

# Reactivity of 2,3-bis(2-pyridyl)pyrazine with $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2]$ : Molecular structures of $[\text{Re}_2(\text{CO})_8(\text{C}_{14}\text{H}_{10}\text{N}_4)]$ and $[\text{Re}_2(\text{CO})_8(\text{C}_{14}\text{H}_{10}\text{N}_4)\text{Re}_2(\text{CO})_8]$

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## Abstract

The reaction of the labile compound  $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2]$  with 2,3-bis(2-pyridyl)pyrazine in dichloromethane solution at reflux temperature afforded the structural dirhenium isomers  $[\text{Re}_2(\text{CO})_8(\text{C}_{14}\text{H}_{10}\text{N}_4)]$  (**1** and **2**), and the complex  $[\text{Re}_2(\text{CO})_8(\text{C}_{14}\text{H}_{10}\text{N}_4)\text{Re}_2(\text{CO})_8]$  (**3**). In **1**, the ligand is  $\sigma, \sigma'-N, N'$ -coordinated to a  $\text{Re}(\text{CO})_3$  fragment through pyridine and pyrazine to form a five-membered chelate ring. A seven-membered ring is obtained for isomer **2** by N-coordination of the 2-pyridyl groups while the pyrazine ring remains uncoordinated. For **2**, isomers **2a** and **2b** are found in a dynamic equilibrium ratio  $[\mathbf{2a}]/[\mathbf{2b}] = 7$  in solution, detected by  $^1\text{H}$  NMR ( $-50^\circ\text{C}$ ,  $\text{CD}_3\text{COCD}_3$ ), coalescence being observed above room temperature. The ligand in **3** behaves as an 8e-donor bridge bonding two  $\text{Re}(\text{CO})_3$  fragments through two ( $\sigma, \sigma'-N, N'$ ) interactions. When the reaction was carried out in refluxing tetrahydrofuran, complex  $[\text{Re}_2(\text{CO})_6(\text{C}_{14}\text{H}_{10}\text{N}_4)_2]$  (**4**) was obtained in addition to compounds **1–3**. The dinuclear rhenium derivative **4** contains two units of the organic ligand  $\sigma, \sigma'-N, N'$ -coordinated in a chelate form to each rhenium core. The X-ray crystal structures for **1** and **3** are reported. © 2006 Elsevier B.V. All rights reserved.

**Keywords:** Rhenium carbonyls;  $\alpha$ -diimines; Crystal structures; Pyridine; Pyrazine

## 1. Introduction

Polypyridyl ligands bridging two or more remote metal centers and containing  $\pi$ -delocalized systems have been the subject of an enormous amount of work [1]. The interest in metallic complexes with this type of ligand has been stimulated due to the strong metal-to-ligand charge transfer normally present in these complexes, which is believed to be potentially useful in molecular materials to promote elec-

tron transfer, magnetic coupling and intervalence transfer [2].

The interaction of  $\pi$ -delocalized organic ligands with metal clusters is well documented [3]. Our interest in the combination of metal clusters and polycyclic aromatic ligands is oriented to produce novel systems with potential electronic properties. A variety of binuclear transition-metal complexes containing  $\alpha$ -diimine ligands has been studied extensively within the past several years [4]. In dimetallic clusters,  $\alpha$ -diimine ligands such as R-DBA (1,4-disubstituted-1,4-diaza-1,3-butadienes), R-Pyca (pyridine-2-carbaldimines 6-R-C<sub>5</sub>H<sub>3</sub>N-2-CH=N-R), bipyridine and phenanthroline, adopt chelating  $\sigma, \sigma'-N, N'$  coordinations to yield complexes formulated as

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$[\text{M}_2(\text{CO})_8(\alpha\text{-diimine})]$  ( $\text{M} = \text{Mn}, \text{Re}$ ) [5]. In this context, when complexes  $[\text{LnM}'\text{M}(\text{CO})_3(\alpha\text{-diimine})]$  ( $\text{LnM}' = (\text{CO})_5\text{Mn}, (\text{CO})_5\text{Re}, (\text{CO})_4\text{Co}, \text{Cp}(\text{CO})_2\text{Fe}, \text{PhSn}$ ;  $\text{M} = \text{Mn}, \text{Re}$ ;  $\alpha\text{-diimine} = \text{bipyridine}, \text{phenanthroline}$ ) are irradiated under visible light, the homolysis of the  $\text{M}'\text{--M}$  bond and/or loss of CO from the  $\text{M}(\text{CO})_3(\alpha\text{-diimine})$  fragment is observed [6]. While the rhenium complex  $[\text{LnM}'\text{Re}(\text{CO})_3(\alpha\text{-diimine})]$  uniquely exhibited  $\text{M}'\text{--Re}$  bond homolysis, both reactions occurred for some others  $[\text{LnM}'\text{Mn}(\text{CO})_3(\alpha\text{-diimine})]$  derivatives [6].

The  $\alpha\text{-diimine}$  2,3-bis(2-pyridyl)pyrazine is a very versatile ligand, widely used to construct supramolecular transition-metal compounds [7]. We have previously studied the interaction of 2,3-bis(2-pyridyl)pyrazine with the labile  $[\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2]$  and have found the formation of two structural isomers  $[\text{Os}_3(\mu\text{-H})(\mu, \eta^3\text{-C}_{14}\text{H}_9\text{N}_4)(\text{CO})_9]$  due to the thermolysis of  $[\text{Os}_3(\text{C}_{14}\text{H}_{10}\text{N}_4)(\text{CO})_{10}]$  [8]. One isomer shows an orthometallated 2-pyridyl group and a N-coordinated 2-pyridyl, forming a seven-membered chelate ring with the pyrazine ring uncoordinated. The other isomer contains a 2-pyridyl-1,4-pyrazine fragment metallated in the pyrazine ring to form a five-membered chelate ring, as the second pyridine ring remains uncoordinated [8].

In this paper we describe the isolation and characterization of new dirhenium complexes showing  $\sigma, \sigma'\text{-N, N}'\text{-4e}$  donor groups, derived from the reaction of  $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2]$  with 2,3-bis(2-pyridyl)pyrazine.

## 2. Experimental

All reactions were carried out under dried and purified nitrogen. Solvents were purified by standard procedures and distilled prior to use [9].  $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2]$  was prepared by the method previously described [10]. 2,3-Bis(2-pyridyl)pyrazine was purchased from Aldrich and used as supplied. Reactions were monitored by FT-IR in the range 2200–1750  $\text{cm}^{-1}$  and the products were separated by TLC ( $\text{SiO}_2$ , Merck 60  $\text{HF}_{254}$ ). IR spectra were recorded on a Nicolet 5DXC FT-IR spectrometer, using 0.5 mm calcium fluoride cells.  $^1\text{H}$  NMR spectra were obtained on a Bruker 300 MHz spectrometer. Elemental analysis was performed on a Fisons EA-1108 instrument. Partial decomposition of the derivatives under sun light was initially observed, so special care was taken to exclude it from the samples.

*Ab initio* quantum chemical calculations were carried out for compound **2**. All geometry optimizations and energy calculations were performed with GAUSSIAN-98 program [11] at unrestricted DFT level of theory using the Becke's three-parameter hybrid functional with Lee, Yang and Parr correlation functionals (UB3LYP functional). The Stevens, Basch and Krauss relativistic compact effective potentials were employed for N, O, C and Re atoms. For Re atoms, the basis set and the effective potential include explicitly the  $5s^2, 5p^6, 5d^5$  and  $6s^2$  electrons.

### 2.1. Reaction of 2,3-bis(2-pyridyl)pyrazine with $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2]$ . Synthesis of complexes **1–4**

A solution of  $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2]$  (0.100 g, 0.145 mmol) and 2,3-bis(2-pyridyl)pyrazine (0.035 g, 0.149 mmol) in THF (50 ml) was refluxed for 5 h, during which time the color of the solution changed from pale yellow to blue. The solvent was removed under reduced pressure and the residue separated by TLC (dichloromethane:*n*-hexane, 2:3/vol:vol) to give four compounds: the blue structural isomers **1** and **2** (0.035 g, 28% and 0.008 g, 7%, respectively) formulated as  $[\text{Re}_2(\text{CO})_8(\text{C}_{14}\text{H}_{10}\text{N}_4)]$ ;  $[\text{Re}_2(\text{CO})_8(\text{C}_{14}\text{H}_{10}\text{N}_4)\text{Re}_2(\text{CO})_8]$  (**3**) (blue, 0.013 g, 6%) and  $[\text{Re}_2(\text{CO})_6(\text{C}_{14}\text{H}_{10}\text{N}_4)_2]$  (**4**) (yellow, 0.008 g, 5%). Complexes **1** and **3** were obtained as blue crystals after recrystallization from dichloromethane:cyclohexane (1:3 by volume). Carrying out the same reaction in refluxing dichloromethane for 2 h only gave **1**, **2** and **3** (40%, 16%, and 10%, respectively). Anal. Found for **1**: C, 31.87; H, 1.16; N, 6.84%. Anal. Found for **2**: C, 31.71; H, 1.26; N, 6.62%. Calc. for  $\text{C}_{22}\text{H}_{10}\text{N}_4\text{O}_8\text{Re}_2$ : C, 31.81; H, 1.20; N, 6.75%. Anal. Found for **3**: C, 25.31; H, 0.68; N, 3.96%.

Table 1

Crystal data, data collection and refinement parameters for  $[\text{Re}_2(\text{CO})_8(\text{C}_{14}\text{H}_{10}\text{N}_4)]$  (**1**) and  $[\text{Re}_2(\text{CO})_8(\text{C}_{14}\text{H}_{10}\text{N}_4)\text{Re}_2(\text{CO})_8] \cdot \text{CH}_2\text{Cl}_2$  (**3**)

	<b>1</b>	<b>3</b>
Formula	$\text{C}_{22}\text{H}_{10}\text{N}_4\text{O}_8\text{Re}_2$	$\text{C}_{31}\text{H}_{12}\text{Cl}_2\text{N}_4\text{O}_{16}\text{Re}_4$
M	839.74	1512.15
Crystal size ( $\text{mm}^3$ )	$0.36 \times 0.24 \times 0.20$	$0.25 \times 0.12 \times 0.10$
Colour	Blue prism	Violet prism
Temperature (K)	$293 \pm 2$	$293 \pm 2$
Crystal system	Triclinic	Monoclinic
Space group	$P(\bar{1})$	$P2_1/n^-$
<i>Unit cell dimensions</i>		
<i>a</i> (Å)	8.2040(16)	9.994(2)
<i>b</i> (Å)	10.474(2)	22.468(5)
<i>c</i> (Å)	14.506(3)	17.525(4)
$\alpha$ (°)	99.43(3)	90
$\beta$ (°)	102.39(3)	102.96(3)
$\gamma$ (°)	105.68(3)	90
<i>V</i> (Å <sup>3</sup> )	1138.9(4)	3835.2(13)
<i>Z</i>	2	4
<i>D<sub>c</sub></i> ( $\text{g cm}^{-3}$ )	2.422	2.619
<i>F</i> (000)	768	2752
$2\theta$ Range (°)	4.16–50.08	3.62–50.02
$\mu$ ( $\text{mm}^{-1}$ )	10.676	12.799
Reflections measured	4252	7153
Independent reflections ( $R_{\text{int}}$ )	4011 (0.0558)	6741 (0.0646)
Data/restraints/parameters	4011/0/325	6741/6/507
GOF on $F^2$	1.070	1.019
Final <i>R</i> index [ $F^2 > 2\sigma$ ]	$R_1 = 0.0696,$ $wR_2 = 0.2218$	$R_1 = 0.0615,$ $wR_2 = 0.1147$
<i>R</i> index (all data)	$R_1 = 0.0808,$ $wR_2 = 0.2039$	$R_1 = 0.1423,$ $wR_2 = 0.0914$
Index ranges	$h -9/9, k 0/12,$ $l -17/17$	$h 0/11, k 0/26,$ $l -20/20$
Maximum peak/hole ( $\text{e} \text{ \AA}^{-3}$ )	3.084 and $-5.941$	1.528 and $-1.262$

Calc. for  $C_{30}H_{10}N_4O_{18}Re_4$ : C, 25.25; H, 0.70; N, 3.93%.  
Anal. Found for **4**: C, 40.51; H, 1.93; N, 11.06%. Calc.  
for  $C_{34}H_{20}N_8O_6Re_2$ : C, 40.48; H, 1.98; N, 11.11%.

### 2.2. Reaction of $[Re_2(CO)_8(C_{14}H_{10}N_4)]$ (**1**) with $[Re_2(CO)_8(CH_3CN)_2]$

A solution of compound **1** (0.035 g, 0.031 mmol) and  $[Re_2(CO)_8(CH_3CN)_2]$  (0.021 g, 0.031 mmol) in dichloromethane (50 ml) was refluxed for 1 h. The solvent was removed under reduced pressure and the residue separated by TLC eluting with dichloromethane:*n*-hexane (2:3 vol: vol) to give **2** and **3** (6% and 14%, respectively).

### 2.3. Thermal treatment of complex $[Re_2(CO)_8(C_{14}H_{10}N_4)]$ (**1**) in THF

A solution of compound **1** (0.035 g, 0.031 mmol) in THF was heated under reflux for 4 h. The solvent was removed under reduced pressure and TLC of the residue (eluant: dichloromethane:*n*-hexane, 7:3 vol:vol) gave  $[Re_2(CO)_{10}]$  and  $[Re_2(CO)_6(C_{14}H_{10}N_4)_2]$  (**4**) (10% and 4% respectively). When the reaction was carried out in the darkness, only a black residue was obtained, probably due to decomposition of **1**.

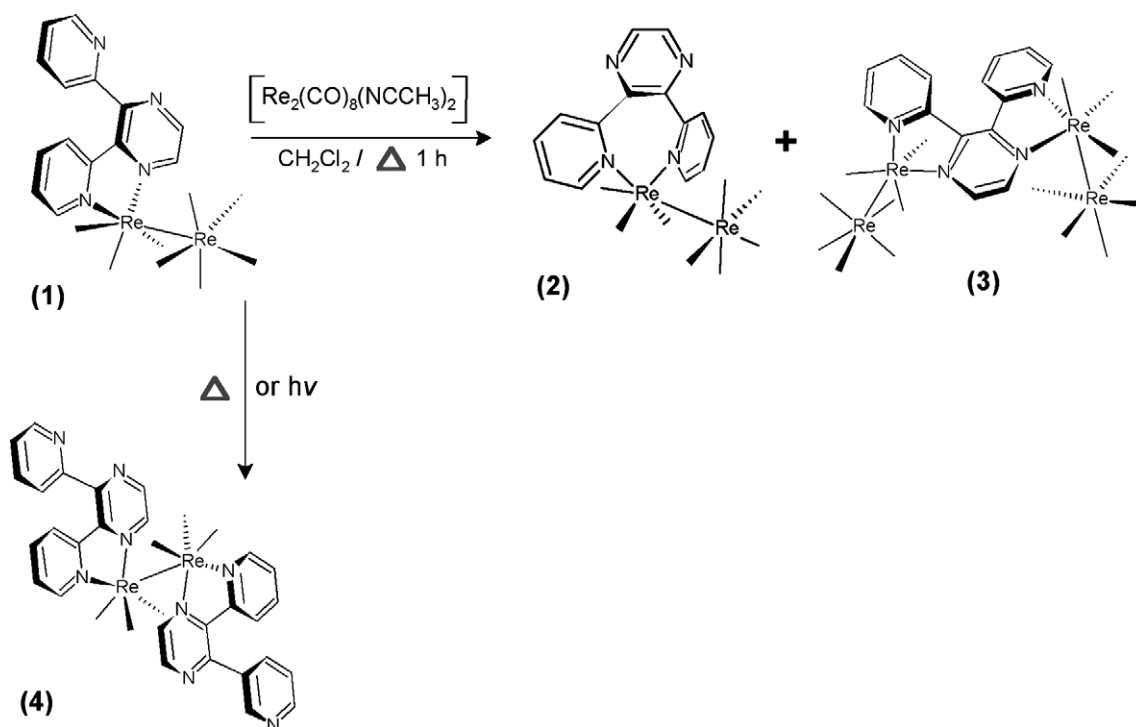
### 2.4. Irradiation of complex $[Re_2(CO)_8(C_{14}H_{10}N_4)]$ (**1**) in dichloromethane

A solution of compound **1** (0.035 g, 0.052 mmol) in dichloromethane was irradiated under visible light (380–

520 nm) for 4 h, during which time the color of the solution changed from blue to orange. The solvent was removed under reduced pressure and TLC of the residue (eluant: dichloromethane:*n*-hexane, 7:3 vol:vol) gave  $[Re_2(CO)_{10}]$  and  $[Re_2(CO)_6(C_{14}H_{10}N_4)_2]$  (**4**) (29% and 26%, respectively).

### 2.5. X-ray crystal structure determinations for compounds **1** and **3**

Data for compounds **1** and **3** were collected using a Rigaku AFC7S diffractometer, provided with a graphite monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Details of the crystal data and structure refinement are shown in Table 1. A semi-empirical absorption correction [12] was applied to both set of data. Crystal structures were solved by direct methods, and the final models were reached by Fourier techniques. The crystals structure of **3** shows a disordered  $CH_2Cl_2$  molecule, which was modeled in two different orientations. All non-H atoms were refined with anisotropic displacement parameters. The H-atoms were included in the last cycle in their calculated positions, except those of the disordered solvent molecule found in **3** that were not considered, and refined using a riding model. The isotropic displacement parameters for the H-atoms were considered according to their parent atoms. The final cycle of full-matrix least-squares was based on  $F^2$ . The data reduction were carried out using the TEXSAN program [13]. All structure solutions and refinements were made using the SHELXTL-PLUS package [14].



Scheme 1.

### 3. Results and discussion

Reaction of  $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2]$  with 2,3-bis(2-pyridyl)pyrazine in dichloromethane solution at refluxing temperature, affords the structural isomers  $[\text{Re}_2(\text{CO})_8(\text{C}_{14}\text{H}_{10}\text{N}_4)]$  (**1** and **2**) and the complex  $[\text{Re}_2(\text{CO})_8(\text{C}_{14}\text{H}_{10}\text{N}_4)\text{Re}_2(\text{CO})_8]$  (**3**). However, if the same reaction is carried out under refluxing THF for 5 h, in addition to complexes **1–3**, compound  $[\text{Re}_2(\text{CO})_6(\text{C}_{14}\text{H}_{10}\text{N}_4)_2]$  (**4**) is obtained. Taking into account the fact that the symmetrical 2,3-bis(2-pyridyl)pyrazine ligand could serve as a versatile bridging ligand and has the potential to act as a linking

group between cluster units, the reaction of **1** with an excess of  $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2]$  in dichloromethane at reflux temperature was carried out, giving compounds **2** and **3**. In a separate experiment, **1** was thermally and photochemically transformed into **4**. The general synthetic route to the rhenium derivatives is depicted in Scheme 1, and their  $^1\text{H}$  NMR and IR data is shown in Table 2.

#### 3.1. Complex $[\text{Re}_2(\text{CO})_8(\text{C}_{14}\text{H}_{10}\text{N}_4)]$ (**1**)

The IR spectrum of **1** in the carbonyl stretching region resembles that for  $[(\text{CO})_5\text{Re}-\text{Mn}(\text{CO})_3(i\text{-Pr-DAB})]$ , whose

Table 2  
IR and  $^1\text{H}$  NMR data for compounds **1–4**

Compound	$\nu(\text{CO})$ ( $\text{cm}^{-1}$ ) <sup>a</sup>	$^1\text{H}$ NMR ( $\delta$ ) <sup>b</sup>	$J_{\text{H-H}}$ (Hz)	
$[\text{Re}_2(\text{CO})_8(\text{C}_{14}\text{H}_{10}\text{N}_4)]$ ( <b>1</b> )	2073 s	9.34 (d, H <sub>a</sub> )	ab 3.3	gh 5.7
	2025 w	8.72 (d, H <sub>b</sub> )	cd 4.8	gi 1.6
	1992 vs	9.23 (ddd, H <sub>g</sub> )	ce 1.7	gj 0.9
	1977 s	7.77 (ddd, H <sub>i</sub> )	cf 1.1	hi 7.5
	1907 m	7.55 (ddd, H <sub>h</sub> )	de 7.7	hj 1.3
		7.29 (ddd, H <sub>j</sub> )	df 1.2	ij 8.5
		8.69 (ddd, H <sub>c</sub> )	ef 7.7	
		8.16 (m, H <sub>e</sub> )		
		7.90 (m, H <sub>f</sub> )		
		7.67 (ddd, H <sub>d</sub> )		
$[\text{Re}_2(\text{CO})_8(\text{C}_{14}\text{H}_{10}\text{N}_4)]$ ( <b>2</b> )	2073 s	9.32 (ddd, H <sub>a</sub> )	ab 5.8	bc 7.5
	1992 vs	9.03 (bs, H <sub>e</sub> )	ac 1.4	bd 1.3
	1976 s	8.93 (bd, H <sub>d</sub> )	ad 0.8	cd 8.5
	1905 m	8.06 (bt, H <sub>c</sub> )		
		7.76 (bt, H <sub>b</sub> )		
		9.33 (ddd, H <sub>a</sub> H <sub>a'</sub> ) <sup>c</sup>		
		9.12 (s, H <sub>e'</sub> )		
		9.08 (d, H <sub>d'</sub> )		
		9.03 (s, H <sub>c</sub> )		
		8.97 (d, H <sub>d</sub> )		
		8.12 (m, H <sub>c</sub> )		
		8.06 (m, H <sub>c'</sub> )		
		7.79 (m, H <sub>b</sub> )		
	7.68 (m, H <sub>b'</sub> )			
$[\text{Re}_2(\text{CO})_8(\text{C}_{14}\text{H}_{10}\text{N}_4)\text{Re}_2(\text{CO})_8]$ ( <b>3</b> )	2082 m	9.09 (d, H <sub>a</sub> )	ab 4.2	gh 5.6
	2072 m	8.91 (d, H <sub>b</sub> )	cd 5.7	gi 1.5
	1999 vs	9.35 (m, H <sub>c</sub> , H <sub>g</sub> )	ce 1.5	hi 7.2
	1989 vs	7.69 (ddd, H <sub>d</sub> )	de 7.5	hj 1.1
	1905 m	8.02 (ddd, H <sub>e</sub> )	df 1.2	ij 8.2
		8.82 (bd, H <sub>f</sub> )	ef 8.6	
		7.75 (ddd, H <sub>h</sub> )		
		8.06 (ddd, H <sub>i</sub> )		
		9.05 (ddd, H <sub>j</sub> )		
$[\text{Re}_2(\text{CO})_6(\text{C}_{14}\text{H}_{10}\text{N}_4)_2]$ ( <b>4</b> )	2026 vs	9.02 (d, H <sub>a</sub> )	ab 3.0	gh 4.9
	1926 s	8.67 (d, H <sub>b</sub> )	cd 5.3	gi 1.7
	1905 s	9.04 (ddd, H <sub>c</sub> )	ce 1.8	gj 1.0
		7.45 (ddd, H <sub>d</sub> )	cf 0.7	hi 6.0
		7.64 (ddd, H <sub>e</sub> )	de 7.0	hj 1.0
		7.12 (ddd, H <sub>f</sub> )	df 1.5	ij 7.7
		8.67 (ddd, H <sub>g</sub> )	ef 8.3	
		7.54 (ddd, H <sub>h</sub> )		
		8:00 (m, H <sub>i</sub> )		
	7.90 (m, H <sub>j</sub> )			

<sup>a</sup>  $\text{CH}_2\text{Cl}_2$ .

<sup>b</sup>  $\text{CDCl}_3$ .

<sup>c</sup>  $(\text{CD}_3)_2\text{CO}$ , 248 K.

structure was determined by X-ray diffraction analysis [15]. The  $^1\text{H}$  NMR spectrum exhibits two doublets ( $\delta = 9.34$  and  $8.72$ ) assigned to pyrazinic protons, and eight different signals in the aromatic region associated to two different pyridine rings. This suggests that the structure of **1** involves a 4e-donating  $\sigma, \sigma'$ - $N, N'$ -bonded 2,3-bis(2-pyridyl)pyrazine ligand. By analogy to the known structure of  $[(\text{CO})_5\text{Re}-\text{Mn}(\text{CO})_3(i\text{-Pr-DAB})]$  [15], **1** may contain a coordinated 2-pyridyl-1,4-pyrazine fragment forming a five-membered chelate ring. The X-ray single-crystal study of **1** (Fig. 1, selected bond lengths and angles are in Table 3) confirmed that the organic ligand is coordinated in a similar way to those observed in the crystal structures of  $[\text{Os}_3(\text{C}_{14}\text{H}_{10}\text{N}_4)(\text{CO})_{10}]$  [8] and  $[\text{Re}(\text{CO})_3\text{Cl}(\text{C}_{14}\text{H}_{10}\text{N}_4)]$  [16]. Therefore, one nitrogen atom of a pyridine ring is axially coordinated [ $\text{Re1}-\text{N3} = 2.174(12)$  Å] and an equatorial site is occupied by a pyrazine nitrogen atom [ $\text{Re1}-\text{N1} = 2.159(12)$  Å]. The second pyridine moiety remains uncoordinated. The bidentate ligand in **1** adopts a conformation statistically equal to that observed for the chloride rhenium complex  $[\text{Re}(\text{CO})_3\text{Cl}(\text{C}_{14}\text{H}_{10}\text{N}_4)]$  [16], even though in this compound the Cl ligand is considerable less voluminous than the  $\text{Re}(\text{CO})_5$  fragment in **1**. For the complex  $[\text{Re}(\text{CO})_3\text{Cl}(\text{C}_{14}\text{H}_{10}\text{N}_4)]$  the dihedral angles between the pyrazine entity and the coordinated and non-coordinated pyridine rings are  $15.3(4)^\circ$  and  $45.8(3)^\circ$ , respectively; for **1**, the corresponding values are  $17.7(8)^\circ$  and  $42.4(7)^\circ$ . As for  $[\text{Re}(\text{CO})_3\text{Cl}(\text{C}_{14}\text{H}_{10}\text{N}_4)]$  [16], the pyrazine ring in **1** is also slightly twisted (rms of the mean plane:  $0.039$  Å) in comparison to the uncoordinated 2,3-bis(2-pyridyl)pyrazine (rms of the mean plane:  $0.007$  Å) [17].

### 3.2. Complex $[\text{Re}_2(\text{CO})_8(\text{C}_{14}\text{H}_{10}\text{N}_4)]$ (**2**)

Spectroscopic data (Table 2) suggest for **2** the presence of a metallocyclic system showing a seven-membered che-

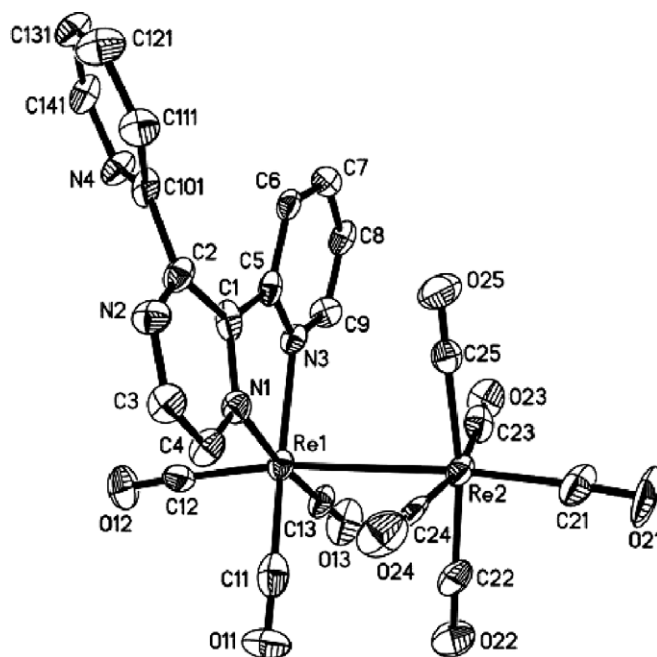


Fig. 1. ORTEP view (30% probability. H atoms omitted for clarity) of the molecular structure of **1** in the crystal.

late ring similar to the coordination found for complexes  $[\text{Os}_3(\text{C}_{14}\text{H}_{10}\text{N}_4)(\text{CO})_9]$  [8],  $\{[\text{Pd}(\text{dpq})_2](\text{PF}_6)_2\}$ ,  $[\text{PdCl}_2(\text{dpq})]$  and  $[\text{ReCl}(\text{CO})_3(\text{tppz})] \cdot 2\text{H}_2\text{O}$  [dpq = 2,3-bis(dipyridyl)quinoxaline; tppz = 2,3,5,6-tetra(2-pyridyl)pyrazine] [18]. The variable temperature  $^1\text{H}$  NMR spectrum of **2** in

Table 3  
Selected bond lengths (Å) and angles ( $^\circ$ ) for compound **1**

Re1–Re2	3.084(1)	N1–Re1–Re2	94.0(3)
Re1–N3	2.17(1)	N3–Re1–Re2	88.7(3)
Re1–N1	2.16(1)		

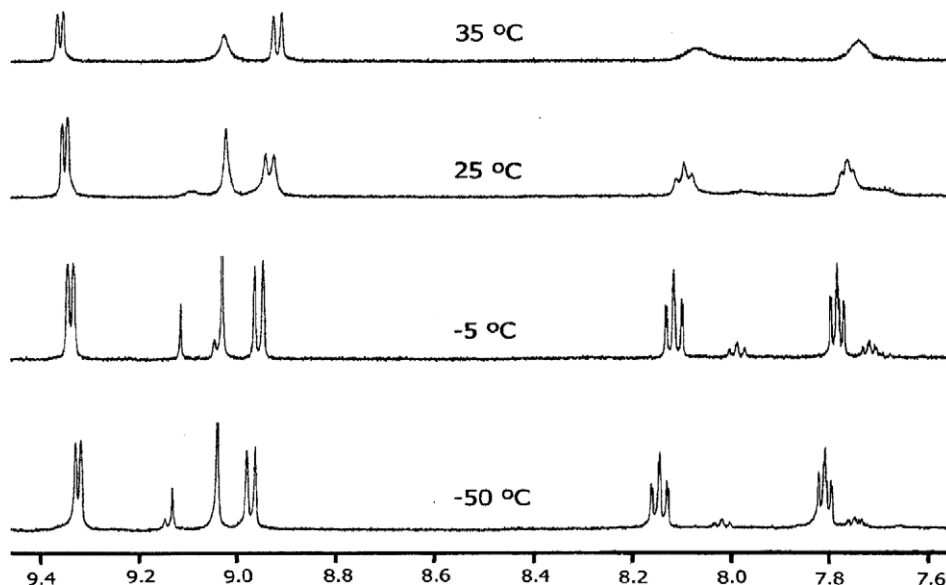


Fig. 2. Variable temperature  $^1\text{H}$  NMR spectra of **2** in  $\text{CD}_3\text{COCD}_3$ .

$\text{CD}_3\text{COCD}_3$  (Fig. 2) shows broad resonances at 35 °C, but at –50 °C sharp resonances are assigned to two highly symmetric isomeric compounds, **2a** and **2b**, where  $[\mathbf{2a}]/[\mathbf{2b}] = 7$ . The major isomer **2a** shows five  $^1\text{H}$  NMR resonances (Table 2) assigned to pyrazinic protons ( $\delta$  9.03) and four C–H signals for the pyridinic protons ( $\delta$  9.33, 8.97, 8.12 and 7.79). Likewise, the minor isomer **2b** shows a set of resonances that can be assigned to pyrazinic protons ( $\delta$  9.12) and four C–H signals for the pyridinic protons ( $\delta$  9.33, 9.08, 8.06 and 7.68). Above 35 °C coalescence is observed (except for the *ortho* protons  $\text{H}_a$  in the pyridine rings) to give four signals. The dynamic behavior between **2a** and

**2b** could be derived from the different conformations adopted by twisting the seven-membered metallocycle (Fig. 2), so the  $\text{Re}(\text{CO})_5$  moiety can be located in an equatorial position relative to the metallocycle mean plane (**2a**), or in an axial position (**2b**). The equatorial orientation of the  $\text{Re}(\text{CO})_5$  fragment leads to the diminishing of the steric repulsion between the carbonyl groups of the  $\text{Re}(\text{CO})_5$  entity and the pyrazine ring, so this conformation is assigned to the major isomer **2a**.

In order to evaluate this hypothesis, *ab initio* quantum chemical calculations were performed at DFT level [11], giving that at 298 K isomer **2a** is thermodynamically more

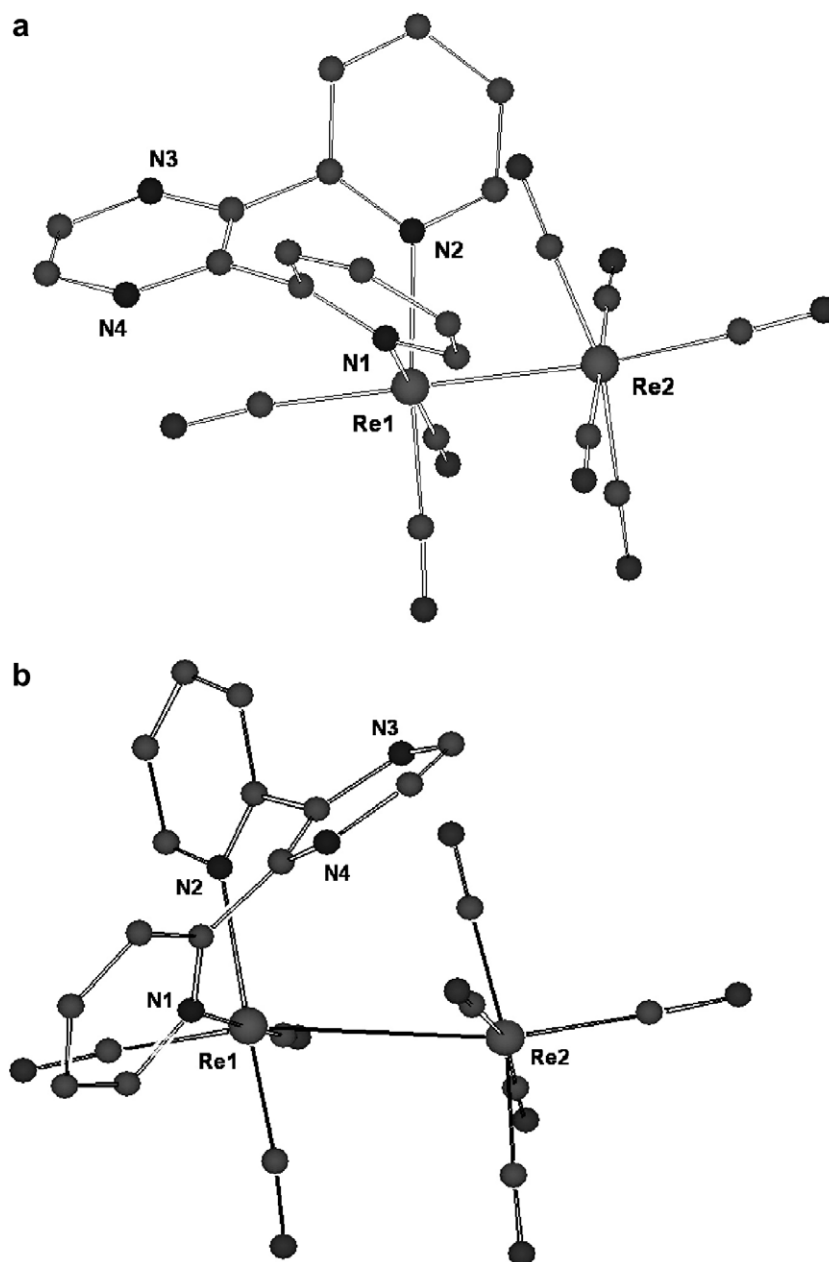


Fig. 3. Structure obtained by *ab initio* quantum chemical calculation: (a) isomer **2a** and (b) isomer **2b**.

stable than isomer **2b** by  $\Delta G = -7.45$  kcal/mol. This theoretical result is in agreement with the  $^1\text{H}$  NMR evidence that in solution the relationship  $[\mathbf{2a}]/[\mathbf{2b}] = 7$ .

### 3.3. Complex $[\text{Re}_2(\text{CO})_8(\text{C}_{14}\text{H}_{10}\text{N}_4)\text{Re}_2(\text{CO})_8]$ (**3**)

The  $\nu(\text{CO})$  absorption spectrum of **3** revealed a pattern similar to that observed for **1** and for  $[(\text{CO})_5\text{ReMn}(\text{CO})_3(i\text{-Pr-DAB})]$  [15]. The  $^1\text{H}$  NMR spectrum of **3** exhibits a group of signals corresponding to eight pyridinic protons, and two doublets for the pyrazinic protons. It is worth mentioning that **3** can also be obtained from the reaction of **1** and  $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2]$  under refluxing dichloromethane. Therefore, the formation of **3** occurs as a consequence of the linkage of a  $\text{Re}_2(\text{CO})_8$  unit to compound **1**, so the organic ligand will be  $\sigma, \sigma'$ - $N, N'$ -coordinated in a chelate form to two  $\text{Re}(\text{CO})_3$  units through the nitrogen atoms of pyrazine and pyridine rings. This coordination mode is also found for the dinuclear complex  $[\text{Re}(\text{CO})_3\text{Cl}(\text{C}_{14}\text{H}_{10}\text{N}_4)\text{Re}(\text{CO})_3\text{Cl}]$  [16] (see Fig. 3).

A single-crystal X-ray study of **3** confirms these observations. Its molecular structure is shown in Fig. 4 and selected bond lengths and angles are in Table 4. The  $(\text{CO})_5\text{Re}-\text{Re}(\text{CO})_3$  fragments [ $\text{Re1}-\text{Re2} = 3.0806(14)$  Å and  $\text{Re3}-\text{Re4} = 3.0676(14)$  Å] are linked by a doubly-chelating bipyridylpyrazine coordinated through all nitrogen atoms [ $\text{Re1}-\text{N1} = 2.125(13)$  Å,  $\text{Re1}-\text{N3} = 2.129(13)$  Å;  $\text{Re3}-\text{N2} = 2.148(14)$  Å,  $\text{Re3}-\text{N4} = 2.179(14)$  Å]. Therefore, two five-membered chelate rings [ $\text{Re1}-\text{N1}-\text{C1}-\text{C5}-\text{N3}$  and  $\text{Re3}-\text{N2}-\text{C2}-\text{C101}-\text{N4}$ ] are formed. The bridging coordination to the metal centers requires the organic ligand to adopt a twisted conformation, in which the dihe-

Table 4  
Selected bond lengths (Å) and angles ( $^\circ$ ) for compound **3**

Re1–Re2	3.081(1)	N1–Re1–Re2	94.2(4)
Re3–Re4	3.068(1)	N3–Re1–Re2	94.2(4)
Re1–N3	2.13(1)	N2–Re3–Re4	93.4(4)
Re1–N1	2.13(1)	N4–Re3–Re4	95.6(4)
Re3–N2	2.15(1)	C4–N1–Re1	124.8(1)
Re3–N4	2.18(1)	C3–N2–Re3	123.7(1)

dral angles between the pyrazine ring and those of the pyridines  $\text{N3}-\text{C5}-\text{C6}-\text{C7}-\text{C8}-\text{C9}$  and  $\text{N4}-\text{C101}-\text{C111}-\text{C121}-\text{C131}-\text{C141}$  are  $24.2(6)^\circ$  and  $22.2(6)^\circ$ , respectively. Both dihedral angles are smaller than those observed in the crystal structure of the complex  $[\text{Re}(\text{CO})_3\text{Cl}(\text{C}_{14}\text{H}_{10}\text{N}_4)\text{Re}(\text{CO})_3\text{Cl}]$  [ $29.7(4)^\circ$  and  $31.6(3)^\circ$ ] [16], possibly due to the presence of the voluminous  $\text{Re}(\text{CO})_5$  units in **3**. In addition, the pyrazine ring in **3** suffers a kind of buckling that leads to deviation from planarity. The average deviation ( $0.056$  Å) from the mean plane of this ring is larger than the value found for **1** ( $0.039$  Å). Maximum deviations are observed for C1 and C2 atoms, which lie below and above the pyrazine mean plane, [ $-0.111(12)$  Å and  $0.081(12)$  Å, respectively].

A possible route for the formation of complexes **1–3** is given in Scheme 2. It is proposed that  $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2]$  dissociates into the coordinatively unsaturated species  $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})]$ , **I** [19]. 2,3-Bis(2-pyridyl)pyrazine (dpp) coordinates *via* a  $\sigma$ -N bond of one pyridyl moiety as shown for intermediate **II**. Complex **1** could be formed from **II** by a concerted process involving CO shift and elimination of  $\text{CH}_3\text{CN}$  (L) from the second rhenium atom [20], followed by chelation through a pyrazine N-atom. For the formation of **2**, the ligand in **II** rotates

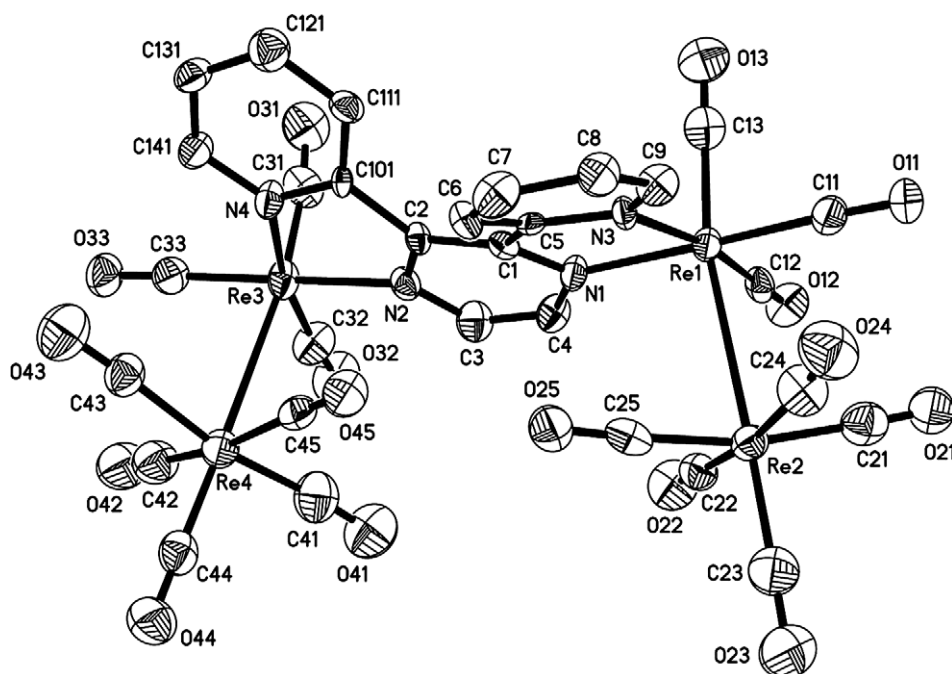
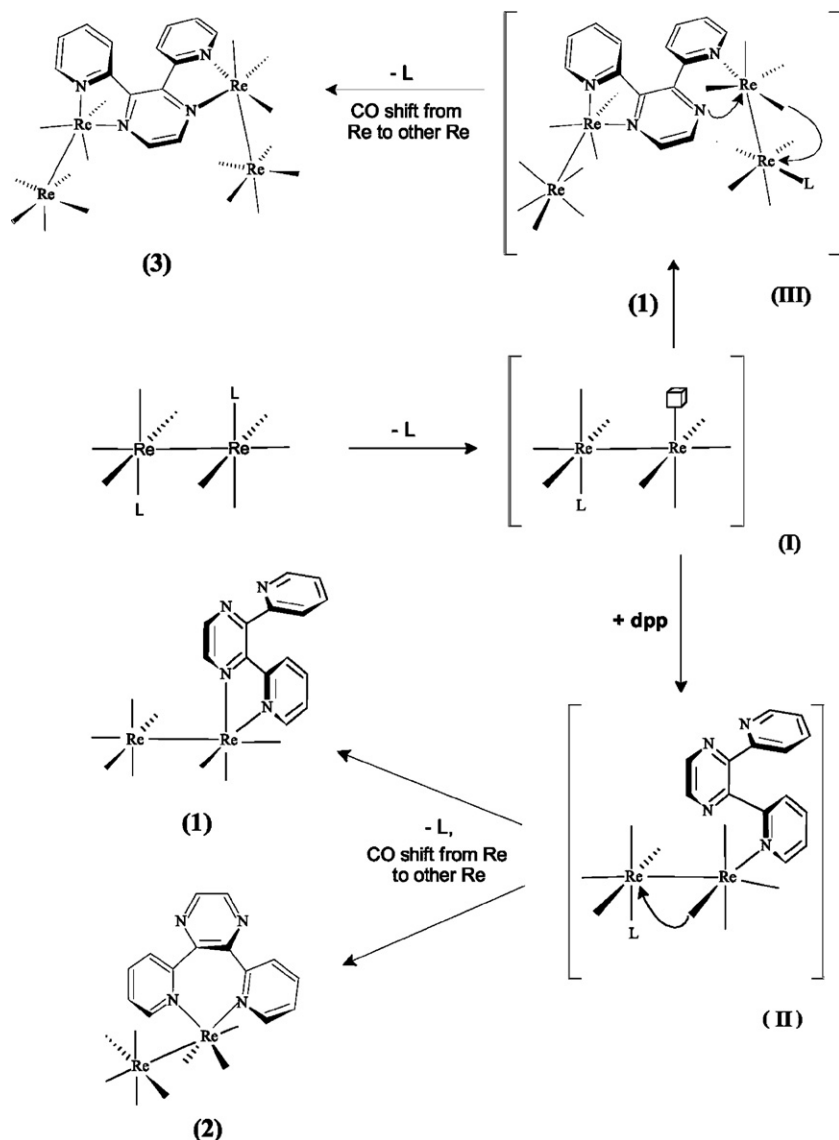


Fig. 4. ORTEP view (30% probability, H atoms omitted for clarity) of the molecular structure of **3** in the crystal.



around the single C–C pyrazine-pyridine bonds, with subsequent pyridine N-coordination. The reaction of complex **1** with the coordinatively unsaturated species **I** gives **III**, which could be converted to **3** by a concerted process similar to that involved in the formation of **1** from **II**.

### 3.4. Complex $[Re_2(CO)_6(C_{14}H_{10}N_4)_2]$ (**4**)

Unlike **1**, the IR carbonyl spectrum of **4** in  $CH_2Cl_2$  shows a very simple band pattern similar to the one observed for  $[Re_2(\mu:\eta^6-C_{24}H_{18}N_4)(CO)_6]$  [21],  $[Re_2(CO)_6(OX)_2]$  ( $X = 8$ -quinoline) [22] and  $[Re(CO)_3-(C_{12}H_8N_2)Cl]_2$  [23], as pseudo-octahedral rhenium complexes with only facial CO ligands usually display three bands in the carbonyl stretching region [24]. The  $^1H$  NMR spectrum of **4** in the aromatic region contains eight different signals associated to two non-equivalent pyridinic systems and two different signals for the four pyrazinic

protons, so the ligand symmetry is lost. The small differences between the chemical shifts observed for **4** compared to **1**, suggest that two organic fragments are coordinated in a  $\sigma, \sigma'$ - $N-N'$ -chelating manner to each  $Re(CO)_3$  moiety.

The structure proposed for compound **4** in Scheme 1 is based on the results obtained when a solution of **1** is thermally treated under visible light. In this case  $[Re_2(CO)_{10}]$  is obtained as a by-product, probably due to a homolytic Re–Re bond cleavage in **1**, where  $[Re(CO)_5]$  radicals so obtained combine to give  $[Re_2(CO)_{10}]$ , easily identified by its  $\nu(CO)$  spectrum [25]. Concomitantly  $[Re(CO)_3-(C_{14}H_{10}N_4)]$  radicals could be formed and self-combined to yield the complex  $[Re_2(CO)_6(C_{14}H_{10}N_4)_2]$  (**4**), in which two equivalent fac- $Re(CO)_3$  subgroups are obtained. The same behavior is observed for the homolytic metal–metal bond cleavage of the complexes  $[(CO)_5MnMn(CO)_3Phen]$ ,  $[(CO)_5ReRe(CO)_3Phen]$  and  $[(CO)_5ReRe(CO)_3Biquin]$  (Phen = 1,10-phenanthroline and Biquin = 2,2'-biquino-



line) when irradiated under visible light to form the corresponding species  $[M_2(CO)_6(\alpha\text{-diimine}_2)]$  [6].

#### 4. Supplementary material

CCDC 285341 and 285342 contain the supplementary crystallographic data for **1** and **3**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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