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Metallic carbonyl complexes containing heterocycles nitrogen ligands[☆]

Part VI. Re(I), Mn(I), Mo(0), and W(0) compounds with 4′-phenyl-2,2′:6′,2″-terpyridine

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Abstract

The synthesis and spectroscopic characterization of new transition metal complexes containing the heterocyclic nitrogen ligand 4′-phenyl-2,2′:6′,2″-terpyridine are reported. Complexes of the [XM(CO)$_3$(L)] type (M = Re(I), Mn(I), Mo(0), or W(0); X = Br or CO; and L = 4′-phenyl-2,2′:6′,2″-terpyridine) were prepared by photosubstitution or by thermolytic reactions. Aspects of the IR, UV–Vis, proton NMR spectra and electrochemistry of the complexes are discussed. Special attention is given to the fact that the heterocyclic nitrogen ligand ph-tpy acts as a bidentate or terdentate chelate in complexes of this type and shows the fluxionality in the coordination. Correlations between redox potentials and spectroscopic measurements indicate the various interactions of the ligand and the metal center, and allow the evaluation of the metal–ligand back-donation. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Metal carbonyl complexes; Rhenium(I); Manganese(I); Molybdenum(0) and Tungsten(0); Heterocyclic nitrogen ligand

1. Introduction

A few examples of transition metal complexes with 2,2′:6′,2″-terpyridine ligand (tpy) coordinated in a bidentate arrangement, leaving off one external pyridyl ring uncoordinated, are known [2]. If the meridional coordination site is available the most current binding mode of this ligand to metals is the terdentate array [3]. The spectroscopic characterization of this type of bidentate species is of interest since they have been postulated to have an important participation as products of photolysis of tridentate terpyridine transition metal complexes [4]. Moreover, the remarkable photophysical and photochemical properties of these complexes are especially convenient for studying the structural modifications of heterocyclic nitrogen ligands with the purpose of causing variations on the electronic properties of these species. Furthermore, systems such as [XRe^{I}(CO)$_3$(L)] type (X = halide and L = 2,2′-bipyridine, 2,2′-biquinoline or their derivatives) have been found to be efficient catalysts for the reduction of CO$_2$ to CO both photochemically [5] and electrochemically [6]. Only scarce examples with the 4′-phenyl-2,2′:6′,2″-terpyridine ligand coordinated to iron(III), ruthenium(II), cobalt(II), and platinum(II) centers are known [7], therefore we have selected this ligand as a

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model to continue our previous work. We study here the reaction of a series of carbonyl transition metal complexes with the 4′-phenyl-2,2′:6′,2″-terpyridine ligand (Fig. 1) to form [XM(CO)$_3$(ph-tpy)] complexes where X = Br or CO; ph-tpy = 4′-phenyl-2,2′:6′,2″-terpyridine and M = Re(I), Mn(I), Mo(0), or W(0); and we report the preparation and the coordination behavior of this heterocyclic nitrogen ligand with different transition metal centers. Part of this work has been reported previously [1d,16d,22c].

2. Experimental

2.1. Materials

All the operations were carried out under purified nitrogen by standard Schlenk and vacuum-line techniques using freshly distilled, dried and degassed solvents. During the synthesis, the solutions of the complexes were protected from light. Molybdenum carbonyl (Aldrich Chemical Co.), tungsten carbonyl (Merck), and manganese pentacarbonyl bromide (Strem) were used without further purification. High purity BrRe(CO)$_5$ was obtained by treating Re$_2$(CO)$_{10}$ (Aldrich Chemical Co.) with Br$_2$ solution in cyclohexane at room temperature (r.t) [8]. Bicyclo[2,2,1]hepta-2,5-diene (NBD) was used as received from Aldrich Chemical Co. The heterocyclic nitrogen ligand 4′-phenyl-2,2′:6′,2″-terpyridine was prepared by modification of literature methods [9]. 2-Acetylpyridine (Aldrich Chemical Co.) and benzaldehyde (Merck) were used as obtained. The solvents used in synthesis, recrystallizations, and spectroscopic analyses (Mallinckrodt, grade HPLC) were treated and distilled prior to use [10]. Anhydrous acetonitrile freshly destilled and dried was used for the electrochemical studies [11]. Tetrabutylammonium perchlorate (TBAP) from Fluka was recrystallized twice from HPLC grade ethyl acetate (Mallinckrodt) before to be used.

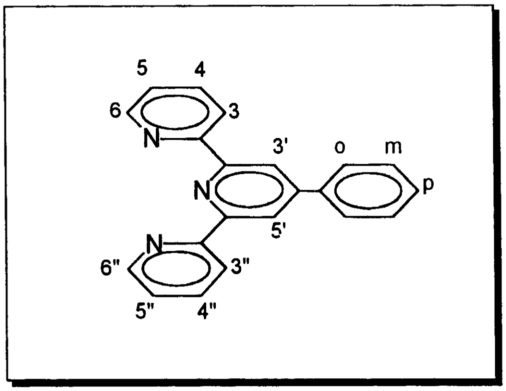

Fig. 1. Heterocyclic nitrogen ligand 4′-phenyl-2,2′:6′,2″-terpyridine (ph-tpy).

2.2. Physical measurements

Irradiation reactions were carried out with a 500 W medium-pressure mercury original Hanau TNN 15/32 lamp that was housed in a glass immersion reactor. The photolysis were performed under dry nitrogen gas atmosphere. All the products of photolysis were handled in the dark. Infrared (IR) spectra (data in cm^{-1}) were run on a Bruker IFS-66V Fourier-transform spectrophotometer using KBr disk and chloroform solutions in NaCl cells or polyethylene pellets (in the far IR region, 450–150 cm^{-1}). The electronic absorption spectra were recorded using a Shimadzu UV-160 spectrophotometer with different solvents in quartz cells on solutions ranging from 1×10^{-5} to 1×10^{-3} mol dm^{-3} at r.t. Proton NMR spectra were recorded on a Bruker DPX 200 operating at 200.131 MHz and a Bruker AMWB 300 operating at 300.134 MHz. Variable-temperature proton NMR spectra were recorded on a Bruker AMWB 300 operating at 300.134 MHz using the Bruker BVT-2000 variable temperature unit to control the probe temperature in CD$_2$Cl$_2$ or DMSO-d$_6$. Homonuclear correlated (COSY) spectra were obtained on a Bruker DPA 200 using the standard Bruker programs NOEXSY.Au and COSY.Au. Molar conductivity measurements were determined in anhydrous acetonitrile in 1×10^{-3} mol dm^{-3} solutions of the complexes at 25°C, using a Cole-Palmer 01481 conductivity meter. Electrochemical data from anhydrous acetonitrile solutions of the complexes containing 0.1 mol dm^{-3} of tetrabutylammonium perchlorate (TBAP) were obtained by cyclic voltammetry using a Bank-Wenking POS 73 potentiostat with a Gould OS 4100 oscilloscope, and a Graphtec XY WX 4301 recorder. A three-electrode configuration was used, where the working electrode was a platinum disk, and the reference and counter electrodes were an aqueous saturated calomel and platinum wire, respectively. The test solution was separated from the reference electrode by a salt bridge containing a Vycor plug and filled with the corresponding solvent/supporting electrolyte system. A sweep rate of 200 mV s^{-1} was used for all the scans. Potentials were reported as $E_{1/2} = 0.5(E_{\mathrm{p_c}} + E_{\mathrm{p_c}})$, where $E_{\mathrm{p_c}}$ and $E_{\mathrm{p_c}}$ were the anodic and cathodic peak potentials, respectively. Ferrocene was used as an internal standard to compensate the junction potential variability among experiments. Elemental analyses were performed by the CNRS analysis laboratory, Villeurbanne (France).

2.3. Preparations

The ligand 4′-phenyl-2,2′:6′,2″-terpyridine (ph-tpy) was prepared by a modified literature method which consisted on two consecutive condensations as follows. A mixture of 2-acetylpyridine (8.4 ml, 74 mmol), benzaldehyde (3.4 ml, 32 mmol) and NaOH (2.0 g) in water (25 ml)/ethanol (35 ml) was stirred for 1 h at r.t. The resulting solution was mixed and stirred with 30 ml of water to obtain a white precipitate of 1,5-bis-(2-pyridyl)-3-pentan-dione. The crude reaction product was filtered, washed extensively with cold ethanol and air-dried. 1,5-bis-(2-pyridyl)-3-pentan-dione (20.0 g, 6.1 mmol) and ammonium acetate (25 g) were dissolved in ethanol (25 ml) and the clear solution heated to 70°C for 2 h. Water (about 20 ml) was slowly added to the cooled solution to give a yellow precipitate. This was filtered, washed with cold ethanol and diethyl ether, and finally dried in vacuum. The 4′-phenyl-2,2′:6′,2″-terpyridine was obtained as pale yellow crystals on recrystallization from hot ethanol. Yield 60%. IR, ν_{C-O} (KBr disk): 1582, 1564, 1548, 1500, 1467,1389, 796, 680, 620 cm^{-1}. ^{1}H NMR (CDCl$_3$, 200 M Hz) δ (ppm): 8.75 (2H, t, H$_{66''}$); 7.97 (2H, d, H$_{55''}$); 7.43 (2H, dd, H$_{44''}$); 8.81 (2H, dd, H$_{33''}$); 8.82 (2H, s, H$_{3'5'}$); 7.43 (2H, m, H$_{oo'+p}$); 8.00 (2H, dd, H$_m$). *Anal.* Calc. for $C_{21}H_{15}N_3$: C, 81.53; H, 4.89; N, 13.58. Found: C, 81.62; H, 4.86; N, 13.08%. M.p. 203–204 °C.

2.3.1. BrRe(CO)$_3$(ph-tpy) (**1**)

BrRe(CO)$_5$ (326 mg, 1 mmol) was dissolved in hot heptane and the heterocyclic nitrogen ligand (ph-tpy) (310 mg, 1 mmol) was slowly added. A yellow color quickly developed which gradually changed to intense orange after 1 h. The solution was concentrated, diethyl ether was added and the mixture was cooled in an ice-bath to obtain a yellow–orange precipitate. The solid was filtered, dissolved in the minimum amount of methylene chloride, and flash precipitated with diethyl ether. The product was collected, washed with diethyl ether and boiling ethanol, recrystallized from acetonitrile/methylene chloride, and dried in vacuum. Yield 90%; IR, ν_{C-O} (KBr disk): 2018, 1909, 1878 cm^{-1}; ν_{C-O} (CHCl$_3$): 2024, 1923, 1905 cm^{-1}; ν_{M-C} (polyethylene pellet): 405 and 187 cm^{-1}. *Anal.* Calc. for [BrRe(CO)$_3$($C_{21}H_{15}N_3$)]: C, 43.71; H, 2.29. Found: C, 44.10; H, 2.48%. Molar conductivity 5.4 Ω^{-1} cm^2 mol^{-1}. M.p. 265°C.

2.3.2. BrMn(CO)$_3$(ph-tpy) (**2**)

To a hot solution of ph-tpy ligand (619 mg, 2.0 mmol) in (30 ml) anhydrous petroleum ether 30–60°C a hot solution of BrMn(CO)$_5$ (548 mg, 2.0 mmol) in hexane (40 ml) was slowly added and stirred under nitrogen atmosphere. The solution was concentrated, diethyl ether was added and the mixture was cooled overnight to obtain an orange–brown precipitate. The solid was collected and purified in a similar procedure as **1**, except ethanol was not used to wash the product. Yield 75%; IR, ν_{C-O} (KBr disk): 2009, 1937, 1912 cm^{-1}; ν_{C-O} (CHCl$_3$ solution): 2009, 1993, 1952 cm^{-1}; ν_{M-C} (polyethylene pellet): 405 and 191 cm^{-1}. *Anal.* Calc. for [BrMn(CO)$_3$($C_{21}H_{15}N_3$)]: C, 54.57; H, 2.86. Found: C, 54.10; H, 2.46%. Molar conductivity 0.0 Ω^{-1} cm^2 mol^{-1}. M.p. 250–275°C (d).

2.3.3. Mo(CO)$_4$(ph-tpy) (**3**)

Mo(CO)$_6$ (1.6 g, 4.0 mmol) was dissolved in tetrahydrofuran (35 ml) and a solution of the ph-tpy ligand (2.5 g, 4.1 mmol) in the same solvent was slowly added. The resulting solution was refluxed under nitrogen and stirred for 5 h, then concentrated, and cooled to obtain a red precipitate. The precipitate was filtered, washed with diethyl ether/ethanol, recrystallized in acetonitrile/methylene chloride, and dried in vacuum. Yield 85%. IR, ν_{C-O} (KBr disk): 2027, 1915, 1861, 1840 cm^{-1}; ν_{C-O} (CHCl$_3$): 2027, 1916, 1861, 1842 cm^{-1}; ν_{M-C} (polyethylene pellet): 382 cm^{-1}. *Anal.* Calc. for [Mo(CO)$_4$($C_{21}H_{15}N_3$)]: C, 58.04; H, 2.92. Found: C, 57.90; H, 3.12%. Molar conductivity 0.0 Ω^{-1} cm^2 mol^{-1}. M.p. 149°C (d).

2.3.4. W(CO)$_4$(ph-tpy) (**4**)

A solution of W(CO)$_6$ (703 mg, 2.0 mmol) in tetrahydrofuran (70 ml) was irradiated at ambient temperature in a Pyrex glass tube for 1.5 h. To the solution bicyclo[2,2,1]hepta-2,5-diene (NBD) was added to obtain the W(CO)$_4$(NBD) complex (ν_{C-O} (CHCl$_3$): 2003 (s), 1984(s), 1884(m), 1838(s) cm^{-1}). The complex was collected and dissolved in tetrahydrofuran and a sample of the ph-tpy ligand (600 mg, 2.0 mmol in 10 ml of THF) was added. The solution was stirred in the dark for 3 h at 50°C. The solution was concentrated, and cooled to obtain the stable W(CO)$_4$(ph-tpy) complex. Yield 83%; IR, ν_{C-O} (KBr disk): 2008, 1990, 1891, 1842 cm^{-1}; ν_{C-O} (CHCl$_3$): 2006, 1990, 1890, 1842 cm^{-1}; ν_{M-C} (polyethylene pellet): 393 cm^{-1}. *Anal.* Calc. for [W(CO)$_4$($C_{21}H_{15}N_3$)]: C, 49.94; H, 2.62; N, 7.28. Found: C, 50.41; H, 2.95; N, 6.71%. Molar conductivity 0.0 Ω^{-1} cm^2 mol^{-1}. M.p. > 300°C.

2.3.5. W(CO)$_3$(ph-tpy) (**5**)

W(CO)$_6$ (704 mg, 2.0 mmol) in acetonitrile (80 ml) was refluxed for 22 h, then a solid sample of ph-tpy (600 mg, 2.0 mmmol in 20 ml of acetonitrile) was added and stirred in the dark at r.t. until IR spectroscopy showed the appearance of the three carbonyl bands for *fac*-W(CO)$_3$(ph-tpy) complex (about 3 h). The solvent was then removed in vacuum and the residue was crystallized in a mixture of acetonitrile/methylene chloride. Yield 70%; IR, ν_{C-O} (KBr disk): 2007, 1895, 1835 cm^{-1}; ν_{C-O} (CHCl$_3$): 2015, 1900, 1817 cm^{-1}; ν_{M-C} (polyethylene pellet): 412 and 179 cm^{-1}. *Anal.* Calc. for [W(CO)$_3$($C_{21}H_{15}N_3$)]: C, 37.70; H, 2.50; N, 6.94. Found: C, 38.25; H, 3.07; N, 7.34%. Molar conductivity 0.0 Ω^{-1} cm^2 mol^{-1}. M.p. > 300°C.

3. Results and discussion

3.1. Spectroscopic characterization of new complexes

The IR spectra in the 2400–1800 cm^{-1} region for the above complexes show the presence of carbonyl stretching frequencies corresponding to terminal carbonyl groups bonded to the metal. In addition, IR spectra of $BrRe(CO)_3$(ph-tpy) and $BrMn(CO)_3$(ph-tpy) complexes show three strong bands, which correspond to carbonyl stretching frequencies of CO groups in a *cis*-conformation, characteristic of a hexacoordinated octahedral species with C_s symmetry [12]. Furthermore, IR spectra of $Mo(CO)_4$(ph-tpy) and $W(CO)_4$(ph-tpy) complexes exhibit three strong bands and one weak ν_{C-O} band, typically generated by vibrational C_{2v} symmetry [13], where the heterocyclic nitrogen ligand acts as a bidentate chelate with the metal in a *cis*-conformation.

In contrast, IR spectrum of the $W(CO)_3$(ph-tpy) complex shows three ν_{C-O} strong bands, involving the ph-tpy ligand in a tridentate chelate bonding [14]. The solution of $W(CO)_6$ in acetonitrile shows one strong ν_{C-O} band at 1979 cm^{-1}, which is transformed in two strong bands (ν_{C-O}, acetonitrile solution: 1940 and 1797 cm^{-1}) after refluxing for 22 h. The latter IR data is indicative of the presence of *fac*-$W(CO)_3$(ph-tpy) species [15]. The addition of the heterocyclic nitrogen ligand to the resulting solution, gives a red-brown product. The IR spectrum of this product shows three ν_{C-O} bands (2015, 1917, 1900 cm^{-1}). This data provides consistent support to suppose that ph-tpy is acting as a tridentate ligand in this complex. Besides, no evidence of bidentate species was observed. These results are in agreement with the stoichiometry given by microanalysis and by molar conductivity measurements for the complexes. The substitution of carbonyl groups by the heterocyclic nitrogen ligand (ph-tpy) produces a decrease in carbonyl stretching frequency values of the complexes with respect to the corresponding precursor ($\Delta\nu_{C-O} = \nu_{C-O}^{precursor} - \nu_{C-O}^{complex}$) due to a higher electron donation from the metal to the remaining ligands carbonyl groups. This increase in the metal back-bonding to vacant π^* orbitals of the CO ligand results from the increase of the electron density at the metal center by the displacement of carbonyl groups by the heterocyclic nitrogen ligand which has less π-acceptor, but greater σ-donor character than the carbonyl groups. Greater electron density supplied by the metal and the other ligands, can be back-donated into π^* orbitals of carbonyl and/or halogen ligands which lowers the C–O bond order and decrease the stretching frequency value [16]. Table 4 shows that the values $\Delta\nu_{C-O}^{1}$ decreases in the order: $W(CO)_3$(ph-tpy) > $Mo(CO)_4$(ph-tpy) > $W(CO)_4$(ph-tpy) > $BrRe(CO)_3$(ph-tpy) > $BrMn(CO)_3$-(ph-tpy). The metal in the molybdenum and tungsten complexes, maintain an excess of negative load due to the competition of d orbitals of metal with the tricoordination of ph-tpy ligand.

The well known fluxionality, that complexes containing terpyridine show, has also been observed for the prepared complexes. The ambient, high and low temperature proton NMR spectrum of these complexes give strong support to suggest that the 2,2′:6′,2″-terpyridine ligand acts as a nitrogen heterocyclic bidentate ligand in some of the prepared complexes. The 4′-phenyl-2,2′:6′,2″-terpyridine, and 2,2′:6′,2″-terpyridine itself, have all coplanar rings with the nitrogen heterocyclic atoms of the peripheral rings in a *trans* position with respect to central pyridyl nitrogen atom. This structural conformation occurs only in the solid state for these ligands [17]. However, the complex formation causes the heterocyclic nitrogen ligand to adopt the *cis*:*cis* configuration and in solution rapid rotation should occurs. Low and ambient proton NMR experiments provide a strong evidence for the fluxionality occurring in the prepared complexes.

Full proton NMR chemical shift data for the complexes and the ligand are given in Table 1. Assignment was based taking in consideration their integration, multiplicity, coupling constant, and value of their chemical shifts and 2D-COSY spectroscopy. The ambient proton NMR spectra show seven groups of signals for the complexes with chemical shifts and forms similar to 2,2′:6′,2″-terpyridine itself. When the ligand bond to metal as a *N*,*N*,*N* terdentate ligand, the ph-tpy should be a symmetrical ligand giving a lower number of signals in the proton NMR spectrum. In spite of the fact that the ph-tpy is coordinated as a *N*,*N* bidentate ligand provides a proton NMR spectrum with a higher number of signals being the chemical shifts of the proton on the uncoordinated side of the terpyridine very similar to those of the free ligand. The protons on the uncoordinated pyridyl ring experience rather smaller positive shifts compared with those protons on the coordinated pyridyl rings. In order to produce the coordination with the metal, the 4′-phenyl-2,2′:6′,2″-terpyridine ligand must modify its conformation from *trans*:*trans* of its heteroatoms to *cis*:*cis*. This change in the ligand conformation is reflected in the chemical shift of the H_3 and $H_{3''}$ protons which are shifted to lower frequencies. On warming, the spectra undergoes changes, coalescence occurring between the corresponding signals pairs ($H_6/H_{6''}$; $H_5/H_{5''}$; $H_4/H_{4''}$; $H_3/H_{3''}$; $H_{3'}/H_{5'}$). The signals for the spectator protons H_o, H_m and H_p remain as sharp multiplets at all temperatures. This behavior indicates, that the terdentate ligand is fluxional and switches its metal coordination between different adjacent pairs of its three nitrogen atoms. The low temperature proton NMR study was carried out at the temperature range of 297 to 183 K. Basically the

Table 1
Proton NMR chemical shift selected data for ph-tpy and its rhenium(I), manganese(I), molybdenum(0), and tungsten(0) complexes

Complex (ligand)	Assignments δ (ppm) [a]						
	$H_{66''}$	$H_{33''}$	$H_{3'5'}$	$H_{44''}$	$H_{55''}$	$H_{mm'}$	$H_{oo'+p}$
BrRe(CO)$_3$(ph-tpy) [b] (**1**)	9.21 8.92	8.42 7.83	8.98 8.00	8.16 7.83	7.61 7.61	8.00 8.00	7.61 7.61
BrMn(CO)$_3$(ph-tpy) [b] (**2**)	9.15 7.89	8.70 8.15	8.26 7.82				
Mo(CO)$_4$(ph-tpy) [c] (**3**)	8.69 8.64	8.68 8.73	8.67 8.66				
W(CO)$_4$(ph-tpy) [c] (**4**)	8.71 8.67	8.67 8.75	8.75				
W(CO)$_3$(ph-tpy) [b] (**5**)	8.77	8.36	8.71				
(ph-tpy) [b]	8.75	8.81	8.82	7.43	7.97		7.47

[a] Referred to SiMe$_4$ (internal) in CDCl$_3$ $\delta = 0$ ppm; see Fig. 1 for hydrogen labeling.
[b] Recorded at 300 MHz.
[c] Recorded at 200 MHz.

spectrum remained the same in all this range of temperature. However an important change was observed in the spectrum, as can be shown in Fig. 2. Cooling this complex to approximately 203 K caused changes in the signals at 9.10 ppm. Initially it broadened or eventually split into an equal intensity doublet at 198 K to produce finally a doublet of doublet at 183 K. This should be attributed to the fact that the pendant pyridyl ring can become locked at low solution temperature with its nitrogen heteroatoms either *syn* or *anti* with respect to the formed plane by the coordination of the metal with the two coordinated nitrogen of the ligand [17d].

The proton NMR spectrum of the W(CO)$_3$(ph-tpy) complex does not present the same behavior observed for the rhenium complex, being the signals similar to those appearing in the spectrum of the ph-tpy free ligand, but slightly shifted by coordination when the complex is formed (Table 2).

The signals of protons 6 and 6″ are deshielded due to a decrease of the electronic density of the rings while the donation takes place [18]. This effect is reinforced by the coordination with metal which results in the displacement of signals to downfield (positive values of $\Delta\delta$ in all spectra of complexes) [12e]. On the other hand, the signals of H_3 and $H_{3''}$ of the external pyridyl rings and $H_{3'}$ and $H_{5'}$ of the central ring, of the coordinated ph-tpy ligand suffer a displacement to high field (negative values of $\Delta\delta$) due to protective effect that causes back donation between the metal and the heterocyclic nitrogen ligand, which is reinforced by anisotropy of neighboring rings [1]. This effect is strong in BrRe(CO)$_3$(ph-tpy), BrMn(CO)$_3$(ph-tpy), and W(CO)$_3$(ph-tpy) complexes, and weak in Mo(CO)$_4$(ph-tpy) and W(CO)$_4$(ph-tpy) complexes, because of the participation of the atom of halogen in complexes **1** and **2** and tricoordination of ph-tpy ligand in the W(CO)$_3$(ph-tpy) complex that leads to an increase in the back-bonding effect and therefore the resulting difference in the negative values of chemical shifts (Table 2). This could discard tricoordination in complexes **1**–**4** and confirm participation of a bidentate chelate mode of ph-tpy ligand in them, and suggest a tricoordination for the W(CO)$_3$(ph-tpy) complex.

In addition, molar conductivity measurements [19] and elemental analysis for the W(CO)$_3$(ph-tpy) complex clearly indicates that the heterocyclic nitrogen ligand

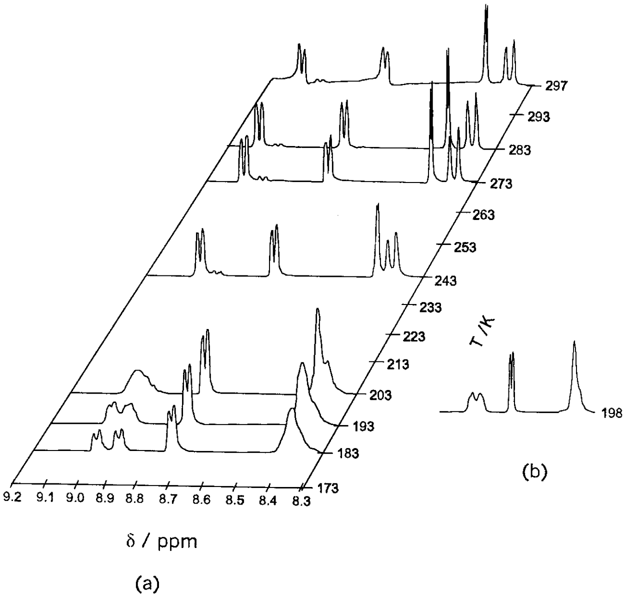

Fig. 2. (a) Temperature-depending proton NMR spectra for the BrRe(CO)$_3$(ph-tpy) complex in the range of 183–297 K. (b) detail of the signal at 198 K, doublet of doublet starts to be formed.

Table 2
Coordination-induced proton NMR chemical shifts for complexes

Complex	$\Delta\delta$ (ppm [a])		
	$H_{66''}$	$H_{33''}$	$H_{3'5'}$
$BrRe(CO)_3$(ph-tpy) (**1**)	+0.49 +0.20	−0.34 −0.76	+0.20 −1.17
$BrMn(CO)_3$(ph-tpy) (**2**)	+0.50 +0.04	−0.44 −0.81	−0.58 −0.91
$Mo(CO)_4$(ph-tpy) (**3**)	+0.03 +0.02	0.00 −0.03	0.00 −0.01
$W(CO)_4$(ph-tpy) (**4**)	+0.05 +0.02	+0.03 +0.02	+0.02
$W(CO)_3$(ph-tpy) (**5**)	+0.12	−0.55	−0.03

[a] $\Delta\delta = \delta_{complex} - \delta_{free\ ligand}$, referred to $SiMe_4$.

Table 3
Electronic absorption data for $[XM(CO)_3$(ph-tpy)] complexes

Complex	λ_{max} (nm) (ε ($dm^3\ mol^{-1}\ cm^{-1}$)) [a,b]
$BrRe(CO)_3$(ph-tpy) (**1**)	387(1960), 280(24 200), 260(25 100), 393(1620)/$CHCl_3$
$BrMn(CO)_3$(ph-tpy) (**2**)	421(2500), 312(21 500), 272(23v600), 425(2730)/CH_3OH
$Mo(CO)_4$(ph-tpy) (**3**)	454(1480), 275(11 720), 251 (12 520), 472(1100)/ether
$W(CO)_4$(ph-tpy) (**4**)	553(1190), 272(19 900), 249 (20 620), 545(1720)/$CHCl_3$
$W(CO)_3$(ph-tpy) (**5**)	559(1950), 276(18 600), 263 (24 120), 571(2100)/$CHCl_3$

[a] In acetonitrile solutions of 2.5 and 5.0×10^{-4} mol dm^{-3}.

[b] Lowest energy absorption band in different solvents (2.5×10^{-4} mol dm^{-3}).

should be tricoordinated to the tungsten center. Support for this conclusion comes also from the IR spectra analysis (vide supra). Proton NMR spectra of this complex showed that signals corresponding to protons of the heterocyclic nitrogen ligand are equivalent. This behavior is typical of tridentate disposition on the part of the terpyridyl derivative ligands in these species.

UV–Vis absorption spectra obtained for complexes in acetonitrile solutions at r.t. (Table 3), showed a group of very intense bands of high energy and a low energy absorption band having a low intensity. The high energy bands would correspond to absorptions due to intraligand transitions and the lowest energy band could be assigned to an absorption due to a charge-transfer from the metal to the heterocyclic nitrogen ligand (MLCT). Both proposals are supported by intensity, position, and solvent dependence of these bands, along with the analysis of the ligand spectrum [13,14].

3.2. Electrochemical properties

The electrochemical properties of this series of complexes **1–5** were studied. The redox potentials were determined by cyclic voltammetry and the number of electrons involved in electronic transfer by coulommetry (Table 4). Quasi-reversibility approaches were determined by the difference of potential between the anodic peak and the cathodic peak current (ΔE_p), the ratio between the intensities of anodic and cathodic peaks (i_{p_a}/i_{p_c}) and the relationship between the current and sweep rate. Relationship between the intensity of average versus $v^{1/2}$ was used to determine that the processes of electron transfer of these complexes were diffusion controlled. Cyclic voltammograms of these systems in the range 0.0 to −2.2 V versus Fc^+/Fc showed a reduction wave which could be assigned to a reversible monoelectronic reduction centered in the heterocyclic nitrogen ligand (Eq. (1)).[1] This agrees well with the fact that the π* molecular orbital of this ligand is the LUMO level of energy, which is confirmed by similar values of $E_{1/2}^{red}$ [20]:

$$XM(CO)_3(\text{ph-tpy}) + e^- \rightarrow [XM(CO)_3(\text{ph-tpy}^\bullet)]^- \qquad (1)$$

All the complexes presented a wave of irreversible oxidation in the region 0.0 to +1.7 V versus Fc^+/Fc. This wave was assigned to a monoelectronic oxidation process centered at the metal atom (M(II)/M(I): M = Re or Mn [6d,10e,21,23c]; M′(I)/M′(0): M′ = Mo or W [22] indicating that there is more electronic density removed from the Mn(I) than from the Re(I) and that of Mo(0) than of W(0). Consistent with a greater extension of d orbitals in the third-row transition metals of a same group, it ensues that the overlap between the metal orbitals and the heterocyclic nitrogen atom orbitals of the polypyridine ligand should be much larger for the metal in the second or third transition series. So, in complex **5** in which the heterocyclic nitrogen ligand ph-tpy is tricoordinated, this type of interaction is increased by the participation of three heterocyclic nitrogen atoms, making more difficult the removal of one electron from the metallic center, and leading to a more positive oxidation potential [23].

Since the potential of oxidation is a measure of the electronic density in the metal center and the electronic process of reduction is centered in the heterocyclic nitrogen ligand ph-tpy, one could establish correlations between the displacement to low frequency ($\Delta\nu_{C-O}$) of the band of C–O stretching for the vibration of dis-

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[1] $i_{p_a}/i_{p_c} \approx 1$, $\Delta E_p = 70–110$ mV.

Table 4
Decrease of carbonyl stretching frequencies ν_{CO} and electrochemical data for [XM(CO)$_3$(ph-tpy] complexes

Complex	$\Delta\nu_1$ [a]	Reduction		Oxidation [b]	
		$E_{1/2}^{\text{red c}}$	i_{p_c}/i_{p_a}	$E_{p_c}^{\text{ox,I}}$	$E_{p_c}^{\text{ox,II}}$
BrRe(CO)$_3$(ph-tpy) (**1**)	134	E_{p_c} −1.78 E_{p_c} −1.68 $E_{1/2}$ −1.73 ΔE_p (100) [e]	1.28	0.84 (i)	1.05 (i) [d]
BrMn(CO)$_3$(ph-tpy) (**2**)	130	E_{p_c} −1.81 E_{p_c} −1.96 $E_{1/2}$ −1.90 ΔE_p (110)	1.11	0.62 (i)	
Mo(CO)$_4$(ph-tpy) (**3**)	145	E_{p_c} −1.75 E_{p_c} −1.85 $E_{1/2}$ −1.85 ΔE_p (100)	1.26	0.75 (i)	
W(CO)$_4$(ph-tpy) (**4**)	136	E_{p_c} −1.89 E_{p_c} −1.81 $E_{1/2}$ −1.80 ΔE_p (80)	1.09	0.87 (i)	
W(CO)$_3$(ph-tpy) (**5**)	147	E_{p_c} −1.79 E_{p_c} −1.71 $E_{1/2}$ −1.75 ΔE_p (75)	1.37	1.07 (i)	
(ph-tpy)		E_{p_c} −2.63 E_{p_c} −2.47 $E_{1/2}$ −2.55 ΔE_p (160)			
(Fc$^+$/Fc)		E_{p_c} E_{p_c} $E_{1/2}$ ΔE_p		0.41 0.35 0.38 (60)	

[a] $\Delta\nu_{CO}^{1} = \nu_{CO}^{\text{precursor}} - \nu_{CO}^{\text{complex}}$ (cm^{-1}).

[b] Redox potentials in V (± 0.030 V) versus Fc$^+$/Fc, in CH$_3$CN 0.1 mol dm^{-3} of TBAP, $v = 200$ mV s^{-1}.

[c] $E_{1/2}^{\text{red}} = 0.5(E_{p_c} - E_{p_c})$, where E_{p_c} and E_{p_c}, are cathodic and anodic peaks, respectively.

[d] Irreversible.

[e] $\Delta E_p = E_{p_c} - E_{p_c}$ in mV.

charge energy (way A_1^1) [24] and the absorbance energy of the band of CTM → heterocyclic nitrogen ligand (ph-tpy) [16d,21c,25], with the difference between the oxidation and the reduction potentials of these complexes. The two plots gave relationships of the form: $\Delta\nu_{C-O}$ (cm^{-1}) $= 25.55 + 43.00$ (E^{ox} (V)) with $r = 0.9505$ and E_{abs} (eV) $= 10.719 + 3.068$ (E^{ox} (V)) with $r = 0.9017$.

4. Conclusion

The bi- or tricoordination of the heterocyclic nitrogen ligand ph-tpy, achieved by synthesis of new complexes, originate important changes in the spectroscopic and electrochemical characteristics, which can be used as a fundamental tool for the design and preparation of new species with predetermined properties.

5. Supplementary material

Additional IR, proton NMR data, including temperature and 2D-COSY information, and electrochemical experiments are available upon request.

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