Synthesis and molecular structure of [Re$_2$(μ:η^6-C$_{24}$H$_{18}$N$_4$)(CO)$_6$] containing the rtct-tetrakis(2-pyridyl)cyclobutandiyl ligand, derived from the reaction of [Re$_2$(CO)$_8$(MeCN)$_2$] and 1,2-bis(2-pyridyl)ethene

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Abstract

The reaction of the labile compound [Re$_2$(CO)$_8$(CH$_3$CN)$_2$] with *trans*-1,2-bis(2-pyridyl)ethene (C$_{12}$H$_{10}$N$_2$) at room temperature in tetrahydrofuran affords the compounds [Re$_2$(μ:η^3-C$_{12}$H$_{10}$N$_2$)(CO)$_8$] (**1**) and the oxidative addition product [Re$_2$(μ-H)(μ:η^3-C$_{12}$H$_9$N$_2$)(CO)$_7$] (**2**). When the reaction is carried out at temperatures of refluxing tetrahydrofuran, besides compounds **1** and **2**, the oxidative addition product [Re$_2$(μ-H)(μ:η^4-C$_{12}$H$_9$N$_2$)(CO)$_6$] (**3**), the insertion product [Re$_2$(μ:η^4-C$_{12}$H$_{10}$N$_2$)(CO)$_8$] (**4**) and [Re$_2$(η^6-C$_{24}$H$_{18}$N$_4$)(CO)$_6$] (**5**) are obtained. Compound **5** contains the organic ligand *rtct*-tetrakis(2-pyridyl)cyclobutandiyl which is derived from a [2 + 2] cycloaddition of 1,2-bis(2-pyridyl)ethene mediated by its coordination to the bimetallic framework. The molecular structures of **1, 2, 4** and **5** were confirmed by X-ray crystallographic studies.
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1. Introduction

Aromatic nitrogen heterocycles represent an important class of ligands in coordination chemistry [1]. Such ligands offer exciting new possibilities for the preparation of binuclear and polynuclear complexes with potential applications as catalysts, photosensitizers or low dimensional conducting polymers. Binuclear and multi-nuclear transition metal complexes comprising two or more metal centers bridged by multidentated ligands have been the subject of enormous amount of work particularly in recent years [2].

We are interested in the interaction of these π-delocalised organic ligands with the dinuclear rhenium complex [Re$_2$(CO)$_8$(CH$_3$CN)$_2$], due to the high reactivity of this labile complex towards oxidative and insertion reactions of such ligands, in order to obtain new complexes that can be used to model important bio-inorganic systems such as some metalloproteins, or to find some applications as catalysts for photosensitization. In this work, we report the synthesis and characterization of new complexes of rhenium derived from the interaction

of the labile $[Re_2(CO)_8(CH_3CN)_2]$ with 1,2-bis(2-pyridyl)ethene.

A variety of oxidative addition reactions involving polynuclear metal carbonyl systems has been studied extensively within the past several years [3]. In particular C–H oxidative addition has been observed for a large number of functionalized organic molecules, including alkenes, alkynes and aromatics. In trimetallic clusters alkenyl ligands adopt bridging coordinations and act as three-electron donors to the metallic atoms [4]. In dinuclear rhenium complexes such species can adopt three possible isomeric forms I–III, with the substituent on either the α-(I) or β-(II–III) carbon, the latter being either *cis* (II) or *trans* (III).
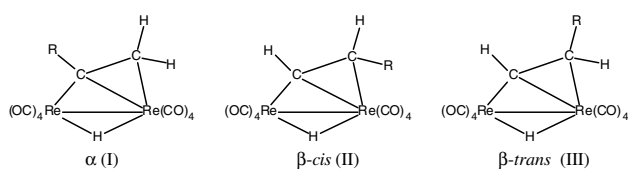
The β forms (*cis* and *trans*) can exchange: for example, the *cis*-$[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}CH\text{=}CHR)]$ (R = Me, Et) converts into the thermodynamically stable *trans* isomer both thermally and photochemically [5].

R = Me, Et
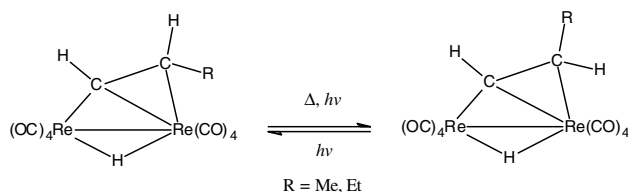
In this work, we have evaluated the coordination ability of the two functionalities in the ligand 1,2-bis(2-pyridyl)ethene upon its interaction with the labile rhenium complex $[Re_2(CO)_8(CH_3CN)_2]$ and have found that coordination to the metal atoms occurs through both the ethenyl function and nitrogen atoms of the pyridine rings, and C–H bonds of the ethenyl moiety are cleaved rather than those of the pyridine rings.

2. Experimental

All reactions were performed under dried and purified nitrogen. Solvents were purified by standard procedures and distilled prior to use [6]. $[Re_2(CO)_8(CH_3CN)_2]$ was prepared by the methods described previously [7]. 1,2-bis(2-pyridyl)ethene was provided by Aldrich. Reactions were monitored by FT–IR in the range 2200–1750 cm^{-1} and the products were separated by TLC (SiO$_2$, Merck 60 HF$_{254}$). IR spectra were recorded on a Nicolet 5DXC FT-IR spectrometer, using 0.5 mm calcium fluoride solution cells. ^{1}H NMR spectra were obtained on a Bruker 300 MHz spectrometer.

2.1. Reaction of 1,2-bis(2-pyridyl)ethene with [Re$_2$-(CO)$_8$(CH$_3$CN)$_2$]: synthesis of the complexes 1, 2, 3, 4 and 5

A solution of $[Re_2(CO)_8(CH_3CN)_2]$ (0.200 g; 0.298 mmol) and 1,2-bis(2-pyridyl)ethene (0.054 g; 0.298 mmol) in THF (50 ml) was refluxed for 3 h during which time the color of the solution changed from pale yellow to light orange. The solvent was removed under reduced pressure and the residue separated by TLC eluting with dichloromethane:*n*-hexane (3:7, v:v) to give five compounds: $[Re_2(\mu:\eta^3\text{-}C_{12}H_{10}N_2)(CO)_8]$ (1) (yellow; 0.055 g, 24%), $[Re_2(\mu\text{-}H)(\mu:\eta^3\text{-}C_{12}H_9N_2)(CO)_7]$ (2) (yellow; 0.033 g, 15%), $[Re_2(\mu\text{-}H)(\mu:\eta^4\text{-}C_{12}H_9N_2)(CO)_6]$ (3) (green; 0.043 g, 20%), $[Re_2(\mu:\eta^4\text{-}C_{12}H_{10}N_2)(CO)_8]$ (4) (yellow; 0.020 g, 9%) and $[Re_2(\mu:\eta^6\text{-}C_{24}H_{18}N_4)(CO)_6]$ (5) (yellow; 0.012 g, 4%). Complexes 1, 2, 4 and 5 were obtained as yellow crystals after recrystallization from CH_2Cl_2:C_6H_{12} (1:3, v:v) at room temperature. When the reaction is carried out in tetrahydrofuran or dichloromethane at room temperature only compounds $[Re_2(\mu:\eta^3\text{-}C_{12}H_{10}N_2)(CO)_8]$ (1) and $[Re_2(\mu\text{-}H)(\mu:\eta^3\text{-}C_{12}H_9N_2)(CO)_7]$ (2) are obtained (25% and 18% respectively). Anal. Found for 1: C, 30.66; H, 1.35; N, 3.40. Calc. for $C_{20}H_{10}N_2O_8Re_2$: C, 30.85; H, 1.29; N, 3.60. Anal. Found for 2: C, 30.58; H, 1.40; N, 3.55. Calc. for $C_{19}H_{10}N_2O_7Re_2$: C, 30.40; H, 1.34; N, 3.73. Anal. Found for 3: C, 30.12; H, 1.47; N, 3.62. Calc. for $C_{18}H_{10}N_2O_6Re_2$: C, 29.92; H, 1.39; N, 3.88. Anal. Found for 4: C, 30.70; H, 1.33; N, 3.35. Calc. for $C_{20}H_{10}N_2O_8Re_2$: C, 30.85; H, 1.29; N, 3.60. Anal. Found for 5: C, 39.72; H, 2.10; N, 5.88. Calc. for $C_{30}H_{18}N_4O_6Re_2$: C, 39.91; H, 2.01; N, 6.21.

2.2. Thermal treatment of [Re$_2$(μ:η^3-C$_{12}$H$_{10}$N$_2$)(CO)$_8$] (1)

A solution of compound 1 (0.012 g; 0.013 mmol) in cyclohexane (30 ml) was heated under reflux for 8 h. The solvent was evaporated under reduced pressure and TLC of the residue (eluant: dichloromethane:*n*-hexane, 7:3, v:v) gave $[Re_2(\mu\text{-}H)(\mu:\eta^4\text{-}C_{12}H_9N_2)(CO)_6]$ (3) (0.005 g; 42%) and $[Re_2(\mu:\eta^4\text{-}C_{12}H_{10}N_2)(CO)_8]$ (4) (0.005 g; 42%).

2.3. Thermal treatment of [Re$_2$(μ-H)(μ:η^3-C$_{12}$H$_9$N$_2$)(CO)$_7$] (2)

Compound 2 (0.010 g; 0.013 mmol) was dissolved in cyclohexane (30 ml). The solution was heated under reflux for 4 h. The solvent was evaporated under reduced

pressure and TLC of the residue (eluant: dichloromethane:*n*-hexane, 3:7, v:v) gave [Re$_2$(μ-H)(μ:η^4-C$_{12}$H$_9$N$_2$) (CO)$_6$] (**3**) (0.007 g; 62%).

2.4. Thermal treatment of [Re$_2$(μ-H)(μ:η^4-C$_{12}$H$_9$N$_2$)-(CO)$_6$] (**3**) under CO atmosphere

Compound **3** (0.010 g; 0.014 mmol) was dissolved in cyclohexane (30 ml) and the solution was taken to reflux under CO atmosphere for 2 h. The solvent was evaporated under reduced pressure and the residue separated by TLC (eluant: dichloromethane:*n*-hexane, 3:7, v:v) yielding [Re$_2$(η^4-C$_{12}$H$_{10}$N$_2$)(CO)$_8$] (**4**) (0.005 g; 48%).

2.5. Carbonylation of [Re$_2$(μ-H)(μ:η^4-C$_{12}$H$_9$N$_2$)-(CO)$_6$] (**3**) at room temperature

A sample of compound **3** (0.010 g; 0.013 mmol) was dissolved in CD$_3$COCD$_3$ (1 ml) in a NMR tube and sealed under CO (1 atm). After 17 days at room temperature, compound **3** was completely converted to [Re$_2$-(μ-H)(μ:η^3-C$_{12}$H$_9$N$_2$)(CO)$_7$] (**2**).

2.6. X-ray crystal structure determinations for compounds **1**, **2**, **4** and **5**

Crystal structures of the four compounds were determined using a Rigaku AFC7S diffractometer provided with a graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at room temperature. X-ray experimental details are collected in Table 1. All data were corrected for Lp effects and semi-empirical absorption corrections [8] were also applied. Crystal structures were solved by direct methods [9] and expanded using Fourier techniques [10]. For each compound all non-H atoms were refined anisotropically. For **2** a cyclohexane molecule of crystallization was found sitting on a local crystallographic center of symmetry. Disorder was observed for the solvent in two positions, so the C atoms were refined with isotropic displacement parameters. The occupancy factors for the solvent positions in the two models were refined to 0.58 and 0.42. A residual peak was observed for **2** in the last cycle of refinement, which was consistent with the expected hydride ligand position. This peak was included without any further refinement. For all crystal structures, H-atoms were included in

Table 1
Crystal data, data collection and refinement parameters for compounds **1**, **2**, **4**, and **5**

	1	**2**	**4**	**5**
Formula	C$_{20}$H$_{10}$N$_2$O$_8$Re$_2$	C$_{19}$H$_{10}$N$_2$O$_7$Re$_2$	C$_{20}$H$_{10}$N$_2$O$_8$Re$_2$	C$_{30}$H$_{18}$N$_4$O$_6$Re$_2$
M	778.70	792.77	778.70	902.88
Crystal size (mm^3)	0.54×0.30×0.24	0.30×0.20×0.10	0.65×0.30×0.26	0.50×0.32×0.44
Color	Yellow	Yellow	Yellow	Yellow
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P1$	$P2_1/n$	$P2_1/n$	$P2_1/n$
Unit cell dimensions				
a (Å)	8.656(3)	9.482(2)	9.505(3)	11.010(2)
b (Å)	10.356(4)	22.707(5)	13.171(6)	14.427(10)
c (Å)	12.714(7)	11.619(2)	17.482(2)	17.161(3)
α (°)	104.01(4)	90	90	90
β (°)	103.87(3)	103.97(3)	93.57(2)	93.567(18)
γ (°)	91.16(3)	90	90	90
V (Å^3)	1069.8(8)	2427.6(8)	2184.4(1)	2720.6(8)
Z	2	4	4	4
D_c (g cm^{-3})	2.417	2.169	2.368	2.204
$F(000)$	716	1472	1432	1696
2θ range (°)	3.42–49.98	3.58–49.98	3.88–49.96	3.70–50.02
μ (mm^{-1})	11.354	10.007	11.122	8.944
Reflections measured	3995	4547	4093	5057
Independent reflections	3776	4276	3847	4791
R(int)	0.0362	0.0161	0.0153	0.0359
Data/restrains/parameters	3776/0/289	4276/0/297	3847/0/289	4791/0/379
GOF on F^2	1.050	1.028	1.090	1.015
Final R index [$I > 2\sigma(I)$]	$R_1 = 0.0596$	$R_1 = 0.0321$	$R_1 = 0.0285$	$R_1 = 0.0354$
	$wR_2 = 0.1698$	$wR_2 = 0.0766$	$wR_2 = 0.0507$	$wR_2 = 0.0823$
R index (all data)	$R_1 = 0.0740$	$R_1 = 0.0500$	$R_1 = 0.0474$	$R_1 = 0.0614$
	$wR_2 = 0.1845$	$wR_2 = 0.0840$	$wR_2 = 0.0554$	$wR_2 = 0.0937$
Extinction coefficients		0.00220		
Largest features in final difference map min. e Å^{-3})	4.167/−3.194	1.183/−1.080	0.907/−0.548	1.262/−1.057

Refinement method: Full-matrix least-squares on F^2.

calculated positions in the last cycle, except for **1** in which the olefinic H-atoms were located. In all cases thermal parameters of these atoms were 1.2 times the U_{eq} of the corresponding C atoms and refined by using a riding model. The final cycle of full-matrix least-squares was based on F^2. All data reduction and graphical representations were performed using teXsan [11] crystallographic software package, whereas refinement calculations were made using SHELXTL-PLUS [10].

3. Results and discussion

The general synthetic route to the rhenium-1,2-bis(2-pyridyl)ethene derivatives is depicted in Scheme 1. Treatment of $[Re_2(CO)_8(CH_3CN)_2]$ with 1.0 eq. of 1,2-bis(2-pyridyl)ethene in tetrahydrofuran or dichloromethane solution at room temperature, affords compounds $[Re_2(\mu:\eta^3-C_{12}H_{10}N_2)(CO)_8]$ (**1**) and $[Re_2(\mu-H)(\mu:\eta^3-C_{12}H_9N_2)(CO)_7]$ (**2**). When the reaction is carried out in refluxing tetrahydrofuran for 3 h, besides **1** and **2**, the compounds $[Re_2(\mu-H)(\mu:\eta^4-C_{12}H_9N_2)(CO)_6]$ (**3**), $[Re_2(\mu:\eta^4-C_{12}H_{10}N_2)(CO)_8]$ (**4**) and $[Re_2(\mu:\eta^6-C_{24}H_{18}N_4)(CO)_6]$ (**5**) are obtained in significant yields. ^{1}H NMR and IR data are shown in Table 2. A mixture of **3** and **4** was isolated from thermolysis of compound **1** in cyclohexane. Thermolysis of complex **2** afforded

quantitatively the hexacarbonyl species **3**. This conversion was completely reversed by treating **3** at room temperature with 1 atm CO. Compound **5** shows the dimetallated organic ligand *rtct*-tetrakis(2-pyridyl)cyclobutandiyl (2,2′-tpcb) with a new mode of coordination. To account for the formation of this species, 1,2-bis(2-pyridyl)ethene was heated in THF reflux, but the 2,2′-tpcb ligand was not obtained, suggesting that its formation is assisted by the presence of $[Re_2(CO)_8(CH_3CN)_2]$.

3.1. Complex $[Re_2(\mu:\eta^3-C_{12}H_{10}N_2)(CO)_8]$ (**1**)

The $v(CO)$ absorption spectrum of **1** indicates that only terminal carbonyl groups are present and its band pattern resembles that for $[Re_2(CO)_8(\mu-MeC_2NMe_2)]$ [12]. The ^{1}H NMR spectrum exhibits two doublets ($\delta = 6.18$ and 4.16 ppm) assigned to the ethylenic protons, and eight different signals in the aromatic region are associated to two different pyridine systems, which implies a loss of the free ligand symmetry. For the olefinic protons, a coupling of $J = 10.7$ Hz and their high field shift suggest the coordination of the *trans*-CH=CH-group to the dirhenium metal system.

The molecular structure of **1** was confirmed by X-ray analysis (Fig. 1). Selected bond lengths and angles are shown in Table 3. The structural analysis revealed that **1** contains two $Re(CO)_4$ groups joined by a Re–Re single bond, and the organic ligand acts as a four-electron donor. The Re_1–Re_2 bond distance [3.0355(12) Å] is similar to the Re–Re distance in the parent compound $[Re_2(CO)_{10}]$ [3.0413(11) Å] [13]. The ligand is η^1-coordinated through the nitrogen of a pyridine ring to one rhenium atom [Re_2–$N_2 = 2.215(13)$ Å] and the olefinic portion is η^2-coordinated to Re_1. An asymmetric triangle is formed by C6A, C7A and Re_1 atoms [Re_1–C6A = 2.318(14) Å, Re_1–C7A = 2.238(16) Å], and as a consequence of the η^2-coordination of the ethylenic moiety, the distance C6A–C7A [1.38(2) Å] is longer than uncoordinated C–C double bond lengths [14].

3.2. Complex $[Re_2(\mu-H)(\mu:\eta^3-C_{12}H_9N_2)(CO)_7]$ (**2**)

The ^{1}H NMR spectrum of **2** in the aromatic region contains a series of signals integrating for eight protons due to two non-equivalent pyridine rings. The broad signal at $\delta = 7.37$ ppm is assigned to an olefinic hydrogen (H_i). The absence of a signal for the second C–H olefinic proton and a doublet at $\delta = -10.68$ ppm ($J = 0.9$ Hz) due to a bridging hydride Re–H–Re, suggest a C–H bond cleavage on the HC=CH fragment. The H–H COSY revealed that the broad olefinic signal for H_i is coupled to the hydride ligand and to the α proton (H_e) of a pyridine ring.

The molecular structure of **2** is shown in Fig. 2 and selected bond distances and angles are collected in Table 4. In **2** the bond length Re1–Re2 [3.256(12) Å] is slightly
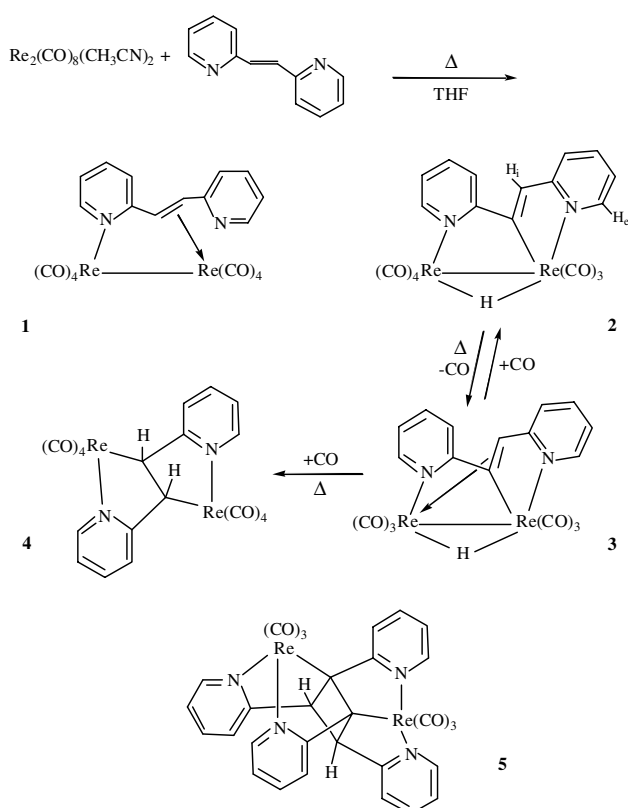
Scheme 1.

Table 2
IR and NMR data for compounds **1–5**

Compound	$v(CO)^a$ (cm^{-1})	^{1}H NMR^b (δ, ppm)	J_{H-H}	(Hz)
[Re$_2$(μ:η^3-C$_{12}$H$_{10}$N$_2$)(CO)$_8$] (**1**)	2087 m	8.84 (ddd, H$_a$)	ab 5.5	ef 4.7
	2044 m	7.22 (ddd, H$_b$)	ac 1.0	eg 1.7
	1993 vs	7.37 (ddd, H$_c$)	ad 1.5	eh 1.0
	1985 s	7.84 (ddd, H$_d$)	bc 7.9	fg 7.5
	1976 m	8.43 (ddd, H$_e$)	bd 1.7	fh 1.1
	1954 m	7.06 (ddd, H$_f$)	cd 7.9	gh 7.9
	1928 m	7.76 (ddd, H$_g$)		ij 10.7
		7.59 (ddd, H$_h$)		
		6.18 (d, H$_i$)		
		4.16 (d H$_j$)		
[Re$_2$(μ-H)(μ:η^3-C$_{12}$H$_9$N$_2$)(CO)$_7$] (**2**)	2105 m	9.13 (ddd, H$_a$)	ab 5.7	ef 5.5
	2013 vs	7.25 (m, H$_b$, H$_f$)	ac 1.5	eg 1.6
	1995 s	8.07 (ddd, H$_c$)	ad 0.9	eh 1.1
	1952 s	7.35 (ddd, H$_d$)	bc 7.7	fg 7.9
	1921 s	9.01 (ddd, H$_e$)	bd 1.4	fh 1.1
	1900 s	7.95 (ddd, H$_g$)	cd 7.7	gh 7.9
		7.65 (ddd, H$_h$)		ij 0.9
		7.37 (br s, H$_i$)		
		−10.68 (d, H$_j$)		
[Re$_2$(μ-H)(μ:η^4-C$_{12}$H$_9$N$_2$)(CO)$_6$] (**3**)	2039 s	8.75 (ddd, H$_a$)	ab 5.5	ef 5.5
	2010 vs	7.12 (ddd, H$_b$)	ac 0.8	eg 1.5
	1948 vs	8.00 (m, H$_c$, H$_g$)	ad 0.8	eh 1.2
	1940 vs	7.86 (ddd, H$_d$)	bc 7.6	fg 7.9
	1925 s	8.35 (ddd, H$_e$)	bd 1.4	fh 1.2
	1918 s	7.23 (ddd, H$_f$)	cd 7.6	gh 7.9
		7.17 (ddd, H$_h$)		
		8.67 (s, H$_i$)		
		−9.42 (s, H$_j$)		
[Re$_2$(μ:η^4-C$_{12}$H$_{10}$N$_2$)(CO)$_8$] (**4**)	2081 m	8.46 (ddd, 2H$_a$)	ab 5.9	bc 7.0
	1990 vs	6.70 (ddd, 2H$_b$)	ac 1.5	bd 1.0
	1979 m	7.59 (ddd, 2H$_c$)	ad 1.0	cd 8.5
	1964 vs	7.25 (ddd, 2H$_d$)		
	1933 vs	4.77 (s, 2H$_e$)		
[Re$_2$(μ:η^6-C$_{24}$H$_{18}$N$_4$)(CO)$_6$] (**5**)	2070 m	8.98 (ddd, 2H$_a$)	ab 5.5	ef 5.9
	2014 vs	7.25 (ddd, 2H$_b$)	ac 1.3	eg 1.8
	1976 m	7.96 (ddd, 2H$_c$)	ad 1.0	eh 1.0
		7.93 (ddd, 2H$_d$)	bc 7.2	fg 7.2
		8.76 (ddd, 2H$_e$)	bd 1.4	fh 1.4
		6.66 (ddd, 2H$_f$)	cd 7.9	gh 8.5
		7.50 (ddd, 2H$_g$)		
		7.32 (ddd, 2H$_h$)		
		4.32 (s, 2H$_i$)		

^{a} In C$_6$H$_{12}$.
^{b} In CD$_3$COCD$_3$, 298 K.

longer than that observed for [Re$_2$(CO)$_{10}$] [13] but compares well with the values reported for other hydride bridged Re–Re single bonds [15]. The organic fragment is η^3-coordinated to the metal centers donating five electrons; two Re–N bonds [Re1–N1 = 2.237(6) Å and Re2–N2 = 2.185(7) Å] and one σ-Re–C bond [Re2–C6A = 2.153(8) Å]. The bond distance [C6A–C7A = 1.357(11) Å] is shorter than that observed for complex **1**, although it is slightly longer than that of a C–C double bond [14]. In contrast to what was observed

for **1**, the C6A–C7A axis is almost perpendicular to the Re–Re axis, with an angle of 82.1°. In **2**, a five-membered ring (Re2–N2–C8A–C7A–C6A) is formed, showing a nearly planar conformation (mean deviation = 0.0372 Å). This metallocycle has a dihedral angle of 3.9° with respect to the pyridine ring N2–C8A–C9A–C10A–C11A–C12A, and of 56.9° to the N1–C1A–C2A–C3A–C4A–C5A heterocycle. Between the pyridine rings a dihedral angle of 53.9° is formed. The hydride ligand position was determined in the X-ray study and is consistent with
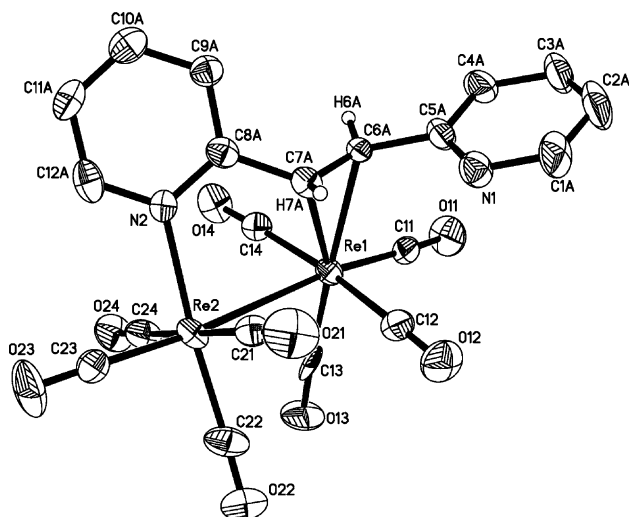
Fig. 1. ORTEP view (35% probability ellipsoids, H atoms omitted for clarity) of the molecular structure of **1** in the crystal.

Table 3
Selected bond lengths (Å) and angles (°) for compound **1**

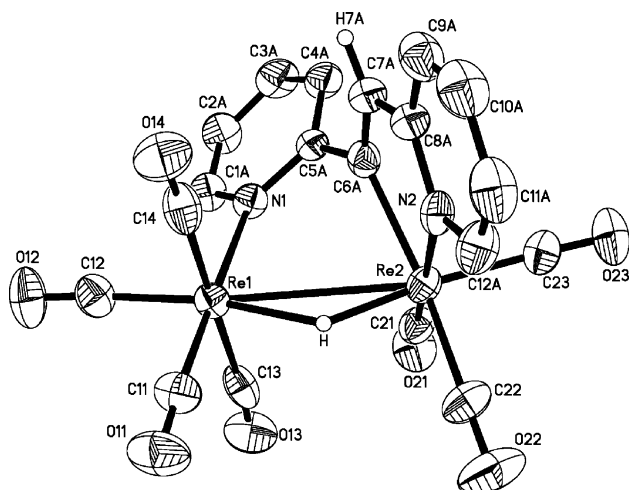| Re1–Re2	3.0355(12)	C6A–Re1–Re2	108.3(4)
Re1–C6A	2.318(14)	C7A–Re1–Re2	73.5(4)
Re1–C7A	2.238(16)	C6A–Re1–C7A	35.2(5)
Re2–N2	2.215(13)	Re1–Re2–N2	81.8(3)
C6A–C7A	1.38(2)	Re1–C6A–C5A	116.3(10)
		Re1–C6A–C7A	69.2(9)
		Re1–C7A–C6A	75.6(9)
		Re1–C7A–C8A	114.9(10)
		C6A–C7A–C8A	120.2(12)
		C7A–C8A–N2	118.3(14)
		Re2–N2–C8A	119.5(10)

Fig. 2. ORTEP view (35% probability ellipsoids, H atoms omitted for clarity) of the molecular structure of **2** in the crystal.

the vacancy around both rhenium centers, close to the *trans* positions given by C12A and C23A carbonyl groups, and oriented on the opposite side to the N1, C5A and C6A atoms of the bipyridyl ligand. The ob-

Table 4
Selected bond lengths (Å) and angles (°) for compound **2**

Re1–Re2	3.256(12)	C6A–Re2–N2	73.9(3)
Re1–N1	2.237(6)	C6A–Re2–H	88.3
Re1–H	1.92	N2–Re2–H	85.4
Re2–C6A	2.153(8)	C6A–C5A–N1	114.8(7)
Re2–N2	2.185(7)	Re2–C6A–C5A	121.7(6)
Re2–H	1.71	Re2–C6A–C7A	117.3(6)
C6A–C7A	1.357(11)	C6A–C7A–C8A	116.4(8)
		C7A–C8A–N2	115.8 (8)
		Re1–N1–C5A	120.7(5)
		Re2–N2–C8A	115.9(5)

served Re–H–Re angle (127.6°) compares well to the values reported for the trinuclear rhenium complex [H$_3$Re$_3$(CO)$_{11}$PPh$_3$] [average = 127.1(5)°], for which the crystal structure was determined by neutron diffraction [c]. In contrast, the Re–H distances (Re$_1$–H = 1.92 Å and Re2–H = 1.71 Å) show a small asymmetry that could be attributed to the different coordination environments around each Re atom.

3.3. Complex [Re$_2$(μ-H)(μ:η^4-C$_{12}$H$_9$N$_2$)(CO)$_6$] (3)

The structure depicted for **3** (Scheme 1) is based on spectroscopic data and the interconversion observed between **2** and **3**, where decarbonylation of **2** in refluxing cyclohexane gives **3**, which easily reverts to **2** under CO atmosphere. The IR spectrum for **3** is quite different to IR spectra reported for rhenium dinuclear complexes. Its ^{1}H NMR spectrum shows a group of signals in the aromatic region accounting for eight protons, a signal at $\delta = 8.67$ ppm corresponding to one olefinic proton and a singlet at $\delta = -9.42$ ppm associated with a bridging hydride. The combination of two coordinated pyridines, a bridging σ, η^2-vinyl group and a hydride results in a total contribution of eight electrons to give a 34-electron count for the dinuclear compound.

3.4. Complex [Re$_2$(μ:η^4-C$_{12}$H$_{10}$N$_2$)(CO)$_8$] (4)

The ^{1}H NMR spectrum of **4** exhibits four aromatic resonances corresponding to eight pyridinic protons indicating equivalent pyridine rings, and a singlet at $\delta = 4.77$ ppm associated with two protons. This high field resonance corresponds to the reduction of the carbon–carbon double bond and a hybridization change from sp^2 to sp^3.

Compound **4** was characterized by a single-crystal X-ray diffraction analysis. An ORTEP drawing of the molecular struture of **4** is shown in Fig. 3 and selected bond lengths and angles are listed in Table 5. The structure reveals the absence of a Re–Re bond (Re$\cdots$Re = 4.565 Å) and each rhenium atom bears four terminal carbonyl ligands. The asymmetric unit in the crystal structure of **4** contains a full crystallographically independent molecule, which sits in a local site with a close to twofold axis
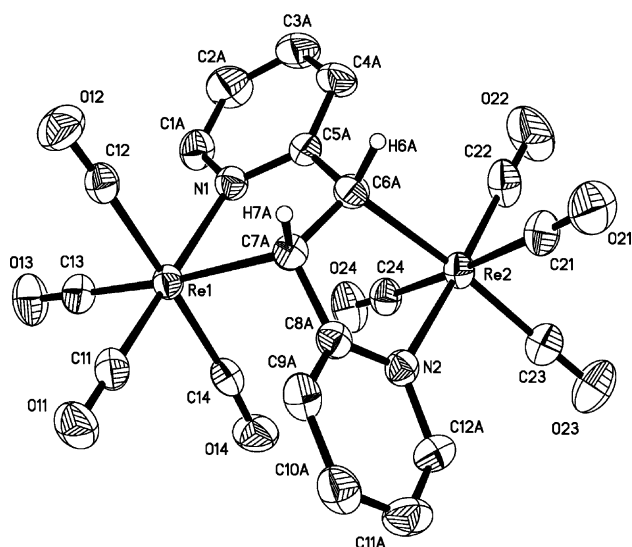
Fig. 3. ORTEP view (35% probability ellipsoids, H atoms omitted for clarity) of the molecular structure of **4** in the crystal.

Table 5
Selected bond lengths (Å) and angles (°) for compound **4**

Re1···Re2	4.565	C7A–Re1–N1	77.7(2)
Re1–C7A	2.271(6)	C6A–Re2–N2	77.7(2)
Re1–N1	2.187(6)	Re2–C6A–C5A	109.1(4)
Re2–C6A	2.270(7)	Re2–C6A–C7A	109.7(4)
Re2–N2	2.181(5)	C5A–C6A–C7A	113.6(6)
C6A–C7A	1.549(9)	Re1–C7A–C6A	109.9(4)
		Re1–C7A–C8A	108.5(4)
		C6A–C7A–C8A	113.3(5)
		C7A–C8A–N2	118.2(6)
		Re1–N1–C5A	117.2(4)
		Re2–N2–C8A	116.9(4)

cutting the C6A–C7A bond, which accounts for the observed symmetry in solution. The ligand forms two five-membered rings involving each rhenium center, Re1–C7A–C6A–C5A–N1 and Re2–C6A–C7A–C8A–N2. These rings are *cis*-fused along the C6A–C7A bond with *cis*-hydrogens on these carbon atoms, and the Re atoms adopt a relative position with a torsion angle Re2–C6A–C7A–Re1 of 103.8°. This value shows that the C6–C7 bond is closer to being eclipsed (120° torsional angle) than staggered (60° torsional angle). Each ring shows a similar envelope conformation, in which the C6A and C7A atoms are found out of the mean plane (mean deviation = 0.070 Å) by an average distance of 0.121 Å. The mean planes of both five-membered rings form a dihedral angle of 69.7°. The pyridine rings are coordinated to the rhenium centers through the nitrogen atoms [Re1–N1 = 2.187(6) Å and Re2–N2 = 2.181(5) Å], forming a dihedral angle of 104.6° between the planes of the heterocycles. The bond distance C6A–C7A [1.549(9) Å] is characteristic of a C–C single bond, and these two carbon atoms are coordinated to rhenium atoms with Re1–C7A and Re2–C6A bond distances of

2.271(6) and 2.270(7) Å respectively. This mode of coordination for the bipyridine ligand in **4** was also observed for the complex [(C$_5$Me$_5$)$_2$Sm]$_2$(μ-η^2:η^2-pyCHCHpy), [16] but the quality of the structural data in that case precludes any further comparison about the intramolecular parameters. In **4**, the ligand is regarded as a six-electron donor (three electrons to each metallic center) and the metal atoms are coordinatively saturated.

3.5. Complex [Re$_2$(μ:η^6-C$_{24}$H$_{18}$N$_4$)(CO)$_6$] (5)

The IR spectrum of **5** in the carbonyl stretching region shows a very simple pattern, consistent with two equivalent *fac*-Re(CO)$_3$ subgroups. The ^{1}H NMR spectrum of **5** shows eight aromatic resonances for two non-equivalent 2-pyridyl ring enviroments (two rings in each enviroment), and a signal at $\delta = 4.32$ ppm corresponding to two equivalent protons, suggesting the change of the C=C in the free ligand into a single C–C bond.

The molecular structure of **5** was determined by a single-crystal X-ray study. The solid-state structure of **5** is illustrated in Fig. 4 and selected bond lengths and angles are given in Table 6. The ligand *rtct*-tetrakis(2-pyridyl)cyclobutandiyl in this dirhenium compound is the
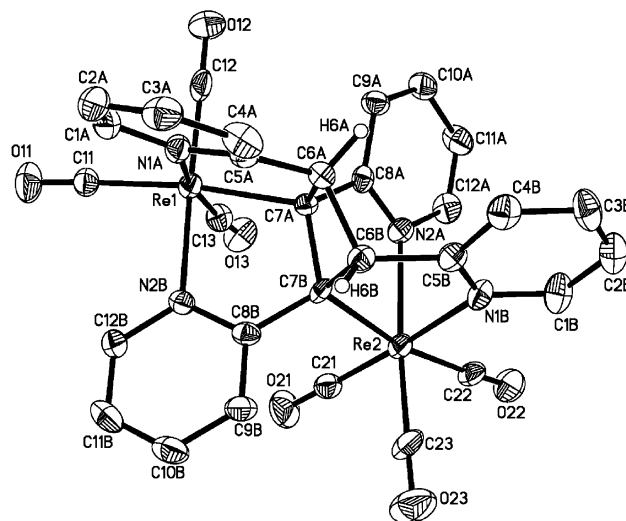

Fig. 4. ORTEP view (35% probability ellipsoids, H atoms omitted for clarity) of the molecular structure of **5** in the crystal.

Table 6
Selected bond lengths (Å) and angles (°) for compound **5**

Re1···Re2	4.718	C7A–Re1–N1A	77.5(3)
Re1–C7A	2.187(8)	C7A–Re1–N2B	77.5(3)
Re1–N1A	2.227(6)	N1A–Re1–N2B	82.1(2)
Re1–N2B	2.209(7)	C7B–Re2–N1B	77.0(3)
Re2–C7B	2.196(7)	C7B–Re2–N2A	77.3(3)
Re2–N1B	2.192(7)	N1B–Re2–N2A	79.1(3)
Re2–N2A	2.209(7)	Re1–N1A–C5A	117.6(5)
C6A–C6B	1.563(11)	Re2–N2A–C8A	117.0(5)
C6A–C7A	1.551(10)	Re2–N1B–C5B	119.2(5)
C6B–C7B	1.552(11)	Re2–N2B–C8B	117.6(5)
C7A–C7B	1.582(11)		

result of a cycloaddition reaction of *trans*-1,2-bis(2-pyridyl)ethene. The cyclobutandiyl fragment shows C–C bond distances [average 1.562(10) Å] similar to the ones observed in the crystal structure of the co-crystal of *rctt*-tetrakis(2-pyridyl)cyclobutane and 1,8-naphthalenedicarboxylic acid (average: 1.562 Å) [17]. Each rhenium has a coordination shell with three terminal carbonyl ligands, a σ-Re–C bond and two nitrogen atoms [Re$_1$–N1A = 2.227(6) Å, Re$_1$–N2B = 2.209(7) Å, Re$_2$–N1B = 2.192(7) Å and Re$_2$–N2A = 2.209(7) Å]. As a result of C–H activation, the complex shows two σ-Re–C bonds within the cyclic system, [Re$_1$–C7A = 2.187(8) Å and Re$_2$–C7B = 2.196(7) Å]. To the best of our knowledge the coordination mode found here for the *rtct*-tetrakis(2-pyridyl)cyclobutandiyl ligand has not been observed previously. The complex contains an approximate twofold axis which bisects the C6A–C6B and C7A–C7B bonds. This result is consistent with what was observed in solution, where the NMR spectrum shows only one set of signals for the two equivalent portions in the molecule. In order to account for the formation of **5**, reaction of compound **1** with the free ligand was carried out but **5** was not obtained. When 1,2-bis(2-pyridyl)ethene was treated under the same reaction conditions but in the absence of [Re$_2$(CO)$_8$(MeCN)$_2$], dimerization did not occur. These results prompt us to propose that the formation of the ligand *rtct*-tetrakis(2-pyridyl)cyclobutandiyl occurs via coordination at rhenium, as has been argued for the dimerization of alkynes at 190 °C in the presence of [Re$_2$(CO)$_{10}$] [18]. We believe that **5** is formed only at previous stages of the reaction when two molecules of the ligand coordinate at the metal framework. A striking feature observed for our system is the stereospecific formation of the *rtct*-derivative in **5**. This isomer has only been observed during the solid-state photodimerization of 1,2-bis(2-pyridyl)ethene, which gives a mixture of *rctt* and *rtct* isomers [19].

4. Supporting material

Complete crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publications Nos. 213660 (**1**), 213662 (**2**), 213663 (**4**), 213661 (**5**).

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