

# W(CO)<sub>5</sub>–Pyridine- $\pi$ -acceptor complexes: synthesis, structure and electronic absorption spectra

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Received 7 May 2002; received in revised form 7 May 2002; accepted 9 May 2002

## Abstract

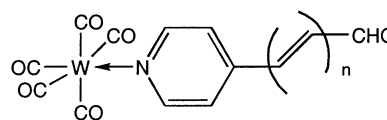
W(CO)<sub>5</sub>-complexes of 3-(4-pyridyl)propenal (**1b**), 5-(4-pyridyl)penta-2,4-dienal (**1c**), dimethyl (4-pyridylmethylene)malonate (**2a**), methyl 2-cyano-3-(4-pyridyl)acrylate (**2b**) and (4-pyridylmethylene)malononitrile (**2c**) have been synthesised. The molecular structures of **2b** and **2c** have been determined by X-ray diffraction. Significant distortions from the coplanarity of the W–N bond and the pyridine rings planes were observed in both structures. Electronic absorption spectra of **1b–c** and **2a–c** display red-shifted MLCT bands and a strong solvatochromism. © 2002 Elsevier Science B.V. All rights reserved.

## 1. Introduction

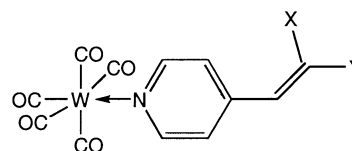
Linear and second-order non-linear optical (NLO) properties of W(CO)<sub>5</sub>L complexes (where L is pyridine or its 4-substituted derivative) have been thoroughly studied and reviewed [1–8]. It is now well established that electronic absorption spectra of these complexes display bands corresponding to d–d metal-centred (or ligand field, LF), as well as metal-to-ligand charge-transfer (MLCT or d– $\pi^*$ ) transitions. When the pyridine ligand bears an electron-withdrawing substituent, the energy of the MLCT excited state is markedly lowered and this state may become the lowest excited state of the complex [1]. With MLCT excitation of W(CO)<sub>5</sub>L are associated their second-order NLO properties [2,4,6].

Up to now the studies on W(CO)<sub>5</sub>–pyridine complexes having a MLCT state as the lowest excited state were limited to complexes of 4-substituted pyridines in which the acceptor group was attached directly to the ring. Since it is now well established that enhanced NLO properties are displayed by molecular systems in which donor and acceptor groups are linked not directly, but via a conjugated  $\pi$ -bridge [2–6] we thought that it would

be interesting to synthesise and study W(CO)<sub>5</sub>–pyridine complexes **1b–c** and **2a–c**. The aim of this work was to obtain complexes having the MLCT band significantly red-shifted and displaying a strong solvatochromism. Both these features promise enhanced second-order NLO properties.



**1**  
(a) n = 0  
(b) n = 1  
(c) n = 2



**2**  
(a) X = Y = COOMe  
(b) X = CN, Y = COOMe N2O  
(c) X = Y = CN

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## 2. Results and discussion

### 2.1. Synthesis of **1** and **2**

Complexes **1b–c** and **2a–c** were synthesised by a standard procedure using photochemically generated  $W(CO)_5(THF)$  and the corresponding pyridine ligands [9,10]. Complex **1a** was described earlier [11]. Unfortunately, crude **2a–c** were always contaminated with variable amounts of uncomplexed ligands. The purification proved troublesome (several crystallisations were required to obtain analytically pure samples) and was accompanied by a significant loss of the products.

The structures of complexes **1b–c** and **2a–c** were confirmed by spectral methods ( $^1H$ - and  $^{13}C$ -NMR, IR), elemental analyses and (for **2b** and **2c**) by X-ray diffraction.

### 2.2. X-ray structures of **2b** and **2c**

The molecular structures of **2b** and **2c** are shown in Figs. 1 and 2 together with the atomic numbering system. Crystallographic data and structure refinement details are collected in Table 1. Selected bond distances and angles are given in Table 2.

Compound **2b** has the (*E*)- configuration, resulting presumably from steric reasons. We think that this results from the same configuration of the precursor pyridine ligand, although X-ray structure of this compound is not known. According to the  $^1H$ -NMR spectrum, the ligand exists in chloroform solution as a one stereoisomer (one set of signals is observed) but the spectrum did not allow configuration assignment.

The W atoms in both complexes exhibit almost ideal octahedral geometry. The bonding W–C and W–N distances are practically the same as those reported for  $W(CO)_5(\text{pyridine})$  [12]:  $W-C_{trans} = 2.00(1)$  Å,  $W-C_{cis} = 2.04(1)$  Å,  $W-N = 2.26(1)$  Å. Therefore, electron-withdrawing substituents in pyridine ligands do not affect the co-ordinating properties of the nitrogen atom.

The peculiar feature of both complexes is that the W–N bonds do not lie in the plane of pyridine ligands. The angles between these bonds and normals to the ring planes (tilt angles) are  $81.9(2)^\circ$  (**2b**) and  $75.4(3)^\circ$  (**2c**).

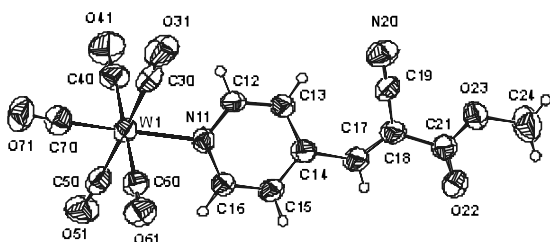


Fig. 1. ORTEP drawing of molecule **2b** with atom labelling scheme. Displacement ellipsoids are drawn at the 40% probability level.

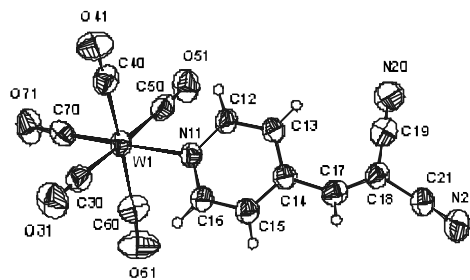


Fig. 2. ORTEP drawing of molecule **2c** with atom labelling scheme. Displacement ellipsoids are drawn at the 40% probability level.

This brings about deviation of the W atoms from the plane of the pyridine ring of  $0.278(3)$  and  $0.495(4)$  Å, respectively. The inspection of the Cambridge Structural Database [13] revealed that in known complexes of the type  $W(CO)_5(\text{pyridine})$  tilt angles was in the range of  $82.4$ – $90^\circ$  and the maximum deviation of W from the ligand plane was  $0.199(1)$  Å. The similar distortion was also reported for  $W(CO)_5(\text{azaferrocene})$  complex: tilt angle  $83.0(3)$ – $85.8(8)^\circ$  and deviation of W  $0.171(1)$ – $0.271(1)$  Å for two crystallographically independent molecules [14]. The planes of vinyl moieties (least-square plane of C17C18C14C19C21) are slightly inclined with respect to the plane of the pyridine ring and dihedral angles between these planes are  $25.6(3)^\circ$  for **2b** and  $25.5(4)^\circ$  for **2c**. The COOMe group in **2b** is practically coplanar with the vinyl moiety (dihedral angle  $2.0(3)^\circ$ ).

The crystal structure of **2b** is composed of molecules arranged in a ‘head-to-tail’ scheme (Fig. 3). The  $W(CO)_5$  moieties are packed between two parallel cyanoester moieties of the molecules related by translation around crystallographic *a* axis.

The crystal structure of **2c** is composed of two alternating layers perpendicular to *b* crystallographic direction: a layer of W atoms with the carbonyl ligands, and a layer of almost parallel pyridine moieties (Fig. 4). The pyridine moiety is bent, because of steric hindrance with carbonyl groups of next layer. Hence, one of the cyano groups—especially N20 atom—is put into ‘pocket’ between three carbonyl ligands of the neighbouring molecule. This arrangement causes an intermolecular interaction between cyano and one of carbonyl group. This results in relatively short distances:  $N20 \cdots C60$   $3.214(17)$  Å;  $N20 \cdots O61$   $3.119(15)$  Å and  $C19 \cdots O61$   $3.207(15)$  Å, respectively. The above pairs of atoms are closer in crystal than sum of their van der Waals radii [15]. Thus, very close crystal packing, as well as avoiding steric crowding, seem to be a reason for tilting pyridine ligands and bending of molecule of **2c**.

Inspection of molecular packing in both structures (especially that of **2c**) led to conclusion that the aforementioned distortions may be (at least in part) due to the packing effects.

Table 1  
Crystallographic data and structure refinement details

	I	II
<i>Crystal data</i>		
Formula	C <sub>14</sub> H <sub>5</sub> N <sub>3</sub> O <sub>5</sub> W	C <sub>15</sub> H <sub>8</sub> N <sub>2</sub> O <sub>7</sub> W
F <sub>w</sub>	479.06	512.08
Crystal description	dark red needle	yellow plate
Crystal size (mm)	0.1 × 0.2 × 0.5	0.1 × 0.3 × 0.5
Space group	P2 <sub>1</sub> /c	P2 <sub>1</sub> /n
a (Å)	6.566(1)	12.290(1)
b (Å)	18.256(2)	6.436(1)
c (Å)	12.815(1)	21.548(2)
β (°)	90.83(1)	92.22(1)
V (Å <sup>3</sup> )	1536.0(3)	1703.1(3)
Z	4	4
d <sub>x</sub> (g cm <sup>-3</sup> )	2.067	1.996
<i>Data collection</i>		
Diffractometer	Rigaku AFC5S	
Radiation type		
λ (Å)	Cu–K <sub>α</sub> (1.54178)	
μ (mm <sup>-1</sup> )	14.188	12.948
Temperature (K)	293(2)	293(2)
Data collected (h, k, l)	–6 ≤ h ≤ 8, –16 ≤ k ≤ 22, –14 ≤ l ≤ 15	–9 ≤ h ≤ 15, –6 ≤ k ≤ 7, –26 ≤ l ≤ 26
Number of reflections measured	3160	3395
Number of independent reflections	2910	3242
R <sub>int</sub>	0.036	0.052
Number of reflections with I > 2σ(I)	2405	2559
<i>Solution and refinement</i>		
Solution	Direct methods	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
H atoms treatment	Constrained	
Number of parameters	209	227
R(F) <sup>a</sup>	0.065	0.055
wR(F <sup>2</sup> ) <sup>b</sup>	0.187 <sup>c</sup>	0.121 <sup>d</sup>
R(F) <sup>a</sup>	0.056 for 2405 reflections	0.041 for 2559 reflections
wR(F <sup>2</sup> ) <sup>b</sup>	0.171 for 2405 reflections <sup>c</sup>	0.116 for 2559 reflections <sup>d</sup>
(Δ/σ) <sub>max</sub>	0.001	0.001
Difference peak/hole (e Å <sup>-3</sup> )	3.151/–2.596	1.127/–1.639

<sup>a</sup>  $R(F) = \Sigma(|F_o - F_c|) / \Sigma|F_o|$ .

<sup>b</sup>  $wR(F^2) = [\Sigma w(|F_o - F_c|)^2 / \Sigma|F_o|^2]^{1/2}$ .

<sup>c</sup>  $w = 1/[\sigma^2(F_o^2) + (0.134P)^2]$  where  $P = [(F_o^2) + 2(F_c^2)]/3$ .

<sup>d</sup>  $w = 1/[\sigma^2(F_o^2) + (0.068P)^2 + 1.139P]$  where  $P = [(F_o^2) + 2(F_c^2)]/3$ .

### 2.3. Electronic absorption spectra of 1 and 2

The electronic absorption spectra in the visible region of **1a–c** in benzene are shown in Fig. 5.

As expected, the spectra consist of two broad bands: the first (~400 nm) attributable to the LF transition and the second (~440 nm) to the MLCT transition. This assignment was earlier reported for **1a** [1]. It is seen

Table 2  
Selected bond lengths (Å) and angles (°)

Parameter	2c	2b
<i>W Coordination</i>		
W1–N11	2.275(7)	2.265(6)
W1–C30	1.996(15)	2.074(11)
W1–C40	2.073(12)	2.070(9)
W1–C50	2.036(17)	2.026(11)
W1–C60	2.070(11)	2.038(8)
W1–C70	1.989(11)	1.982(10)
<i>Pyridine ligands</i>		
C17–C14	1.464(13)	1.465(11)
C17–C18	1.307(16)	1.328(11)
C18–C19	1.417(15)	1.431(11)
C19–N20	1.168(13)	1.146(11)
C18–C21	1.449(13)	1.496(11)
C21–N22	1.135(14)	
C21–O22		1.199(10)
C21–C23		1.308(11)
C14–C17–C18	130.7(10)	127.8(8)
C17–C18–C19	124.4(9)	124.2(8)
C17–C18–C21	121.4(10)	120.1(8)
C19–C18–C21	113.9(9)	115.7(8)
C18–C21–O22		123.8(9)
C18–C21–O23		111.3(8)
C14–C17–C18–C19	5.0(18)	1.2(15)
C14–C17–C18–C21	–169.0(11)	178.8(8)
C17–C18–C21–O22		–0.8(15)
C17–C18–C21–O23		179.4(8)
C19–C18–C21–O22		177.0(9)
C19–C18–C21–O23		–2.7(11)

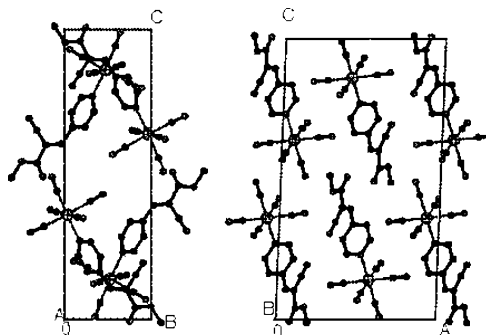


Fig. 3. Crystal packing of **2b**. Hydrogen atoms are omitted.

from Fig. 1 the elongation of the length of the conjugated chain between the pyridine ring and the aldehyde function does not bring about a significant bathochromic shift of the MLCT band. Only a hyperchromic effect (increase of  $\epsilon_{\max}$ ) is observed.

The electronic absorption spectra in the visible region of **2a–c** in benzene are shown in Fig. 6.

It is seen from Fig. 6 the MLCT bands of these complexes are significantly shifted toward lower wavelengths in comparison to the analogous bands in **1a–c**, whereas the position of the LF bands practically does not depend on the ligand. Furthermore, the bands

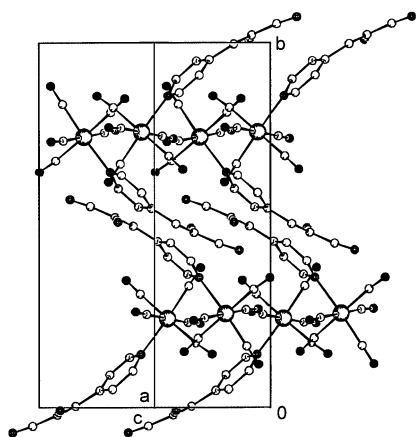


Fig. 4. Crystal packing of **2c**. Hydrogen atoms are omitted.

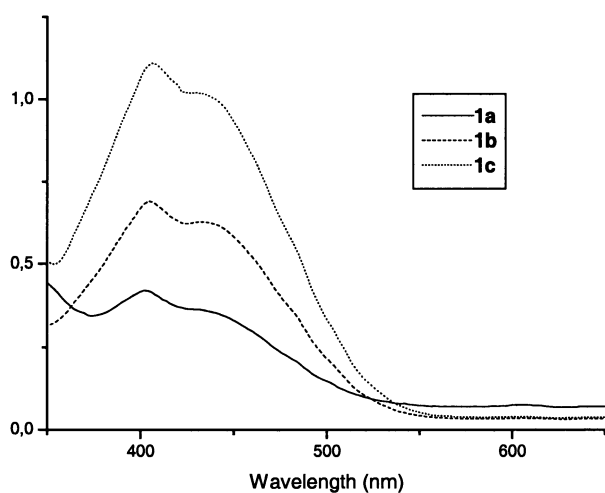


Fig. 5. Electronic absorption spectra of **1a–c** in benzene ( $c = 10^{-4}$  M).

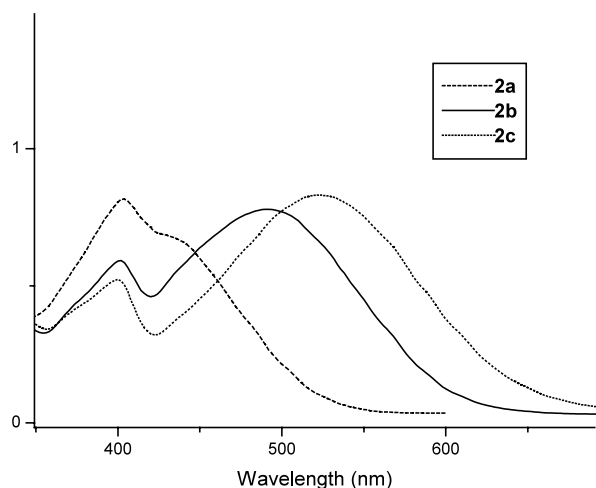


Fig. 6. Electronic absorption spectra of **2a–c** in benzene ( $c = 10^{-4}$  M).

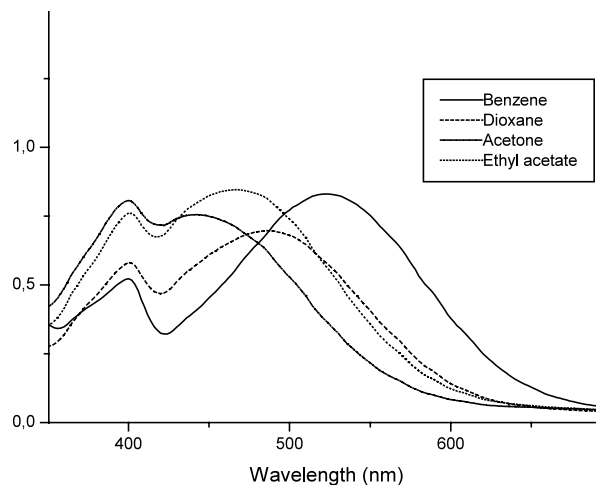


Fig. 7. Electronic absorption spectra of **2c** in various solvents ( $c = 10^{-4}$  M).

display a pronounced solvatochromic behaviour. It is presented in Fig. 7 for **2c** and in Table 3.

As for other  $W(CO)_5L$  complexes [1], a negative solvatochromism (i.e. shift toward higher energy with increasing polarity of the solvent) is observed. For **2b** and **2c** a good linear correlation between energy of the lowest transition and the polarity of the solvent (expressed as  $1/n^2 - 1/D$  (where  $n$  is the refractive index and  $D$  is the dielectric constant of the solvent [16]) was observed (Fig. 8).

This correlation provides another evidence for the CT nature of these bands.

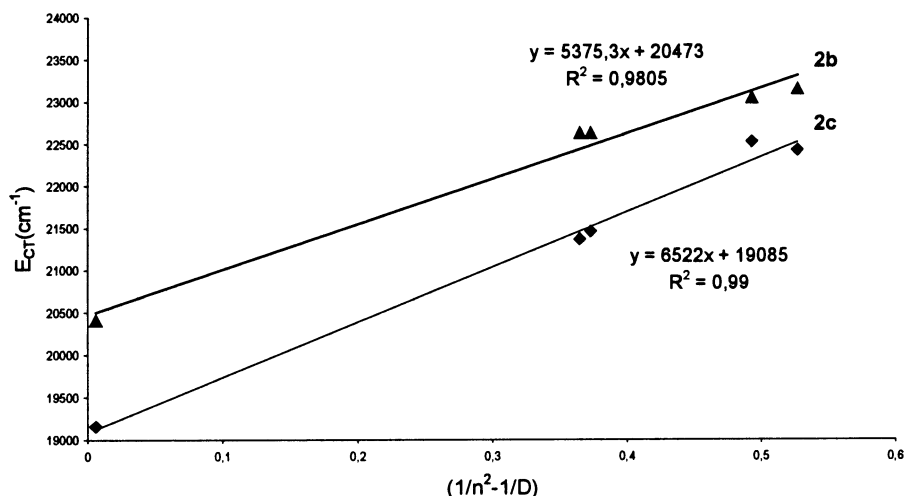
Preliminary EFISH experiments showed that unfortunately NLO properties (measured as  $\mu\beta(2\omega)$ ) of **2c** are negligible. However, this may not result from negligible first hyperpolarisability ( $\beta$ ) but from negligible dipole moment ( $\mu$ ), or from unfavourable spatial orientation between the dipole moment vector and the main component of the  $\beta$  tensor.

In conclusion, we have synthesised a series of  $W(CO)_5$  (4-substituted pyridine) complexes exhibiting very low-

Table 3  
Electronic absorption spectra of complexes **2a–c**

Solvent	$\lambda_{\max}$ (nm) ( $\epsilon_{\max}$ ( $M^{-1} \text{ cm}^{-1}$ ))		
	<b>2a</b>	<b>2b</b>	<b>2c</b>
Benzene	404 (8160)	402 (5920)	400 (5220)
	430 (6840) <sup>a</sup>	490 (7790)	522 (8300)
Ethyl acetate	400 (9580)	402 (7790)	400 (7610)
		442 (7650)	468 (8460)
THF	400 (7880)	402 (7420)	402 (6740)
		442 (7260)	466 (7200)
Acetone	398 (8640)	400 (8980)	402 (8040)
		434 (7890)	444 (7550)
Acetonitrile	396 (7600)	400 (7220)	398 (7390)
		432 (6500)	446 (7530)

<sup>a</sup> Shoulder.

Fig. 8. Solvatochromic behaviour of **2b** and **2c**.

energy MLCT transitions and enhanced solvatochromism, which promise enhanced first hyperpolarisabilities ( $\beta$ ).

### 3. Experimental

All reactions were carried out under argon. Tetrahydrofuran was distilled before use from sodium/benzophenone. Chromatographic separations were carried out on silica gel 60 (Merck, 230–400 mesh ASTM) using chloroform as eluent. Evaporations were carried out under reduced pressure on rotary evaporators. NMR spectra were recorded on a Varian Gemini 200 BB spectrometer (200 MHz for <sup>1</sup>H, 50 MHz for <sup>13</sup>C) in CDCl<sub>3</sub> solutions and were referenced to internal TMS. Electronic absorption spectra (VIS) were recorded on a Helios Alfa (Unicam) spectrometer. Infrared (IR) spectra were recorded in CHCl<sub>3</sub> on a Specord 75 IR and a Bio-Rad spectrometer. NMR labelling scheme is shown in Fig. 9. Elemental analyses were done by the Analytical Services of the CBMiM PAN (Łódź). Complex **1a** and pyridine ligands for complexes **2b–c** were prepared according to published procedures [9–11].

#### 3.1. X-ray structure determination

Data were collected on a Rigaku AFC5S diffractometer [17] using Cu–K $\alpha$  X-ray source and a graphite monochromator. The unit cell dimensions were obtained from a least-squares fit to setting angles of 25 reflections. The crystals of both compounds show no significant decay under X-ray radiation. Analytical absorption correction was applied [18]. A summary of X-ray details is given in Table 1. The structures were solved by direct methods using SHELXS86 [19] and

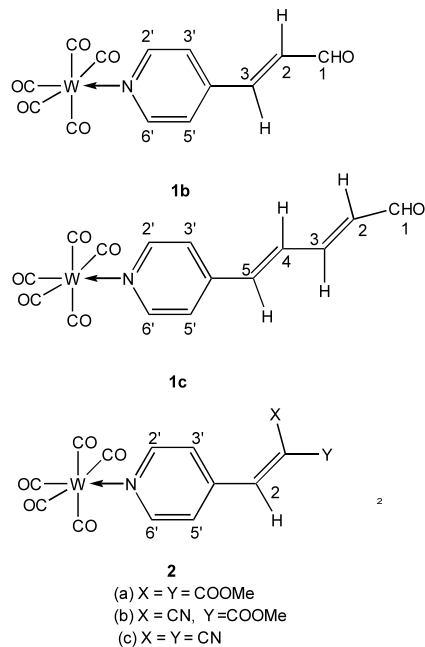


Fig. 9. NMR labelling scheme.

refined by full-matrix least-square method using SHELXL97 [20].

In the final step of refinement procedure, all non-hydrogen atoms for both structures were refined with anisotropic thermal displacement parameters. Hydrogen atoms were introduced in calculated positions with idealised geometry and refined using riding body model. They were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl group) of the equivalent isotropic displacement parameter of the C atom to which they are attached. The molecular geometry was calculated by PARST [21] and PLATON [22]. The drawings were made by PLATON.

### 3.2. General procedure

An argon saturated solution of  $W(CO)_6$  (177 mg, 0.45 mmol) in THF (50 ml) was irradiated through Pyrex with a high pressure Hg lamp for 1.5 h. To a resulting yellow solution of  $W(CO)_5(THF)$  the appropriate ligand (0.45 mmol) was added and the solution was stirred for 1.5 h. The solvent was evaporated to dryness and the residue chromatographed (complexes **1b–c**) or crystallised several times from dichloromethane–hexane (complexes **2a–c**).

#### 3.2.1. Compound **1b**

$^1H$ -NMR; 9.81(1H, d,  $J = 7.2$  Hz) H-1; 8.91 (2H, d,  $J = 5.5$  Hz) pyridine H-2' and H-6'; 7.40 (1H, d,  $J = 16.4$  Hz) H-3; 7.37 (2H, d,  $J = 5.5$  Hz) pyridine H-3' and H-5'; 6.85 (1H, dd,  $J = 7.2, 16.4$  Hz) H-2. Elemental analysis: Calc. for  $C_{13}H_7NO_6W$ : C, 34.16, H, 1.54. Found: C, 34.13; H, 1.63%.

#### 3.2.2. Compound **1c**

$^1H$ -NMR: 9.69 (1H, d,  $J = 7.5$  Hz) H-1; 8.80 (2H, d,  $J = 6.5$  Hz) pyridine H-2' and H-6'; 7.29 (2H, d,  $J = 6.5$  Hz) H-3' and H-5'; 7.23–7.18 (2H, m) H-4 and H-5; 6.90 (1H, d,  $J = 14.0$  Hz) H-3; 6.41 (1H, dd,  $J = 7.5, 14.0$  Hz) H-2. Elemental analysis: Calc. for  $C_{15}H_9NO_6W$ : C, 37.29, H, 1.88. Found: C, 37.33; H, 1.87%.

#### 3.2.3. Compound **2a**

$^1H$ -NMR: 8.85 (2H, d,  $J = 5.5$  Hz) pyridine H-2' and H-6'; 7.69 (1H, s) H-2; 7.24 pyridine (2H, d,  $J = 5.5$  Hz) H-3' and H-5'; 3.90 (6H, s) OMe.  $^{13}C$ -NMR: 202 (C≡O *trans* to the pyridine ring); 198.5 (C=O *cis* to the pyridine ring); 164 (C=O); 156.4 (C2' and C6'); 150 (C1); 141.5 (C4'); 137.2 (C2); 124.5 (C3' and C5'); 53.2 (Me). IR (CHCl<sub>3</sub>,  $\nu$  (cm<sup>-1</sup>)): 2072, 1960, 1909 (C≡O); 1734 (C=O). Elemental analysis: Calc. for  $C_{16}H_{11}NO_9W$ : C, 35.25, H, 2.03. Found: C, 35.53; H, 2.08%.

#### 3.2.4. Compound **2b**

$^1H$ -NMR: 9.02 (2H, d,  $J = 6.8$  Hz) H-2' and H-6'; 8.15 (1H, s) H-3; 7.72 (2H, d,  $J = 6.8$  Hz) H-3' and H-5'; 3.97 (3H, s) OMe.  $^{13}C$ -NMR: 202.1 (C≡O *trans* to the pyridine ring); 198.4 (C=O *cis* to the pyridine ring); 161 (C=O); 157 (C2' and C6'); 156 (C2); 149.1 (C4'); 139.1 (C3); 125 (C3' and C5'); 113.8 (C≡N); 54.1 (CH<sub>3</sub>). IR (CHCl<sub>3</sub>,  $\nu$  (cm<sup>-1</sup>)): 2236 (C≡N); 2070, 1975, 1916, 1869 (C≡O); 1731 (C=O); Elemental analysis: Calc. for  $C_{15}H_8N_2O_7W$ : C, 35.18, H, 1.57, N, 5.47. Found: C, 35.16; H, 1.56, N, 5.47%.

#### 3.2.5. Compound **2c**

$^1H$ -NMR: 9.08 (2H, d,  $J = 6.0$  Hz) pyridine H-2' and H-6'; 7.77 (1H, s) H-2; 7.65 (2H, d,  $J = 6.0$  Hz) pyridine H-3' and H-5'.  $^{13}C$ -NMR: 201.9 (C≡O *trans* to the pyridine ring); 198.3 (C=O *cis* to the pyridine ring); 157.4 (C2' and C6'); 154.3 (C1); 151.3 (C4'); 137.8 (C2); 124.3 (C3' and C5'); 112.0 (C≡N); 111.0 (C≡N). IR (CHCl<sub>3</sub>,  $\nu$  (cm<sup>-1</sup>)): 2074, 1975, 1926 (C≡O); 2229 (C≡N). Elemental analysis: Calc. for  $C_{14}H_5N_3O_5W$ : C, 35.10, H, 1.05, N, 8.77. Found: C, 35.08; H, 0.74, N, 8.75%.

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