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Synthesis and X-ray structures of some metal carbonyl complexes containing dipyridylformamidine ligands

Hsiu-Chi Liang [a], Ying-Yann Wu [a], Fang-Chu Chang [a], Pang-Yen Yang [a], Jhy-Der Chen [a,*], Ju-Chun Wang [b]

[a] Department of Chemistry, Chung-Yuan Christian University, Chung-Li, Taiwan, ROC
[b] Department of Chemistry, Soochow University, Taipei, Taiwan, ROC

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Abstract

Five metal carbonyl complexes of *N*,*N′*-di(2-pyridyl)formamidine (HDpyF) and *N*,*N′*-di(6-methyl-2-pyridyl)formamidine (HDMepyF) are reported. Complexes of the type $ReBr(CO)_3L$ (L = HDpyF, **1**; L = HDMepyF, **2**) were prepared by the reactions of $ReBr(CO)_5$ with HDpyF and HDMepyF in THF, respectively, while the complexes $M(CO)_4(L)$ (M = Mo, L = HDpyF, **3**; M = Mo, L = HDMepyF, **4**; M = W, L = HDMepyF, **5**) were prepared by the reactions of HDpyF or HDMepyF with corresponding Group 6 metal hexacarbonyls. The neutral dipyridylformamidine ligands in **1** and **2** adopt the *s-cis-syn-s-cis* and *s-trans-anti-s-trans* conformations, respectively, while those in complexes **3**–**5** adopt the *s-trans-anti-s-cis* conformation.

Keywords: Metal carbonyl complexes; Dipyridylformamidine; Conformation; X-ray structure

1. Introduction

In a previous paper, we reported the synthesis and X-ray structures of some Group 6 metal carbonyl complexes of the types $M(CO)_4(HDpyF)$(M = Cr and W; HDpyF = *N*,*N′*-di(2-pyridyl)formamidine) and $Mo(CO)_3(HDpyF)(CH_3CN)$ [1]. The neutral HDpyF ligands in the Cr and W complexes chelate the metal centers through the first and the second nitrogen atoms to form four-membered rings and the third and the fourth nitrogen atoms are not coordinated, while in the Mo complex, the HDpyF ligand chelates the metal center through the first and the third nitrogen atoms to form a six-membered ring. All the three complexes show supramolecular structures in the solid state by intermolecular hydrogen bonding and aromatic π–π interactions.

As an extension of this chemistry, we have synthesized metal carbonyl complexes containing *N*,*N′*-di(6-methyl-2-pyridyl)formamidine (HDMepyF) ligand which has methyl groups *ortho* to the pyridine nitrogen atoms. The conformations adopted by the neutral HDpyF and HDMepyF ligands in these metal carbonyl complexes are in marked contrast to those found for anionic diarylformamidine bearing an *m*-alkoxy substituent, proposed by Ren and co-authors [2]. The syntheses structures, and ligand conformations of $ReBr(CO)_3L$ and $M(CO)_4(L)$ (M = Mo, W; L = HDpyF; HDMepyF) form the subject of this report.

2. Experimental

2.1. General procedures

All manipulations were carried out under dry, oxygen-free nitrogen by using Schlenk techniques, unless otherwise noted. Solvents were dried and deoxygenated by refluxing over the appropriate reagents before use. Diethyl ether, hexanes and THF were purified by distillation from sodium–benzophenone. The IR spectra were recorded on a JASCO FTIR-460 plus spectrometer. The ^{1}H-NMR spectra were measured from a Bruker Avance 300 MHz spectrometer.

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[*] Corresponding author. Fax: +886-3-456-3160.
E-mail address: jdchen@cycu.edu.tw (J.-D. Chen).

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2.2. Materials

The complexes $ReBr(CO)_5$ [3], *N*,*N′*-di(2-pyridyl)formamidine (HDpyF) [4], and *N*,*N′*-di(6-methyl-2-pyridyl)formamidine (HDMepyF) [5] were prepared according to known procedures. $Mo(CO)_6$ and $W(CO)_6$ were purchased from Strem Chem. Co.

2.3. Preparations

2.3.1. $ReBr(CO)_3(HDpyF)$

In a 50 ml flask, $ReBr(CO)_5$ (0.10 g, 0.25 mmol) and HDpyF (0.10 g, 0.52 mmol) were suspended in 15 ml of THF. The mixture was refluxed for 3 days. Upon heating, the color of mixture changed from light yellow to dark orange. The yellow solid was collected by filtration and washed repeatedly with ether and then dried under vacuum. Yield: 0.068 g (50%). Anal. Found: C, 30.48; H, 1.80; N, 9.70. Calc. for $C_{14}H_{10}N_4O_3BrRe$ (MW = 548.37): C, 30.66; H, 1.84; N, 10.22%. ^{1}H-NMR (300 MHz, DMSO-d_6): 7.28 (t, 1H, pyridyl), 7.36 (t, 1H, pyridyl), 7.43 (d, 1H, pyridyl), 7.61 (d, 1H, pyridyl), 7.96 (t, 1H, pyridyl), 8.10 (t, 1H, pyridyl), 8.18 (d, 1H, C*H*), 8.48 (d, 1H, pyridyl), 8.72 (d, 1H, pyridyl), 11.79 (d, 1H, N*H*). IR (cm^{-1}, KBr disk): ν 3378br (NH), 2024s (CO), 1913s (CO), 1897s (CO).

2.3.2. $ReBr(CO)_3(HDMepyF)$

In a 50 ml flask, $ReBr(CO)_5$ (0.10 g, 0.25 mmol) and HDMepyF (0.10 g, 0.45 mmol) were suspended in 15 ml of THF. The other procedures for **2** were similar to those for **1**. Yield: 0.079 g (52%). Anal. Found: C, 33.53; H, 2.59; N, 9.70. Calc. for $C_{16}H_{14}N_4O_3BrRe$ (MW = 576.42): C, 33.34; H, 2.45; N, 9.72%; ^{1}H-NMR (300 MHz, DMSO-d_6): 2.41 (s, 3H, C*H*$_3$), 2.46 (overlapped s, 3H, C*H*$_3$), 7.10 (d, 1H, pyridyl), 7.24 (t, 2H, pyridyl), 7.53 (d, 1H, pyridyl), 7.76 (t, 1H, pyridyl), 7.92 (t, 1H, pyridyl), 9.59 (d, 1H, C*H*), 10.69 (d, 1H, N*H*). IR (cm^{-1}, KBr disk): ν 3364br (NH), 2025s (CO), 1933s (CO), 1910s (CO).

2.3.3. $Mo(CO)_4(HDpyF)$

$Mo(CO)_6$ (0.26 g, 1.00 mmol) and HDpyF (0.20 g, 1.00 mmol) were placed in a flask containing 10 ml of THF. The mixture was refluxed for 3 h to yield yellow solution. The solvent was reduced and hexane added to induce precipitation. The solid was filtered, washed with ether and then dried under reduced pressure. Yield: 0.18 g (43%). Anal. Found: C, 43.87; H, 2.78; N, 14.18. Calc. for $C_{15}H_{10}N_4O_4Mo$ (MW = 406.21): C, 44.35; H, 2.48; N, 13.79%. ^{1}H-NMR (300 MHz, CD_2Cl_2): 8.82 (s, 1H, C*H*), 7.01 (m, 1H, pyridyl), 7.78 (m, 1H, pyridyl), 8.28 (m, 1H, pyridyl), 9.21 (s, 1H, N*H*). IR (cm^{-1}, KBr disk): ν 3337s (NH), 2013s (CO), 1906s (CO), 1868s (CO), 1809s (CO).

2.3.4. $Mo(CO)_4(HDMepyF)$

$Mo(CO)_6$ (0.26 g, 1.00 mmol) and HDMepyF (0.23 g, 1.00 mmol) were placed in a flask containing 10 ml of THF. The mixture was refluxed for 3 h to yield yellow solution. The solvent was reduced and hexane added to induce precipitation. The solid was filtered, washed with ether and then dried under reduced pressure. Yield: 0.21 g (48%). Anal. Found: C, 46.84; H, 3.46; N, 13.21. Calc. for $C_{17}H_{14}N_4O_4Mo$ (MW = 434.26): C, 47.02; H, 3.25; N, 12.90%. ^{1}H-NMR (300 MHz, CD_2Cl_2): 2.40 (s, 3H, C*H*$_3$), 6.87 (m, 1H, pyridyl), 7.05 (m, 1H, pyridyl), 7.65 (m, 1H, pyridyl) 9.78 (s, 1H, C*H*), 10.85 (m, 1H, N*H*). IR (cm^{-1}, KBr disk): ν 3333s (NH), 2014s (CO), 1874s (CO), 1868s (CO), 1804s (CO).

2.3.5. $W(CO)_4(HDMepyF)$

$W(CO)_6$ (0.35 g, 1.00 mmol) and HDMepyF (0.28 g, 1.00 mmol) were placed in a flask containing 15 ml of toluene. The mixture was refluxed for 6 h to yield yellow solution. The solvent was reduced and hexane added to induce precipitation. The solid was filtered, washed with ether and then dried under reduced pressure. Yield: 0.30 g (57%). Anal. Found: C, 38.94; H, 2.51; N, 11.01. Calc. for $C_{17}H_{14}N_4O_4W$ (MW = 522.17): C, 39.10; H, 2.70; N, 10.73%. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.45 (s, 3H, C*H*$_3$), 2.46 (s, 3H, C*H*$_3$), 6.80 (d, 1H, pyridyl), 6.98 (d, 1H, pyridyl), 7.17 (d, 1H, pyridyl), 7.24 (d, 1H, pyridyl), 7.61 (t, 1H, pyridyl), 7.71 (t, 1H, pyridyl), 8.01 (d, 1H, C*H*), 9.65 (d, 1H, N*H*). IR (cm^{-1}, KBr disk): ν 3347s (NH), 2003m (CO), 1892m (CO), 1873m (CO), 1830m (CO).

2.4. X-ray crystallography

The diffraction data of **1** was collected on a Bruker AXS P4 diffractometer, which was equipped with a graphite-monochromated Mo–K$_\alpha$ ($\lambda_\alpha = 0.71073$ Å) radiation. Data reduction was carried out by standard methods with use of well-established computational procedures [6]. The structure factors were obtained after Lorentz and polarization corrections. The positions of the heavier atoms, including the rhenium and bromide atoms, were located by the direct method. The remaining atoms were found in a series of alternating difference Fourier maps and least-squares refinements [7]. Since the uncoordinated pyridine ring are free to rotate about the C–N uncoordinated ring, C(11) and N(4) are possible positions for the nitrogen atom before the structure was determined. These two conformations were assumed and the structures were refined. The structure depicted in Fig. 1 is the best fit to the final refinement result. The conformation of the HDpyF ligand in Fig. 1 is also the one found directly from the electron density map, i.e. by identifying the position of the hydrogen atom. The final residuals were $R_1 = 0.0567$ and $wR_2 = 0.1373$, respectively, for **1**. The X-ray crystal-

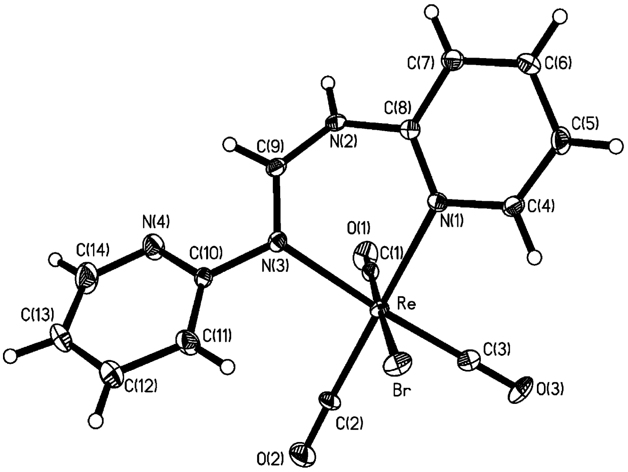

Fig. 1. An ORTEP diagram of **1**.

lographic procedures for the other complexes were similar to those for **1**. Basic information pertaining to crystal parameters and structure refinement is summarized in Table 1.

3. Results and discussion

3.1. Syntheses and spectroscopic studies

Complexes of the type $ReBr(CO)_3L$ (L = HDpyF, **1**; L = HDMepyF, **2**) were prepared by the reactions of $ReBr(CO)_5$ with HDpyF and HDMepyF in THF, respectively. The complexes $M(CO)_4(L)$ (M = Mo, L = HDpyF, **3**; M = Mo, L = HDMepyF, **4**; M = W, L = HDMepyF, **5**) were prepared by the reactions of HDpyF or HDMepyF with corresponding Group 6 metal hexacarbonyls. These complexes are stable as solids but slowly decompose in solution. The solid state IR spectra of complexes **1** and **2** exhibit three characteristic $\nu_{C\equiv O}$ in the range 2200–1850 cm^{-1}, indicating a facial configuration for the carbonyl groups. Four $\nu_{C\equiv O}$ vibrations were observed for complexes **3**–**5**, as expected for the octahedral complex with C_1 symmetry.

3.2. Structures of **1** and **2**

Crystals of **1** conform to the space group $P2_1/c$ with four molecules in a unit cell, while crystals of **2** conform to the space group $P\bar{1}$ with two molecules in a unit cell. Figs. 1 and 2 show the ORTEP diagrams for **1** and **2**, respectively. Selected bond distances and angles for **1** and **2** are listed in Table 2. It is seen from Figs. 1 and 2 that three carbonyl groups, one bromide ligand and one HDpyF (or HDMepyF) ligand coordinate to the Re atoms in complexes **1** and **2**. The three carbonyl groups in each complex are located in a *fac* position. The HDpyF ligand in **1** chelates to the Re center through the first and the third nitrogen atoms to form a six-membered ring, leaving the second and the fourth nitrogen atoms uncoordinated. The N(1)–Re–N(3)

Table 1
Crystal data for complexes **1**–**5**

Complex	**1**	**2**	**3**	**4**	**5**
Formula	$C_{14}H_{10}BrN_4O_3Re$	$C_{16}H_{14}BrN_4O_3Re$	$C_{15}H_{10}N_4O_4Mo$	$C_{17}H_{14}N_4O_4Mo$	$C_{17}H_{14}N_4O_4W$
Formula weight	548.37	576.42	406.21	434.26	522.17
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	10.761(1)	7.044(2)	7.392(2)	7.226(1)	7.184(1)
b (Å)	9.065(2)	10.170(3)	9.869(2)	10.201(1)	10.132(1)
c (Å)	16.189(2)	13.302(5)	12.059(3)	13.314(1)	13.276(2)
α (°)	90	83.07(2)	80.514(3)	79.997(1)	79.877(9)
β (°)	91.523(8)	82.54(3)	79.805(3)	80.293(1)	80.251(11)
γ (°)	90	77.35(2)	69.297(3)	72.122(1)	72.116(13)
V (Å^3)	1578.7(4)	917.8(5)	805.0(3)	912.9(1)	898.5(2)
Z	4	2	2	2	2
μ(Mo–K$_\alpha$) (mm^{-1})	10.247	8.819	0.842	0.748	6.458
Temperature (°C)	25	25	25	25	25
Independent reflections	2769[$R_{int} = 0.0628$]	3188[$R_{int} = 0.0237$]	2715[$R_{int} = 0.0522$]	3168[$R_{int} = 0.0250$]	3147[$R_{int} = 0.0298$]
Data/restraints/parameters	2769/0/209	3188/0/226	2715/0/258	3168/0/291	3147/0/247
Quality-of-fit indicator [a]	1.108	1.037	1.190	1.047	1.033
Final R indices [$I > 2\sigma(I)$] [b,c]	$R_1 = 0.0567$, $wR_2 = 0.1373$	$R_1 = 0.0426$, $wR_2 = 0.1130$	$R_1 = 0.0468$, $wR_2 = 0.0937$	$R_1 = 0.0256$, $wR_2 = 0.0692$	$R_1 = 0.0568$, $wR_2 = 0.1454$
R indices (all data)	$R_1 = 0.0588$, $wR_2 = 0.1399$	$R_1 = 0.0485$, $wR_2 = 0.1178$	$R_1 = 0.0573$, $wR_2 = 0.1009$	$R_1 = 0.0262$, $wR_2 = 0.0699$	$R_1 = 0.0627$, $wR_2 = 0.1500$

$w = 1/[\sigma^2(F_o^2)+(ap)^2+(bp)]$, $p = [\max(F_o^2 \text{ or } 0)+2(F_c^2)]/3$. $a = 0.1081$, $b = 2.5563$, **1**; $a = 0.0858$, $b = 1.7115$, **2**; $a = 0.0000$, $b = 2.2340$, **3**; $a = 0.3068$, $b = 0.511$, **4**; $a = 0.1280$, $b = 0.6850$, **5**.

[a] Quality-of-fit = $[\Sigma w(|F_o^2|-|F_c^2|)^2/N_{observed}-N_{parameters})]^{1/2}$.

[b] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$.

[c] $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

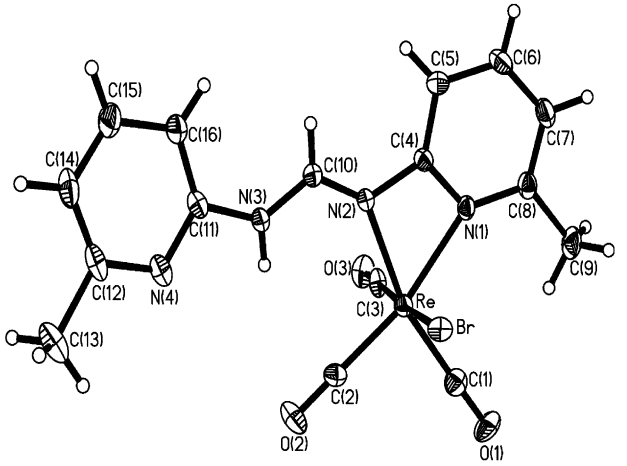

Fig. 2. An ORTEP diagram of **2**.

angle is 82.9(3)°, and N(1)–Re–Br and N(3)–Re–Br are 85.1(2) and 92.3(2)°, respectively. The HDMepyF ligand in **2** chelates to the Re center through the first and the second nitrogen atoms to form a four-membered ring. The N(2)–Re–N(1) angle is 59.6(2)°, and the N(1)–Re–Br and N(2)–Re–Br angles are 83.3(2) and 82.0(2)°, respectively. In both complexes, the three Re–C distances *trans* to the two nitrogen and bromide ligands are similar, indicating that the *trans* influence from the bromide ligand is similar to those from the nitrogen atoms. The bidentate HDpyF and HDMepyF ligands in each complex is not flat, but twisted around the C–N bonds, with a dihedral angle between the planes of the two pyridine rings of 40.1° for **1** and 20.0° for **2**, respectively.

Table 2
Selected bond distances (Å) and bond angles (°) for complexes **1** and **2**

1		**2**	
Bond distances			
Re–C(1)	1.925(10)	Re–C(1)	1.911(10)
Re–C(2)	1.906(9)	Re–C(2)	1.894(9)
Re–C(3)	1.918(11)	Re–C(3)	1.921(10)
Re–N(1)	2.189(7)	Re–N(1)	2.200(7)
Re–N(3)	2.201(8)	Re–N(2)	2.186(7)
Re–Br	2.625(1)	Re–Br	2.615(1)
Bond angles			
C(1)–Re–N(1)	92.5(3)	C(1)–Re–N(1)	106.1(3)
C(1)–Re–N(3)	87.5(3)	C(1)–Re–N(2)	165.3(3)
C(1)–Re–Br	177.5(2)	C(1)–Re–Br	93.9(3)
C(2)–Re–C(1)	91.4(4)	C(1)–Re–C(3)	90.1(4)
C(2)–Re–C(3)	87.1(4)	C(2)–Re–C(1)	89.6(4)
C(2)–Re–N(1)	175.9(3)	C(2)–Re–C(3)	89.9(4)
C(2)–Re–N(3)	96.3(4)	C(2)–Re–N(1)	163.8(3)
C(2)–Re–Br	91.0(3)	C(2)–Re–N(2)	104.5(3)
C(3)–Re–C(1)	90.2(3)	C(2)–Re–Br	91.5(3)
C(3)–Re–N(1)	93.9(4)	C(3)–Re–N(1)	94.2(3)
C(3)–Re–N(3)	176.0(3)	C(3)–Re–N(2)	93.7(4)
C(3)–Re–Br	89.8(3)	C(3)–Re–Br	175.7(3)
N(1)–Re–N(3)	82.9(3)	N(1)–Re–Br	83.3(2)
N(1)–Re–Br	85.1(2)	N(2)–Re–N(1)	59.6(2)
N(3)–Re–Br	92.3(2)	N(2)–Re–Br	82.0(2)

Figs. 3 and 4 show the packing diagrams of **1** and **2**, respectively. It is seen from Figs. 3 and 4 that while the molecules of **1** are interlinked through a series of trifurcated hydrogen bondings involving two C–H···Br (H···Br = 3.031 and 3.029 Å and ∠C–H···Br = 131.3 and 142.8°, respectively) and one N–H···Br (H···Br = 2.572 Å and ∠N–H···Br = 1551°) hydrogen bonds, the molecules of **2** are interlinked through tetrafurcated hydrogen bondings involving four C–H···Br (H···Br = 2.850, 2.846, 2.804 and 3.005 Å and ∠C–H···Br = 164.7, 159.2, 176.9 and 127.4°, respectively) hydrogen bonds.

3.3. Structures of 3–5

Crystals of **3**–**5** conform to the space groups $P\bar{1}$ with two molecules in a unit cell. Fig. 5 shows the ORTEP diagram for complex **3**, while Fig. 6 shows a representative ORTEP diagram for complexes **4** and **5**. Selected bond distances and angles for **3** are listed in Table 3 and those for **4** and **5** are listed in Table 4, respectively. It is seen from Figs. 5 and 6 that the metal atoms adopt a distorted octahedron, which are coordinated to four COs and one HDpyF (or HDMepyF) ligand. The HDpyF (HDMepyF) ligand chelates the metal atom through the first and the second nitrogen atoms to form a four-membered ring, and the third and the fourth nitrogen atoms are not coordinated. The successful synthesis and structural characterization of complex **3** complete the series of complexes $M(CO)_4(HDpyF)$ (M = Cr [1], Mo and W [1]). The M–C and M–N distances in this series are Cr < Mo ≅ W, while the chelating angle of N–M–N is Cr > Mo ≅ W. The bonding mode of the HDMepyF ligands in complexes **4** and **5** are similar to those of HDpyF in $M(CO)_4$(HDpyF), indicating that introduction of the methyl groups to the pyridyl rings of the HDpyF ligands has no effect on their bonding modes. Due to the formation of the

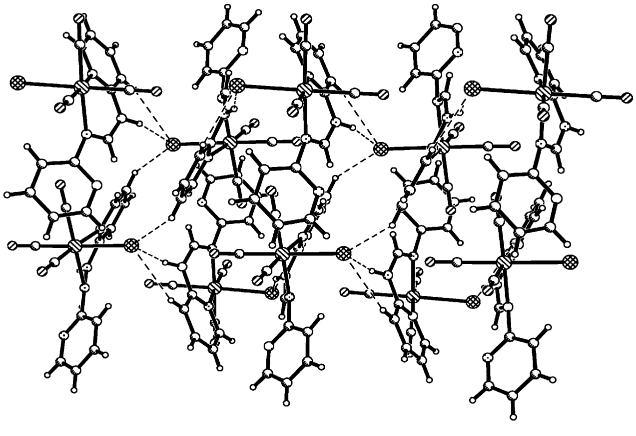

Fig. 3. A packing diagram of **1**.

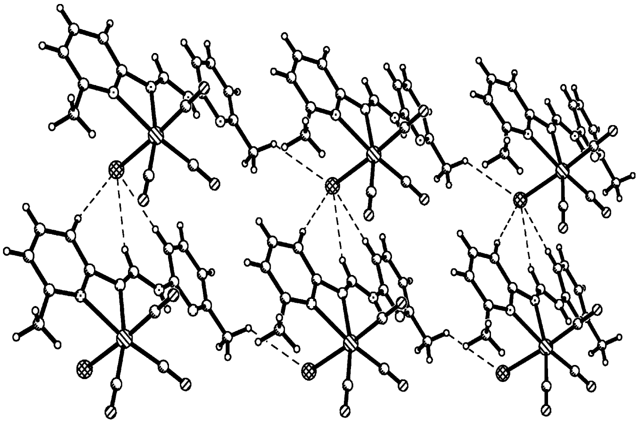

Fig. 4. A packing diagram of **2**.

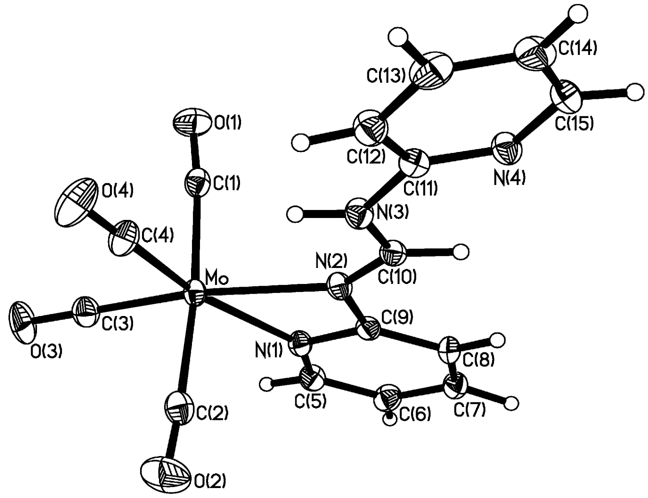

Fig. 5. An ORTEP diagram of **3**.

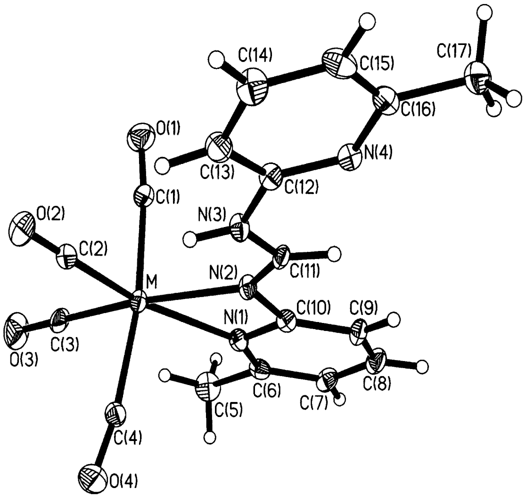

Fig. 6. A representative ORTEP diagram for **4** and **5**.

Table 3
Selected bond distances (Å) and bond angles (°) for **3**

Bond distances			
Mo–C(1)	2.038(7)	Mo–C(4)	1.945(6)
Mo–C(2)	2.040(7)	Mo–N(1)	2.287(4)
Mo–C(3)	1.966(6)	Mo–N(2)	2.274(4)
Bond angles			
C(4)–Mo–C(3)	86.6(3)	C(1)–Mo–N(2)	93.9(2)
C(4)–Mo–C(1)	87.3(2)	C(2)–Mo–N(2)	90.8(2)
C(3)–Mo–C(1)	87.3(2)	C(4)–Mo–N(1)	164.7(2)
C(4)–Mo–C(2)	88.9(3)	C(3)–Mo–N(1)	108.7(2)
C(3)–Mo–C(2)	88.7(2)	C(1)–Mo–N(1)	93.7(2)
C(1)–Mo–C(2)	174.6(2)	C(2)–Mo–N(1)	91.0(2)
C(4)–Mo–N(2)	106.4(2)	N(2)–Mo–N(1)	58.3(2)
C(3)–Mo–N(2)	167.0(2)		

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

	M = Mo	M = W
Bond distances		
M–C(1)	2.042(3)	2.007(11)
M–C(2)	1.951(3)	1.953(13)
M–C(3)	1.948(3)	1.952(9)
M–C(4)	2.049(3)	2.023(10)
M–N(1)	2.289(2)	2.264(8)
M–N(2)	2.273(2)	2.233(8)
Bond angles		
C(3)–M–C(2)	88.35(12)	88.0(5)
C(3)–M–C(1)	85.46(11)	86.9(5)
C(2)–M–C(1)	88.16(11)	88.0(4)
C(3)–M–C(4)	85.06(11)	84.0(5)
C(2)–M–C(4)	88.70(11)	88.9(4)
C(1)–M–C(4)	170.10(10)	170.5(4)
C(3)–M–N(2)	167.61(10)	168.5(4)
C(2)–M–N(2)	104.01(9)	103.4(4)
C(1)–M–N(2)	93.87(9)	92.7(4)
C(4)–M–N(2)	96.00(9)	96.8(4)
C(3)–M–N(1)	109.43(10)	109.9(4)
C(2)–M–N(1)	162.21(10)	162.1(4)
C(1)–M–N(1)	92.63(9)	92.6(4)
C(4)–M–N(1)	93.23(9)	93.2(4)
N(2)–M–N(1)	58.20(7)	58.7(3)

four-membered ring, the chelating angles N–M–N are 58.3(2), 58.20(7) and 58.7(3)° for complexes **3**, **4** and **5**, respectively. It is also interesting to note that the M–C distance *trans* to the carbonyl group is longer than those *trans* to the nitrogen atoms of the HDpyF (HDMepyF) ligand. The differences are about 0.08 Å in **3**, 0.1 Å in **4** and 0.06 Å in **5**, respectively. As seen in Figs. 5 and 6, the two *trans* carbonyl groups are obviously bent away from the ligand pyridyl rings, with C–M–C angles of 174.6(2), 170.1(1) and 170.5(4)° for complexes **3**, **4** and **5**, respectively. This may be ascribed to the crowding effect of the HDpyF and HDMepyF ligands. The bidentate HDpyF and HDMepyF ligands in each molecule is not flat, but twisted around the C–N bonds, with dihedral angles between the planes of the two pyridine rings of 20.6, 18.2 and 18.6°, for complexes **3**, **4** and **5**, respectively.

Similar to $Cr(CO)_4(HDpyF)$ and $W(CO)_4(HDpyF)$, the packing diagram (Fig. 7) of complex **3** shows supramolecular structures in the solid state by intermolecular hydrogen bonding between C–H groups of the pyridine rings and the oxygen atoms in the adjacent molecules ($H\cdots O = 2.338$ and 2.559 Å and $\angle C–H\cdots O = 157.1$ and 134.6°, respectively) and aromatic $\pi–\pi$ interactions. However, in complexes **4** and **5**, the molecules are only subjected to $\pi–\pi$ interactions (Fig. 8). The interplanar distances between the pyridyl rings are 4.068, and 3.849 Å for **3**, 3.627, and 3.597 Å for **4** and 3.620 and 3.638 Å for **5**, respectively.

3.4. *Conformations of the ligands*

A conformational descriptor for diarylformamidine bearing an *m*-alkoxy substituent has been proposed by Ren and co-authors [2]. Based on their proposition, three stable conformations exist for diarylformamidine which are defined as (a) *s-cis*, *s-cis*- (*s-cis*-/*s-trans*- are defined between the N–C (methine) bond and the ring C–C bond prioritized by the OR group), (b) *s-cis*, *s-trans*-, and (c) *s-trans*, *s-trans*- [2]. This descriptor is suitable for describing the conformation of anionic diarylformamidine. To describe the conformations for neutral HDpyF and HDMepyF ligands, we have modified this descriptor, shown in Fig. 9, where *syn* and *anti* indicate the relative positions of the methine and amine hydrogen atoms, respectively. Eight possible conformations for the neutral dipyridylformamidine ligands are proposed, which can inter-convert among themselves by rotating either one or both pyridyl groups 180° about the N–C(pyridyl) or N–C(methine) bonds. Table 5 lists the conformations of the neutral HDpyF and HDMepyF ligands adopted by the metal carbonyl complexes reported so far. The neutral dipyridylformamidine ligands in complexes of the types $M(CO)_4(HDpyF)$ ($M = Cr$, Mo and W) and $M(CO)_4(HDMepyF)$ ($M = Mo$ and W) adopt the *s-trans-anti-s-cis* conformation, while those in $Mo(CO)_3(HDpyF)(CH_3CN)$ and $ReBr(CO)_3(HDpyF)$ adopt the *s-cis-syn-s-cis* conformation. Only one complex, $ReBr(CO)_3(HDMepyF)$,

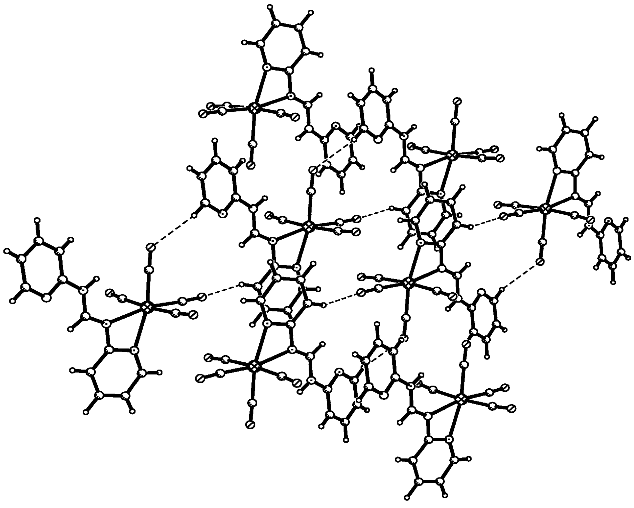

Fig. 7. A packing diagram of **3**.

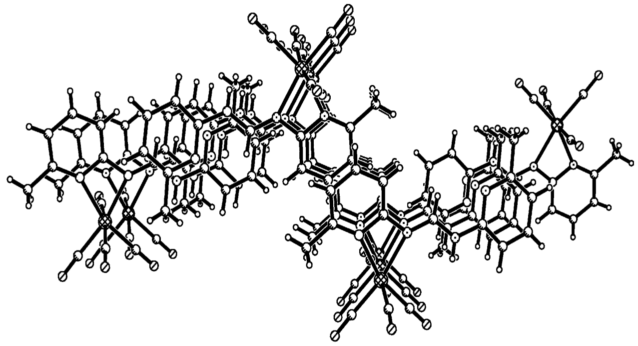

Fig. 8. A representative packing diagram of **4** and **5**.

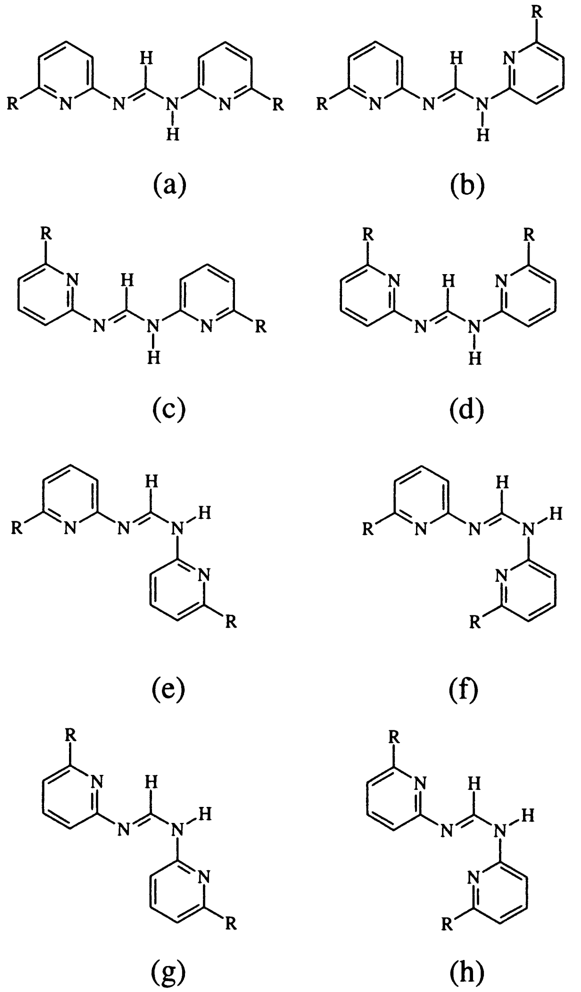

Fig. 9. Possible conformation for the neutral dipyridylformamidine ligands ($R = H$ or CH_3). (a) *s-trans-anti-s-trans* (b) *s-trans-anti-s-cis* (c) *s-cis-anti-s-trans* (d) *s-cis-anti-s-cis* (e) *s-trans-syn-s-trans* (f) *s-trans-syn-s-cis* (g) *s-cis-syn-s-trans* (h) *s-cis-syn-s-cis*.

Table 5
Conformations of the neutral HDpyF and HDMepyF ligands adopted in the metal carbonyl complexes

Compound	Conformation	Reference
$Cr(CO)_4(HDpyF)$	s-*trans*-*anti*-*s*-*cis*	[1]
$Mo(CO)_4(HDpyF)$	*s*-*trans*-*anti*-*s*-*cis*	This paper
$W(CO)_4(HDpyF)$	s-*trans*-*anti*-*s*-*cis*	[1]
$Mo(CO)_3(HDpyF)(CH_3CN)$	*s*-*cis*-*syn*-*s*-*cis*	[1]
$ReBr(CO)_3(HDpyF)$	*s*-*cis*-*syn*-*s*-*cis*	This paper
$Mo(CO)_4(HDMepyF)$	*s*-*trans*-*anti*-*s*-*cis*	This paper
$W(CO)_4(HDMepyF)$	*s*-*trans*-*anti*-*s*-*cis*	This paper
$ReBr(CO)_3(HDMepyF)$	*s*-*trans*-*anti*-*s*-*trans*	This paper

adopts the *s*-*trans*-*anti*-*s*-*trans* conformation and there are five conformations left to be investigated.

4. Conclusions

The syntheses and structures of $ReBr(CO)_3(HDpyF)$, **1**, $ReBr(CO)_3(HDMepyF)$, **2**, and $M(CO)_4(L)$ ($M = Mo$, $L = HDpyF$, **3**; $M = Mo$, $L = HDMepyF$, **4**; $M = W$, $L = HDMepyF$, **5**) have been successfully accomplished. The molecules of the complexes are interlinked through intermolecular hydrogen bonding and/or $\pi - \pi$ interactions in the solid state. The neutral dipyridylformamidine ligands in **1** and **2** adopt the *s*-*cis*-*syn*-*s*-*cis* and *s*-*trans*-*anti*-*s*-*trans* conformations, respectively, while those in complexes **3**–**5** adopt the *s*-*trans*-*anti*-*s*-*cis* conformation.

5. Supplementary material

Crystallographic data (CIF files) for the structures **1**–**5** have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 199225–199229. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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