472(9)	C(23)–O(23)	1.164(4)
Rh(2)–Rh(1)–Cl(1)	121.62(2)	N(1)–Rh(1)–N(2)	91.19(9)
Rh(2)–Rh(1)–N(1)	126.41(7)	N(1)–Rh(1)–C(21)	91.4(1)
Rh(2)–Rh(1)–N(2)	125.39(7)	N(1)–Rh(1)–C(22)	176.3(1)
Rh(2)–Rh(1)–C(21)	50.31(9)	N(1)–Rh(1)–C(23)	96.5(1)
Rh(2)–Rh(1)–C(22)	49.94(9)	N(2)–Rh(1)–C(21)	175.6(1)
Rh(2)–Rh(1)–C(23)	50.58(9)	N(2)–Rh(1)–C(22)	92.0(1)
Cl(1)–Rh(1)–N(1)	90.24(7)	N(2)–Rh(1)–C(23)	92.4(1)
Cl(1)–Rh(1)–N(2)	91.79(7)	C(21)–Rh(1)–C(22)	85.3(1)
Cl(1)–Rh(1)–C(21)	91.75(9)	C(21)–Rh(1)–C(23)	83.8(1)
Cl(1)–Rh(1)–C(22)	91.62(9)	C(22)–Rh(1)–C(23)	81.4(1)
Cl(1)–Rh(1)–C(23)	171.97(9)		

NC$_5$H$_4$PPh$_2$-2)$_2$Cl$_2$][14] and 2.639 Å in [Rh$_2$(μ-CO)(μ-NC$_5$H$_4$-PPh$_2$-2)$_2$(η^2-H$_2$BH$_2$)$_2$].[15]

Complex **4** is insoluble in most polar solvents (*e.g.* thf, MeOH, Me$_2$CO and MeCN) and non-polar solvents (*e.g.* C$_6$H$_6$, MeC$_6$H$_5$) but slightly soluble in CH$_2$Cl$_2$. Using a freshly prepared solution in CH$_2$Cl$_2$ the spectroscopic data are entirely consistent with the solid-state structure. Thus, there are two almost equally intense ν(CO) bands in the bridging region and the ^{13}C NMR spectrum consists of two triplets in the ratio 1:2 due to the bridging carbonyls (see Table 1); it was unfortunately impossible to obtain ^{15}N NMR data because of the low solubility and long collection times required.

Under an atmosphere of CO complex **4** is converted quantitatively into **3** whereas, under a nitrogen atmosphere, it undergoes slow disproportionation [equation (2)]. The resultant

$$\underset{\mathbf{4}}{[Rh_2(\mu\text{-}CO)_3Cl_2(py)_4]} \xrightarrow[N_2]{CH_2Cl_2} \underset{\mathbf{3}}{[Rh(CO)_2Cl(py)_2]} + \underset{\mathbf{5}}{trans\text{-}[Rh(CO)Cl(py)_2]} \qquad (2)$$

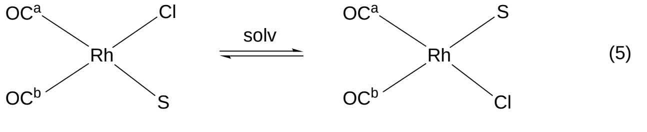
solution shows, in addition to the expected carbonyl IR bands and ^{13}C NMR resonances due to **3**, a band at 1962 cm^{-1} and a doublet in the ^{13}C NMR spectrum [δ 184.5, $^1J(Rh–CO)$ 83.9 Hz)] of half the intensity of the other carbonyl resonance due to **3**; we attribute these additional bands to *trans*-[Rh(CO)Cl(py)$_2$] **5**. This formulation is further substantiated by bubbling CO through this solution which results in the formation of **3** and complete disappearance of the ν(CO) band/^{13}C NMR resonance attributed to **5**, equation (3). However, the reverse is not observed on bubbling N_2 through a solution of **3**.

$$\underset{\mathbf{5}}{trans\text{-}[Rh(CO)Cl(py)_2]} \xrightarrow{CH_2Cl_2/CO} \underset{\mathbf{3}}{[Rh(CO)_2Cl(py)_2]} \qquad (3)$$

(b) Reaction in polar solvents (MeOH, thf). Dissolution of complex **1** in either MeOH or thf under N_2 results in bridge cleavage to give the lightly stabilised solvento-complex **6** [equation (4)]. It is surprising that this reaction has not previously been reported since both the IR and ^{13}CO resonances of **6** are significantly different to the analogous data for **1** in CH_2Cl_2 or $CHCl_3$ solution (see Table 1). Unambiguous evidence of the formulation of **6** comes from the variable-temperature ^{13}CO NMR spectra of $[Rh_2(\mu\text{-}Cl)_2(^{13}CO)_4]$ at low temperature (see Fig. 3) which for both MeOH and thf show two equally intense resonances (see Table 1); at room temperature there is rapid solvent exchange giving rise to a time-averaged carbonyl chemical shift [equation (5)]. The low-temperature chemical shift differences between C^{a}O and C^{b}O for solv = thf or MeOH is rather similar but the coalescence temperature of the two doublets is 213 and 203 K for MeOH and thf respectively. This implies that thf is slightly more labile than MeOH. Unfortunately, isolation of **6a** and **6b** proved impossible.

$$\underset{\mathbf{1}}{[Rh_2(\mu\text{-}Cl)_2(CO)_4]} \xrightarrow{solv/N_2} 2\ cis\text{-}[Rh(CO)_2Cl(solv)] \qquad (4)$$

6a solv = thf
6b solv = MeOH



solv = thf or MeOH

Addition of 2 equivalents of $AgClO_4$ to solutions of complex **1** in MeOH or thf under a nitrogen atmosphere produces slightly different results. The cleanest reaction occurs in thf to give *cis*-$[Rh(CO)_2(solv)_2]^+$ **7a** (solv = thf) which has IR and NMR data entirely consistent with this formulation. A similar reaction occurs in MeOH to give predominantly **7b** but there is also evidence for the formation of minor amounts of $[Rh_2(\mu\text{-}CO)_x(MeOH)_y]^{2+}$ **8** as evidenced by a weak band at 1865 cm^{-1} in the IR spectrum and the presence of a triplet at δ 198.4 [$^1J(Rh–CO)$ 30.1 Hz] in the low-temperature ^{13}C NMR spectrum. On the basis of the spectroscopic evidence we cannot presently be sure of the values of x and y which are likely to be either $x = 2$ and $y = 4$ or $x = 3$ and $y = 6$. However, bubbling CO through a MeOH solution containing **8** results in the immediate transformation into **7b**.

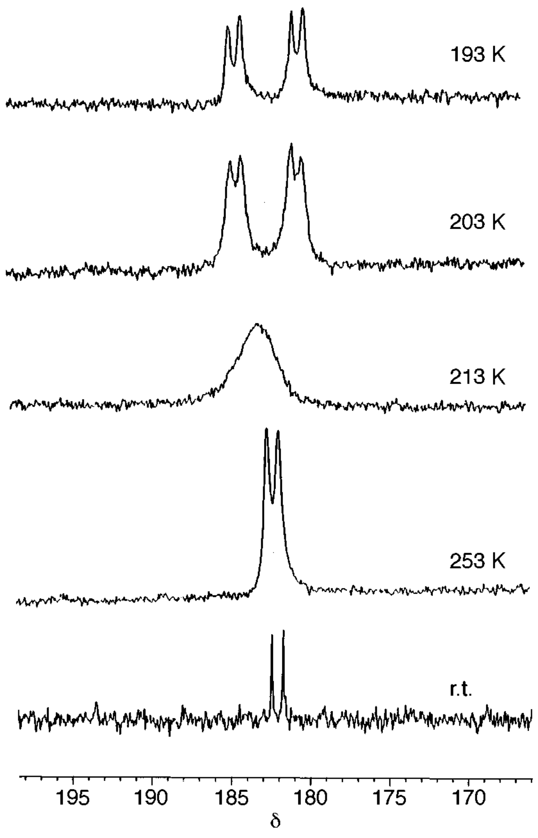


Fig. 3 Variable-temperature ^{13}C NMR spectra of *cis*-$[Rh(^{13}CO)_2Cl(MeOH)]$ **6a** in MeOH; r.t. = room temperature

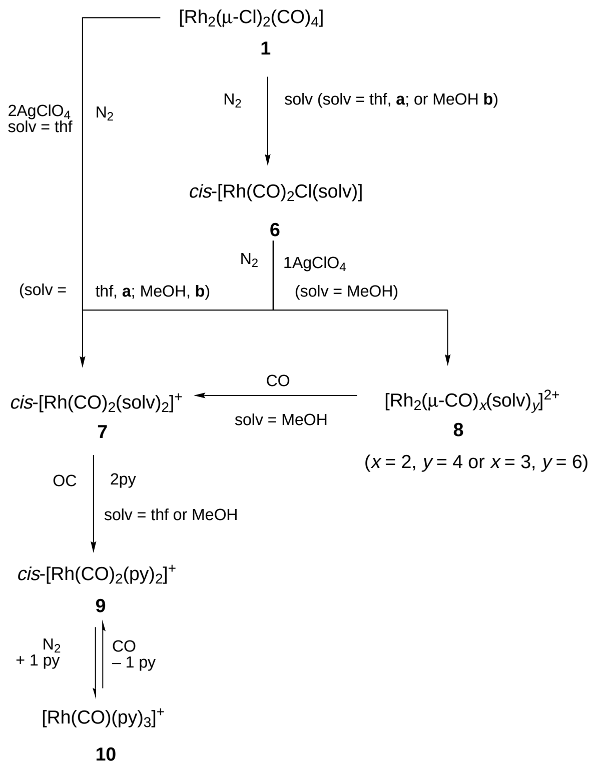
Addition of pyridine (Rh : py = 1 : 2) to a solution of complex **7a** in thf or **7b** in MeOH under CO gives the same product, $[Rh(CO)_2(py)_2]^+$ **9** and the IR data of this complex are in agreement with previously reported results.[12] We have recorded the $^{15}N\text{-}\{^1H\}$ NMR spectrum of **9** which, as expected, consists of one doublet (see Table 1). This complex can also be prepared by bubbling CO into a solution of *cis*-$[Rh(diene)(py)_2]^+$ (diene = cod or nbd) in thf. However, it should be noted that **9** is unstable under N_2 and is transformed overnight into presently unidentified products. Nevertheless, immediate addition of 1 equivalent of py to a solution of **9** in thf or MeOH under N_2 produces a new band in the IR spectrum at 1991 cm^{-1} and the $^{13}C\text{-}\{^1H\}$ NMR spectrum of the solution at 223 K shows a new doublet at δ 189.8 [$^1J(Rh–CO)$ 79 Hz]; we attribute these to $[Rh(CO)(py)_3]^+$ **10** (see Table 1). Reaction of **10** with CO immediately gives **9**.

The reactions of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ **1** with py in polar solvents (thf or MeOH) are summarised in Scheme 3.

trans-$[Rh_2(\mu\text{-}Cl)_2(CO)_2(C_xH_y)_2]$ 11 ($C_xH_y = C_2H_4$ a or C_8H_{14} b) + py

Mixing equimolar amounts of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ and $[Rh_2(\mu\text{-}Cl)_2(C_xH_y)_4]$ ($C_xH_y = C_2H_4$ or C_8H_{14}) in CH_2Cl_2 solution has previously been reported[10] on the basis of IR measurements to give exclusively $[Rh_2(\mu\text{-}Cl)_2(CO)_2(CH_y)_2]$ **11** ($C_xH_y = C_2H_4$ **a** or C_8H_{14} **b**). This result is a little surprising since a statistical distribution of products might have been expected but we only find the presence of one carbonyl doublet in the ^{13}C NMR spectrum both at room and low temperature (see Table 1) consistent with the presence of only the *trans* isomer.

Previous IR and ^1H NMR measurements[10] suggest that addition of pyridine to a solution of complex **11a** in CH_2Cl_2 solution under N_2 (Rh : py = 1 : 1) results in retention of C_2H_4 and formation of $[Rh_2(\mu\text{-}Cl)_2(CO)_2(C_2H_4)_2(py)_2]$ **12**. We have confirmed these measurements and, in addition, the presence



Scheme 3 Products resulting from the reaction of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ **1** with pyridine in polar solvents (thf or MeOH)

of one doublet [δ 184.7, ^1J(Rh–CO) 68 Hz] in the ^{13}C NMR spectrum is consistent with the product shown in Scheme 4. On standing the above solution under a reduced nitrogen pressure a very insoluble black precipitate **13** is formed. Microanalysis of **13** is consistent with the empirical formula $[\{Rh(CO)Cl(py)\}_n]$ and the mass spectrum is consistent with $n = 2$ as reported previously. However, IR data on **13** had not been reported previously and we find that the IR spectrum in Nujol contains no bands in the terminal carbonyl region and only one strong ν(CO) band at 1789 cm^{-1}. As a result **13** must be formulated as shown in Scheme 4 rather than *trans*-$[Rh_2(\mu\text{-}Cl)_2(CO)_2(py)_2]$ as previously reported.[10] Bubbling CO through a suspension of **13** in CH_2Cl_2 gives *cis*-$[Rh(CO)_2Cl(py)]$ **2** and addition of py to **12** (Rh : py = 1 : 2) results in the formation of **5**. This has been reported previously[10] on the basis of IR and elemental analysis and our ^{13}C and ^{15}N NMR data (Table 1) are entirely consistent with this formulation.

Retention of cyclooctene does not occur on addition of pyridine to complex **11b** (Rh : py = 1 : 1) under a nitrogen atmosphere. In this case immediate loss of cyclooctene occurs to give *trans*-$[Rh_2(\mu\text{-}Cl)_2(CO)_2(py)_2]$ **14**. It should be noted in this case that there is only spectroscopic evidence for terminal COs (see Table 1) and surprisingly we have no evidence for rearrangement of **14** to **13** or *vice versa*. Complex **14** reacts with py (Rh : py 1 : 1) to give **5** which reacts further with an excess of pyridine in MeOH to give the ionic species $[Rh(CO)(py)_3]Cl$ **10**.

Experimental

All manipulations involving solutions or solids were performed under an atmosphere of N_2 or CO as appropriate, using standard Schlenk-line techniques. All solvents were dried and distilled under N_2 immediately prior to use. Deuteriated solvents were stored over activated molecular sieves (4 Å) for at least 24 h prior to use. Manipulations using ^{13}CO were carried out using standard vacuum-line techniques.

The ^{13}C NMR spectra were obtained on Bruker WM200, 250 and AMX400 spectrometers using internal $SiMe_4$ as reference, ^{15}N INEPT spectra on a Bruker AMX400 spectrometer using the previously published method[16] with chemical shifts referenced to external $MeNO_2$ and ^{103}Rh NMR spectra on a Bruker WM360 spectrometer using a 15 mm NMR tube {7 cm^3 of a *ca.* 0.8 mmol solution containing *ca.* 25 mg of $[Cr(acac)_3]$ as relaxing agent} with shifts referenced to 3.16 MHz (δ 0) at such a magnetic field that the protons in $SiMe_4$ resonate at exactly 100 MHz. The IR spectra were obtained in solution with CaF_2 windows on a Perkin-Elmer 1720x FTIR spectrometer.

The starting materials were prepared using literature methods: $[Rh_2(\mu\text{-}Cl)_2(C_2H_4)_4]$,[17] $[Rh_2(\mu\text{-}Cl)_2(C_8H_{14})_4]$[18] and $[Rh_2(\mu\text{-}Cl)_2(nbd)_2]$.[19] In order to avoid using expensive $RhCl_3\cdot3H_2O$, $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ was prepared by heating $[Rh_2(\mu\text{-}Cl)_2(nbd)_2]$ to 100 °C in a stream of CO whereupon the product sublimed, yield 80%. The preparation of $[Rh_2(\mu\text{-}Cl)_2(^{13}CO)_4]$ was carried out by stirring a suspension of $[Rh_2(\mu\text{-}Cl)_2(C_2H_4)_4]$ in light petroleum (b.p. 40–60 °C) with a slight excess of ^{13}CO. On cooling this solution to −78 °C the product precipitated and removal of the solvent by a syringe left the pure product, yield 65%.

Preparation of complexes

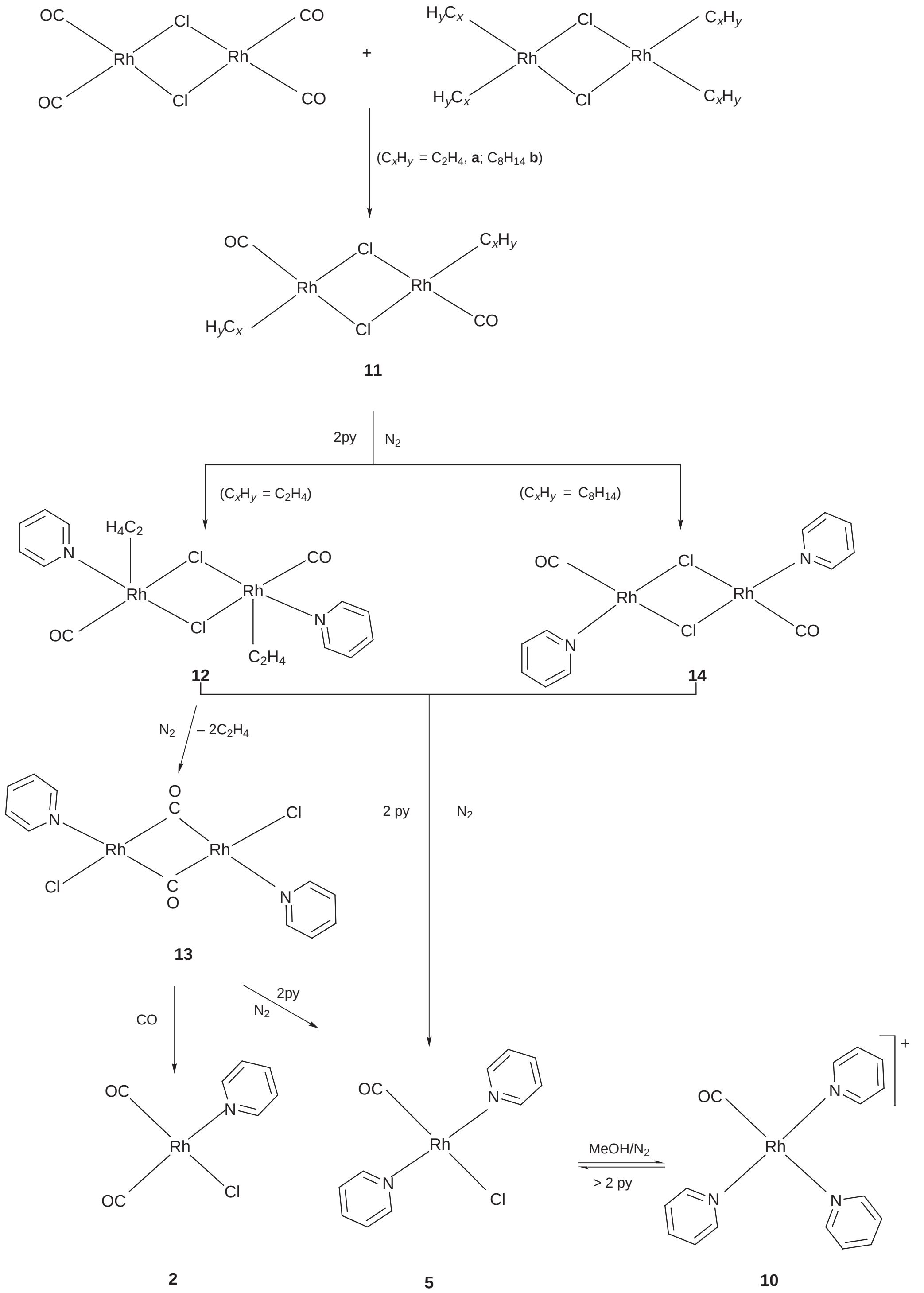
***cis*-$[Rh(CO)_2Cl(py)]$ 2.** Pyridine (83 μl, 1.0 mmol) was added to a solution of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ (200 mg, 0.5 mmol) in CH_2Cl_2 (5 cm^3), under a nitrogen atmosphere, to give a pale yellow solution. X-Ray-quality orange crystals of *cis*-$[Rh(CO)_2Cl(py)]$ were obtained on adding diethyl ether (10 cm^3) and leaving the solution to evaporate slowly under a nitrogen atmosphere. The product was filtered off and dried under vacuum (260 mg, 93%) (Found: C, 30.7; H, 1.8; N, 5.1. $C_7H_5ClNO_2Rh$ requires C, 30.7; H, 1.8; N, 5.1%).

$[Rh(CO)_2Cl(py)_2]$ 3. Pyridine (210 μl, 2.57 mmol) was added to a solution of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ (250 mg, 0.64 mmol) (Rh : py = 1 : 2) in CH_2Cl_2 (3 cm^3) under a nitrogen atmosphere to give a yellow solution of the product. Yellow crystals were obtained by layering this solution with light petroleum but unfortunately they were unsuitable for X-ray analysis (395 mg, 87%) (Found: C, 40.5; H, 2.8; N, 7.5. $C_{12}H_{10}ClN_2O_2Rh$ requires C, 40.9; H, 2.9; N, 7.95%).

$[Rh_2(\mu\text{-}CO)_3Cl_2(py)_4]$ 4. Pyridine (310 μl, 3.86 mmol) was added dropwise to a solution of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ (250 mg, 0.64 mmol) in CH_2Cl_2 (3 cm^3) under a nitrogen atmosphere. The IR and ^{13}C NMR measurements showed the formation of $[Rh_2(\mu\text{-}CO)_3Cl_2(py)_4]$. X-Ray-quality yellow crystals were obtained from this solution by leaving it under a slow flow of N_2. The product was filtered off and dried under vacuum (380 mg, 87%) (Found: C, 40.8; H, 2.9; Cl, 10.7; N, 8.3. $C_{23}H_{20}Cl_2N_4O_3Rh_2$ requires C, 40.8; H, 3.0; Cl, 10.5; N, 8.3%).

***trans*-$[Rh(CO)Cl(py)_2]$ 5.** Pyridine (225 μl, 2.8 mmol) was added to a solution containing $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ (135 mg, 0.35 mmol) and $[Rh_2(\mu\text{-}Cl)_2(C_xH_y)_4]$ where $C_xH_y = C_8H_{14}$ (250 mg, 0.35 mmol) or $C_xH_y = C_2H_4$ (135 mg, 0.35 mmol) (Rh : py = 1 : 2) in CH_2Cl_2 (2 cm^3) under a nitrogen atmosphere and addition of diethyl ether gave yellow crystals of the product which were filtered off and dried under vacuum (370 mg, 87%) (Found: C, 41.0; H, 3.1; N, 8.5. $C_{11}H_{10}ClN_2ORh$ requires C, 40.7; H, 3.1; N, 8.6%).

***cis*-$[Rh(^{13}CO)_2Cl(solv)]$ 6 (solv = thf a or MeOH b).** The complex $[Rh_2(\mu\text{-}Cl)_2(^{13}CO)_4]$ (200 mg, 0.5 mmol) was dissolved in thf or MeOH (5 cm^3) under a nitrogen atmosphere and stirred for 2 h to give *cis*-$[Rh(^{13}CO)_2Cl(solv)]$. The IR and variable-temperature ^{13}C-{^1H} NMR measurements were consistent with the formulation but attempts to isolate the product through either slow evaporation or layering with either diethyl ether or light petroleum always resulted in reformation of the starting material.



Scheme 4 Products resulting from the progressive addition of py to an equimolar mixture of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ **1** and $[Rh_2(\mu\text{-}Cl)_2(C_xH_y)_4]$ ($C_xH_y = C_2H_4$ or C_8H_{14})

***cis*-$[Rh(CO)_2(solv)_2][ClO_4]$ 7 (solv = thf a or MeOH b).** Addition of $AgClO_4$ (210 mg, 1.0 mmol) to a solution of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ (200 mg, 1.0 mmol) in thf (or MeOH) (5 cm^3) under a nitrogen atmosphere gave a yellow solution and a white precipitate (AgCl). The yellow solution was syringed off and concentrated to 2 cm^3. The IR and ^{13}C NMR measurements were consistent with the formulation of the product as *cis*-$[Rh(CO)_2(solv)_2][ClO_4]$ but attempts to isolate it by layering the solution with either diethyl ether or light petroleum failed.

***cis*-$[Rh(CO)_2(py)_2][ClO_4]$ 9.** *Method A.* The salt $AgClO_4$ (315 mg, 1.5 mmol) was added to a solution of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ (300 mg, 0.75 mmol) in thf (5 cm^3) under a CO atmosphere to give a yellow solution with a white precipitate (AgCl). The yellow solution was filtered and concentrated to 2 cm^3. Pyridine (240 μl, 3 mmol) was then added under a CO atmosphere followed by diethyl ether (5 cm^3) which gave the product as a yellow precipitate; this was filtered off and dried under vacuum (445 mg, 71%) (Found: C, 34.5; H, 2.4; N, 6.7. $C_{12}H_{10}ClN_2O_6Rh$ requires C, 34.6; H, 2.4; N, 6.7%).

Method B. The salt $AgClO_4$ (275 mg, 1.3 mmol) was added to a thf solution (6 cm^3) containing $[Rh_2(\mu\text{-}Cl)_2(nbd)_2]$ (300 mg, 0.65 mmol) and pyridine (210 μl, 2.6 mmol) under a nitrogen atmosphere to give a yellow solution with a white precipitate (AgCl). The yellow solution was concentrated under vacuum to give a yellow precipitate. The precipitate was washed with diethyl ether (2 × 3 cm^3), redissolved in thf (5 cm^3) and CO

Table 4 Crystal structure analysis, crystal data and experimental details for complexes **2** and **4***

	2	**4**
Formula	$C_7H_5ClNO_2Rh$	$C_{23}H_{20}Cl_2N_4O_3Rh_2$
M	273.48	677.15
Appearance	Red plate crystal	Yellow prism
a/Å	9.784(6)	11.023(1)
b/Å	13.59(1)	13.395(1)
c/Å	7.446(5)	9.012(3)
α/°	103.73(5)	91.89(2)
β/°	93.45(6)	94.05(2)
γ/°	108.42(7)	71.570(8)
U/Å^3	903(1)	1259.2(4)
Z	4	2
D_c/g cm^{-3}	2.012	1.786
F(000)	528	668
μ(Mo-Kα)/cm^{-1}	21.18	15.36
Crystal dimensions/mm	0.20 × 0.050 × 0.250	0.20 × 0.10 × 0.20
Reflections measured	3386	4661
h,k,l Ranges	0 to 12, −16 to 16, −9 to 9	0 to 13, −16 to 16, −11 to 11
Unique reflections	3182	4409
R_{merg}	0.037	0.013
T_{max}, T_{min}	0.74, 1.0	0.88, 1.0
Observed reflections [$I > 3\sigma(I)$]	1768	3765
Number parameters refined	157	307
R	0.039	0.022
R'	0.039	0.028
Final difference electron density (maximum, minimum)/e Å^{-3}	0.521, −0.54	0.37, −0.42

* Details in common: triclinic, space group $P\bar{1}$ (no. 2).

bubbled through the solution for 30 min. The product was isolated by layering the solution with diethyl ether (605 mg, 84%) (Found: C, 34.55; H, 2.4; N, 6.7. $C_{12}H_{10}ClN_2O_6Rh$ requires C, 34.6; H, 2.4; N, 6.7%).

[Rh(CO)(py)$_3$][ClO$_4$] 10. The salt $AgClO_4$ (215 mg, 1.02 mmol) was added to a thf solution (10 cm^3) containing [Rh$_2$(μ-Cl)$_2$(CO)$_4$] (200 mg, 0.51 mmol) and pyridine (320 μl, 3.95 mmol) under a nitrogen atmosphere to give a reddish orange solution with a white precipitate. Addition of diethyl ether (20 cm^3) to the thf solution gave a reddish orange precipitate which was filtered off, washed with diethyl ether and dried in vacuum (338 mg, 69%) (Found: C, 42.2; H, 3.6; N, 9.3. $C_{16}H_{15}ClN_3O_5Rh$ requires C, 41.1, H, 3.2; N, 9.0%).

***trans*-[Rh$_2$(μ-Cl)$_2$(CO)$_2$(C$_x$H$_y$)$_2$] 11 (C$_x$H$_y$ = C$_2$H$_4$ a or C$_8$H$_{14}$ b).** Dichloromethane (2 cm^3) was added to a mixture of [Rh$_2$(μ-Cl)$_2$(CO)$_4$] (135 mg, 0.35 mmol) and [Rh$_2$(μ-Cl)$_2$(C$_x$H$_y$)$_4$] (C$_x$H$_y$ = C$_2$H$_4$, 135 mg, 0.35 mmol; C$_8$H$_{14}$, 250 mg, 0.35 mmol) under a nitrogen atmosphere and spectroscopic measurements confirmed that *trans*-[Rh$_2$(μ-Cl)$_2$(CO)$_2$(C$_x$H$_y$)$_2$] was formed exclusively. No attempt was made to isolate these products which were used directly for further reactions and monitored using IR and NMR spectroscopy.

[Rh$_2$(μ-Cl)$_2$(CO)$_2$(C$_2$H$_4$)$_2$(py)$_2$] 12. Pyridine (82 μl, 2.0 mmol) was added to a solution containing [Rh$_2$(μ-Cl)$_2$(CO)$_4$] (100 mg, 0.25 mmol) and [Rh$_2$(μ-Cl)$_2$(CO)$_2$(C$_2$H$_4$)$_4$] (100 mg, 0.25 mmol) (Rh : py = 1 : 1) in CH_2Cl_2 (2 cm^3) under a nitrogen atmosphere to give a clear yellow solution. The IR and ^{13}C-{^{1}H} NMR measurements (which showed the presence of co-ordinated C_2H_4) were entirely consistent with the formation of [Rh$_2$(μ-Cl)$_2$(CO)$_2$(py)$_2$(C$_2$H$_4$)$_2$] (see Table 1).

***trans*-[Rh$_2$(μ-CO)$_2$Cl$_2$(py)$_2$] 13.** Addition of pyridine (82 μl, 2.0 mmol) to a mixture containing [Rh$_2$(μ-Cl)$_2$(CO)$_4$] (100 mg, 0.25 mmol) and [Rh$_2$(μ-Cl)$_2$(C$_2$H$_4$)$_4$] (100 mg, 0.25 mmol) (Rh : py = 1 : 1) in CH_2Cl_2 (5 cm^3) under a nitrogen atmosphere gave a clear yellow solution. When left under a reduced pressure of N_2 this solution formed a violet precipitate of *trans*-[Rh$_2$(μ-CO)$_2$Cl$_2$(py)$_2$] which was filtered off and dried under vacuum (181 mg, 72%) (Found: C, 29.4; H, 2.1; N, 5.5. $C_{12}H_{10}Cl_2N_2O_2Rh_2$ requires C, 29.2; H, 2.4; N, 5.6%).

***trans*-[Rh$_2$(μ-Cl)$_2$(CO)$_2$(py)$_2$] 14.** Pyridine (115 μl, 1.4 mmol) was added to a solution containing [Rh$_2$(μ-Cl)$_2$(CO)$_4$] (135 mg, 0.35 mmol) and [Rh$_2$(μ-Cl)$_2$(C$_8$H$_{14}$)$_4$] (250 mg, 0.35 mmol) (Rh : py = 1 : 1) in CH_2Cl_2 (2 cm^3) under a nitrogen atmosphere. The IR, ^{13}C-{^{1}H} and ^{15}N-{^{1}H} INEPTRD (insensitive nuclei enhanced by polarisation transfer, refocussed and decoupled) NMR measurements were entirely consistent with the formation of *trans*-[Rh$_2$(μ-Cl)$_2$(CO)$_2$(py)$_2$] (see Table 1).

Crystallography

Crystal data, data collection and processing details are given in Table 4. All data were recorded on a Rigaku AFC6S diffractometer at −120 °C using graphite-monochromatised Mo-Kα radiation, $\lambda = 0.710\,69$ Å and 50 kW sealed-anode generator, scan width between 1.10 + 0.30 tan θ for complex **2** and 0.89 + 0.30 tan θ for **4**, scan speed 4° min^{-1} for both (2 rescans), $2\theta_{max} = 50°$. Three standard reflections were measured after every 150 scans; no significant decay was observed. An empirical absorption correction (ψ scans[20]) was applied by the TEXSAN[21] system. The unit cells were determined from diffractometer angles for 25 automatically centred reflections with 2θ 7.29–18.76° for **2** and 38.3–44.13° for **4**.

Structure analysis and refinement. Direct methods by full-matrix refinement on F. All non-hydrogen atoms were treated as anisotropic and hydrogen atoms placed in geometric ideal positions and assigned isotropic thermal parameters 20% greater than the B equivalent value of the atom to which they were bonded. The weighting scheme was based on counting statistics and included a factor ($P = 0.03$) to downweight the intense reflections. Plots of $\Sigma w(|F_o| - |F_c|)^2$ *versus* $|F_o|$, reflection order in data collection, $(\sin\theta)/\lambda$, and various classes of indices showed no unusual trends. Neutral atom scattering factors were taken from Cromer and Waber.[22] Anomalous dispersion effects were included in F_c. All calculations were performed using the TEXSAN[21] software package and ORTEP[23] was used to produce Figs. 1 and 2.

CCDC reference number 186/884.

See http://www.rsc.org/suppdata/dt/1998/1403/ for crystallographic files in .cif format.

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