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Synthesis and electrochemistry of Group 6 tetracarbonyl (*N*,*N*′-bis(ferrocenylmethylene)ethylenediamine)metal(0) complexes

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Abstract

Thermal substitution reaction of $Cr(CO)_4(\eta^{2:2}$-1,5-cyclooctadiene), $Mo(CO)_4(\eta^{2:2}$-norbornadiene), and $W(CO)_5(\eta^2$-bis(trimethylsilyl)ethyne) with *N*,*N*′-bis(ferrocenylmethylene)ethylenediamine (bfeda) yields $M(CO)_4$(bfeda) complexes which could be isolated from the reaction solution and characterized by elemental analysis, MS, IR, and NMR spectroscopy. In the case of tungsten, $W(CO)_5$(bfeda) is formed as intermediate and then undergoes the ring closure reaction yielding the ultimate product $W(CO)_4$(bfeda). The electrochemical behavior of the $M(CO)_4$(bfeda) complexes was studied by using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in dichloromethane with tetrabutylammonium tetrafluoroborate as electrolyte. Constant potential electrolysis of the complexes was performed successively at their peak potentials at 0 °C in their CH_2Cl_2 solution and the electrolysis was followed by in situ recording the electronic absorption spectra in every 5 mC. In the electrolysis of $Cr(CO)_4$(bfeda), the central Cr(0) is oxidized first and electrolysis continues with oxidations of two ferrocenyl groups until the end of totally three moles of electron passage per mole of complex. In the electrolysis of $Mo(CO)_4$(bfeda) and $W(CO)_4$(bfeda) the first oxidation occurs on the central atom forming a short-lived species which undergoes an intramolecular one-electron transfer and is reduced back to M(0) while one of the ferrocene units is oxidized to the ferrocenium cation at the same time. This indicates that the electron is transferred from iron to the central metal atom.

Keywords: Chromium; Molybdenum; Tungsten; Carbonyl; Ferrocene; Diimine; Bis(ferroceneylmethylene)ethylenediamine; Cyclic voltammetry

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1. Introduction

Ferrocene containing complexes are currently undergoing something of a renaissance due to their increasing role in the rapidly growing area of materials science and have been used in the preparation of many new materials [1], such as homogeneous catalysts [2], molecular sensors [3], molecular magnets [4], non-linear optic materials [5], and liquid crystals [6]. Transition metal complexes of N,N-, P,N-, and P,P-chelate ligands containing ferrocene unit [7,8] show superior catalytic activity compared to the complexes of the parent bidentate ligands [9]. This unusual catalytic activity is likely due to the availability of different but cooperatively conjugated metal sites [2]. It seems to be vital that the ferrocenyl unit is in conjugation with the ligating atoms of the bidentate ligand which has the ability to accept π-electron density from the second transition metal, thus, two metal centers would be electronically communicating to each other. Since ferrocene unit can easily provide an electron to the transition metal it can be considered as a one-electron reservoir. The presence of two ferrocene units in the same ligand can provide the opportunity for the molecule to be a two-electron reservoir. *N*,*N*′-Diferrocenyl-1,4-diaza-1,3-butadiene has been reported as the first example of such ligand [10]. However, its tetracarbonylmetal(0) complexes of Group 6 have been found to be instable because of the conjugated diene unit [11]. Another problem with this ligand is that two ferrocenyl centers can communicate with each other via the diene unit and, thus, the oxidation of one ferrocenyl group can affect the other. Indeed, this ligand exhibits two well resolved sequential oxidations

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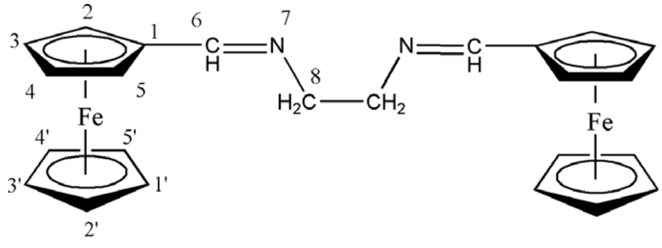
for the ferrocenyl groups [11]. In order for a molecule to act as a real two-electron reservoir, it needs to have two chemically equivalent and isolated ferrocene units. *N*,*N*′-Bis(ferrocenylmethylene)ethylenediamine (bfeda) appears to be a potential candidate for such ligands since it has two isolated but chemically equivalent ferrocene units attached to the imine nitrogen atoms [12]. This prompted us to start a study on the synthesis and characterization of the tetracarbonyl(*N*,*N*′-bis(ferrocenylmethylene)ethylenediamine)metal(0) complexes of Group 6 elements and to test whether the two metal centers are communicating to each other. $M(CO)_4$(bfeda) complexes of M = Cr, Mo, W could be isolated from the appropriate ligand substitution reaction of $Cr(CO)_4(\eta^{2:2}$-1,5-cyclooctadiene), $Mo(CO)_4(\eta^{2:2}$-norbornadiene), and $W(CO)_5(\eta^2$-bis(trimethylsilyl)ethyne), respectively, with *N*,*N*′-bis(ferrocenylmethylene)ethylenediamine and characterized by using spectroscopic techniques. A recent paper has already reported the synthesis and cyclodextrin-encapsulation of two complexes for chromium and molybdenum, though on a different route [13]. Here we report the synthesis and characterization of $M(CO)_4$(bfeda) for all the three metals of Group 6 along with the results of electrochemical investigation. In the case of $W(CO)_4$(bfeda), there exists indeed evidence for the electron transfer from iron to tungsten.



N,N'-bis(ferrocenylmethylene)ethylenediamine, bfeda

2. Experimental

2.1. General remarks

All reactions and manipulations were carried out either in a vacuum or under a dry and oxygen-free nitrogen atmosphere. Solvents were distilled after refluxing over metallic sodium or phosphorous pentoxide for 3–4 days and stored under nitrogen until used.

Analytical grade and deuterated solvents, hexacarbonylchromium(0), hexacarbonylmolybdenum(0), hexacarbonyltungsten(0), 1,5-cyclooctadiene, norbornadiene, bis(trimethylsilyl)ethyne, and ferrocenecarboxaldehyde were purchased from Aldrich Chemical Co. Ltd., Dorset, England, and used as received. The ethylenediamine was purchased from Merck, Darmstadt, Germany. The thermal reactions and other treatments of organometallic compounds such as purification and crystallization were followed by taking IR spectra from solutions on a Perkin–Elmer 16 PC FT-IR spectrometer. The Raman spectrum was recorded by using a Bruker FRA 106/S Spectrometer with Opus software. NMR spectra were recorded on a Bruker Avance DPX 400 (400.1 MHz for ^1H; 100.6 MHz for ^{13}C). TMS was used as internal reference for ^1H and ^{13}C NMR chemical shifts. FAB-MS was done on a Fisons VG Autospec with *m*-nitrobenzylalcohol as matrix. Elemental analyses were performed on a LECO CHNS-932 instrument. The UV–Vis electronic absorption spectra were taken on Hewlett–Packard 8452A Model Diode Array Spectrophotometer with UV–Vis ChemStation software. Electrochemical measurements were performed using either Gammry potentiostat (equipped with PHE 200 Physical Electrochemistry software and PV220 Pulse voltammetry software) or HEKA IEEE 488 model potensiostat. A Pt disc ($d = 1$ mm) working, a Pt coil counter, and a SCE reference electrode were used for cyclic voltammetry (CV) and differential pulse voltammetry (DPV) studies.

The starting complexes, tetracarbonyl($\eta^{2:2}$-1,5-cyclooctadiene)chromium(0), $Cr(CO)_4(\eta^{2:2}$-cod) [14], tetracarbonyl(bicyclo[2.1.1]hepta-2,5-diene)molybdenum(0), $Mo(CO)_4(\eta^{2:2}$-NBD) [15], and tetracarbonyl(bis(trimethylsilyl)ethyne)tungsten(0), $W(CO)_5(\eta^2$-btmse) [16] were prepared as described in the literature.

2.2. *N,N′-Bis(ferrocenylmethylene)ethylenediamine (bfeda)*

N,*N*′-Bis(ferrocenylmethylene)ethylenediamine (bfeda) was prepared by using the procedure given for similar ferrocenylimines [13,17]. Ferrocenecarboxaldehyde (1.01 g, 4.71 mmol) was dissolved completely in benzene (30 mL) at room temperature. Then, 0.152 g (2.35 mmol) of ethylenediamine was added to the solution. The flask containing the reaction mixture was connected to a condenser equipped with a Dean–Stark apparatus and refluxed for 4 h in a glycerin bath. The solvent was evaporated and the residue was dissolved in 10 mL of CH_2Cl_2 and left at −35 °C. After decantation of the mother liqueur, the crystals were dried in vacuum: 0.90 g, 85% yield. IR (benzene) ν(C=N): 1644 cm^{-1}. Raman ν(C=N): 1644 cm^{-1}; UV–Vis (λ nm in CH_2Cl_2): 234 ($\varepsilon = 2.96 \times 10^4$ L mol^{-1} cm^{-1}), 267 ($\varepsilon = 1.65 \times 10^4$ L mol^{-1} cm^{-1}), 346 ($\varepsilon = 0.27 \times 10^4$ L mol^{-1} cm^{-1}) and 460 nm ($\varepsilon = 0.11 \times 10^4$ L mol^{-1} cm^{-1}). ^1H NMR (δ ppm, relative to TMS, in $CDCl_3$): 8.11 (s, H6), 3.74 (s, H8), 4.10 (s, H1′–H5′), 4.72 (s, H2, H5), 4.33 (s, H3, H4) ppm; ^{13}C NMR (δ ppm, relative to TMS, in $CDCl_3$): 162.7 (C6), 80.9 (C1), 70.7 (C2, C5), 69.4 (C1′–C5′), 68.7 (C3, C4), and 62.7 (C8) ppm; CV (200 mV/s, relative to SCE, in CH_2Cl_2): oxidation potential: 0.803 V; reduction potential: 0.574 V.

2.3. *Tetracarbonyl(N,N′-bis(ferrocenylmethylene)-ethylenediamine)chromium(0) $Cr(CO)_4$(bfeda) (**1**)*

A quantity of 0.100 g (0.365 mmol) of $Cr(CO)_4(\eta^{2:2}$-COD) was dissolved in toluene (15 mL) and 0.113 g

(0.250 mmol) of bfeda was added gradually to this solution. The mixture was stirred for 2 h with a magnetic stirrer at 38 °C until the starting material was no longer observed in the IR spectrum (ca. 4 h). When the reaction was completed, volatiles were removed by evaporation under vacuum, the dark red residue was dissolved in 1:1 CH_2Cl_2/toluene mixture, and the solution was left overnight at −35 °C. The yellow precipitate was separated from the supernatant solution and dried under vacuum: 0.14 g, 62% yield. Anal. Calc. for $C_{28}H_{24}O_4N_2Fe_2Cr$ (MW: 616.2): C, 54.58; H, 3.93; N, 4.55. Found: C, 54.9; H, 4.02; N, 4.42%. MS: *m*/*z* 616 (M^+). IR (in CH_2Cl_2): $\nu(CO) = 2004, 1887, 1870, 1822\ cm^{-1}$; $\nu(C{=}N) = 1620\ cm^{-1}$. ^1H NMR (δ ppm, relative to TMS, in CD_2Cl_2): 8.50 (s, H6), 5.09 (s, H2, H5), 4.59 (s, H3, H4), 4.26 (s, H1′–H5′), 3.67 (s, H8). ^{13}C NMR (δ ppm, relative to TMS, in CD_2Cl_2): 228.5 (CO *trans* to bfeda), 217.3 (CO *cis* to bfeda), 171.1 (C6), 78.3 (C1), 72.5 (C2, C5), 72.3 (C3, C4), 70.1 (C1′–C5′), 66.1 (C8). UV–Vis (λ nm in CH_2Cl_2): 233 ($\varepsilon = 3.92 \times 10^4\ L\ mol^{-1}\ cm^{-1}$), 269 ($\varepsilon = 2.31 \times 10^4\ L\ mol^{-1}\ cm^{-1}$), 340 ($\varepsilon = 0.62 \times 10^4\ L\ mol^{-1}\ cm^{-1}$) and 450 nm ($\varepsilon = 0.27 \times 10^4\ L\ mol^{-1}\ cm^{-1}$). CV (200 mV/s, relative to SCE, in CH_2Cl_2): oxidation potential: 0.397, 0.718, 0.930, 1.13 V; reduction potential: 0.273, 0.636, 0.726 V.

2.4. Tetracarbonyl(N,N′-bis(ferrocenylmethylene)-ethylenediamine)molybdenum(0) Mo(CO)4(bfeda) (2)

A quantity of 0.450 g (1.42 mmol) of $Mo(CO)_4(\eta^{2:2}$-NBD) was dissolved in toluene (15 mL) and 0.580 g (1.28 mmol) of *N*,*N*′-bis(ferrocenylmethylene)ethylenediamine (bfeda) was added to the solution with stirring at room temperature. The mixture was stirred with a magnetic stirrer until the starting material was no longer observed in the IR spectrum (ca. 3 days). After the reaction was completed the solvent was evaporated in a vacuum. The solid residue was dissolved in *n*-hexane and the solution was left overnight at −35 °C. An orange precipitate was separated from the supernatant solution and dried under vacuum: 0.64 g, 68% yield. Anal. Calc. for $C_{28}H_{24}O_4N_2Fe_2Mo$ (MW: 662.0): C, 50.95; H, 3.66; N, 4.24. Found: C, 49.5; H, 3.60; N, 4.20%. MS: *m*/*z* 662 (M^+). IR (in CH_2Cl_2): $\nu(CO) = 2011, 1894, 1875, 1824\ cm^{-1}$; $\nu(C{=}N) = 1618\ cm^{-1}$. UV–Vis (λ nm in CH_2Cl_2): 236 ($\varepsilon = 4.78 \times 10^4\ L\ mol^{-1}\ cm^{-1}$), 259 ($\varepsilon = 3.68 \times 10^4\ L\ mol^{-1}\ cm^{-1}$), 304 ($\varepsilon = 1.41 \times 10^4\ L\ mol^{-1}\ cm^{-1}$), 348 ($\varepsilon = 1.25 \times 10^4\ L\ mol^{-1}\ cm^{-1}$), 480 nm ($0.24 \times 10^4\ L\ mol^{-1}\ cm^{-1}$). ^1H NMR (δ ppm, relative to TMS, in CD_2Cl_2): 8.44 (s, H6), 5.15 (t, H2, H5, $J = 2.4$ Hz), 4.61 (t, H3, H4 $J = 2.4$ Hz), 4.27 (s, H1′–H5′), 3.76 (s, H8). ^{13}C NMR (δ ppm, relative to TMS, in CD_2Cl_2): 222.5 (CO *trans* to bfeda), 207.9 (CO *cis* to bfeda), 170.8 (C6), 77.7 (C1), 72.6 (C2, C5), 72.3 (C3, C4), 70.1 (C1′–C5′), 66.6 (C8) ppm. CV (200 mV/s, CH_2Cl_2): oxidation potential: 0.680, 0.845, 0.973, 1.100 V; reduction potential: 0.990, 0.704 V.

2.5. Tetracarbonyl(N,N′-bis(ferrocenylmethylene)-ethylenediamine)tungsten(0) W(CO)4(bfeda) (3)

An amount of 0.1 g (0.20 mmol) of $W(CO)_5(\eta^2$-btmse) was dissolved in dicholoromethane (25 mL). To this solution, 0.09 g (0.20 mmol) of bfeda was added and stirred for 3 days with magnetic stirrer. The formation of $W(CO)_4$(bfeda) with some side products and $W(CO)_6$ were observed from IR spectrum on the following day. The solution was then dried in vacuum and washed with *n*-hexane for several times. The purification process was continued by recrystallization of the remaining residue in CH_2Cl_2 solution at −35 °C: 0.09 g, yield 65%. Anal. Calc. for $C_{28}H_{24}O_4N_2Fe_2W$ (M = 748.1): C, 44.96; H, 3.23; N, 3.74. Found: C, 45.1; H, 3.24; N, 3.81%. MS: *m*/*z* 748 (M^+). IR (in CH_2Cl_2): $\nu(CO) = 2005, 1882, 1863, 1819\ cm^{-1}$; $\nu(C{=}N) = 1614\ cm^{-1}$. UV–Vis (λ nm in CH_2Cl_2): 237 ($\varepsilon = 3.53 \times 10^4\ L\ mol^{-1}\ cm^{-1}$), 250 ($\varepsilon = 3.37 \times 10^4\ L\ mol^{-1}\ cm^{-1}$), 277 ($\varepsilon = 1.83 \times 10^4\ L\ mol^{-1}\ cm^{-1}$), 306 ($\varepsilon = 0.96 \times 10^4\ L\ mol^{-1}\ cm^{-1}$), 351 ($\varepsilon = 0.11 \times 10^4\ L\ mol^{-1}\ cm^{-1}$), 477 nm ($\varepsilon = 0.28 \times 10^4\ L\ mol^{-1}\ cm^{-1}$). ^1H NMR (δ ppm, relative to TMS, in CD_2Cl_2): 8.43 (s, H6), 5.16 (s, H2, H5), 4.64 (s, H3, H4), 4.27 (H1′–H5′), 3.84 (s, H8). ^{13}C NMR (δ ppm, relative to TMS, in CD_2Cl_2): 214.1 (CO *trans* to bfeda), 204.9 (CO *cis* to bfeda), 170.6 (C6), 77.2 (C1), 72.6 (C2, C5), 72.4 (C3, C4), 69.8 (C1′–C5′), 67.5 (C8) ppm. CV (200 mV/s, CH_2Cl_2): oxidation potential: 0.648, 0.810, 0.973, 1.08 V; reduction potential: 0.754, 0.998 V.

2.6. Pentacarbonyl(N,N′-bis(ferrocenylmethylene)-ethylenediamine)tungsten(0) W(CO)5(bfeda) (4)

A quantity of 0.1 g (0.20 mmol) $W(CO)_5(\eta^2$-btmse) complex was dissolved in toluene (25 mL). To this solution, 0.09 g (0.20 mmol) of bfeda was added and the mixture was stirred with a magnetic stirrer until the starting material was no longer observed in the IR spectrum (ca. 1 day). The solution was dried in vacuum. The solid residue was dissolved in *n*-hexane and crystallized at −35 °C. Red crystals were obtained: 9.2 mg, 6% yield. IR (in *n*-hexane): $\nu(CO) = 2067$ s, 1966 vw, 1960 vs, 1922 s, 1915 sh cm^{-1}; $\nu(C{=}N) = 1605, 1652\ cm^{-1}$; ^1H NMR (δ ppm, relative to TMS, in *d*-toluene): 8.51 (s, H6), 8.16 (s, H11), 4.55 (s, H2, H5), 4.40 (s, H3, H4), 4.10 (s, H13, H16), 4.08 (s, H14, H15), 4.02 (s, H8), 4.00 (s, H1′–H5′), 3.91 (s, H12′–H16′), 3.85 (s, H9); ^{13}C NMR (δ ppm, relative to TMS, in *d*-toluene): 201,6 (CO *trans* to bfeda), 199.6 (CO *cis* to bfeda), 175.0 (C6), 162.6 (C11), 80.6 (C1), 74.1 (C12), 72.7 (C2, C5), 72.4 (C3, C4), 70.3 (C13, C16), 69.7 (C1′–C5′), 69.0 (C12′–C16′), 68.6 (C14, C15), 62.9 (C8), 59.9 (C9).

3. Results and discussion

The ligand substitution reactions of the following complexes result in the formation of tetracarbonyl(*N*,*N*′-

bis(ferrocenylmethylene)ethylenediamine)metal(0) in high yield:

$$\mathrm{Cr(CO)_4(\eta^{2:2}\text{-}COD) + bfeda} \xrightarrow[\text{toluene}]{} \underset{\mathbf{1}}{\mathrm{Cr(CO)_4}}\mathrm{(bfeda) + COD} \tag{1}$$

$$\mathrm{Mo(CO)_4(\eta^{2:2}\text{-}NBD) + bfeda} \xrightarrow[\text{toluene}]{} \underset{\mathbf{2}}{\mathrm{Mo(CO)_4}}\mathrm{(bfeda) + NBD} \tag{2}$$

$$\mathrm{W(CO)_5(\eta^{2}\text{-}btmse) + bfeda} \xrightarrow[\text{toluene}]{} \underset{\mathbf{3}}{\mathrm{W(CO)_4}}\mathrm{(bfeda) + btmse + CO} \tag{3}$$

In the case of $W(CO)_5(\eta^2\text{-btmse})$, the alkyne substitution occurs first forming pentacarbonyl(*N*,*N*′-bis(ferrocenylmethylene)ethylenediamine)tungsten(0), $W(CO)_5$(bfeda) (**4**), as intermediate which undergoes the ring closure reaction yielding the ultimate product $W(CO)_4$(bfeda) (**3**). All three tetracarbonyl(bfeda)metal(0) complexes **1**, **2**, and **3** plus the intermediate complex $W(CO)_5$(bfeda) (**4**) could be isolated from the reaction solution as analytically pure crystalline materials and characterized by elemental analysis, MS, UV–Vis, IR, ^{1}H and ^{13}C NMR spectroscopy.

The infrared spectra of three $M(CO)_4$(bfeda) complexes (M = Cr, Mo, W) exhibit four absorption bands in the CO stretching region along with a band due to the C=N stretching (Table 1). The observation of four CO stretching bands indicates a C_{2v} symmetry for the $M(CO)_4$ moiety with vibrational modes of $2A_1 + B_1 + B_2$ [18]. The C=N stretching frequency of the imine bonds in bfeda molecule decreases by 30–24 cm^{-1} upon coordination to the $M(CO)_4$ fragment [19] indicating a weakening of C=N bond. The decrease in the C=N stretching frequencies is in the order $Cr < Mo < W$ which can be attributed to the increasing π-back bonding.

As illustrated in Fig. 1 for **2**, the ^{13}C NMR spectra of all three complexes **1**–**3** exhibit one signal for the imine carbons (C6), one signal for the ethylene carbons (C8), four signals for the ferrocenyl groups and two signals for the carbonyl ligands (Table 2). Of the latter two, the signal at higher chemical shift can readily be assigned to the CO groups *trans* to the bfeda ligand, as observed for similar complexes [20]. With the exception of C1, all the carbons of bfeda show deshielding upon coordination, indicating that the bfeda molecule acts mainly as a σ-donor ligand. It is noteworthy that the deshielding of the C6 atoms upon coordination of free bfeda molecule to the metal centers decreases on going from chromium to molybdenum and tungsten (Δδ; 8.6, 8.1, 7.9 ppm, respectively). This might be attributed to the increasing π-contribution to the metal–ligand bond by going down in Group 6 metals.

Table 1
The CO and C=N stretching frequencies (cm^{-1}) of $M(CO)_4$(bfeda) complexes (M = Cr, Mo, W) in CH_2Cl_2

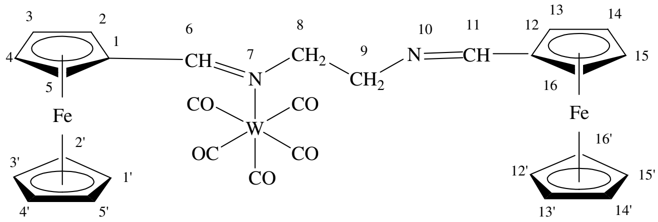
Complex	ν(CO)				ν(C=N)
	$A_1^{(2)}$	B_1	$A_1^{(1)}$	B_2	
$Cr(CO)_4$(bfeda) (**1**)	2004	1887	1870	1822	1620
$Mo(CO)_4$(bfeda) (**2**)	2011	1894	1875	1824	1618
$W(CO)_4$(bfeda) (**3**)	2005	1882	1863	1819	1614

The ^{1}H NMR spectra of the $M(CO)_4$(bfeda) complexes show a pattern similar to that of the free bfeda molecule, except that all signals are shifted to the lower field as expected for a σ-donor ligand (Table 3). Assignment of the signals was made by comparing the chemical shifts of hydrogen nuclei with the values reported for the substituted ferrocenes [21].

The complex $W(CO)_5$(bfeda) (**4**) was also characterized by spectroscopic techniques. The IR spectrum of **4**, Fig. 2, essentially shows five absorption bands in the CO stretching region indicating a distorted C_{4v} symmetry with a split E mode and a weakly allowed B_2 mode for the $W(CO)_5$ moiety [16]. Two absorption bands are observed for the C=N stretching; one for the uncoordinated imine group (1652 cm^{-1}) and one for the imine group coordinated to the tungsten metal center (1605 cm^{-1}).

The ^{13}C–{^{1}H} NMR spectrum gives two signals with a relative intensity ratio of 1:4 for the carbonyl ligands and 12 signals for the bfeda ligand indicating that the bfeda molecule is coordinated asymmetrically as monodentate ligand. The imine carbons of bfeda resonate at 175.0 and 162.6 ppm; the signal at lower field is due to the coordinated one. All the other signals were assigned by comparing them with the respective signals of the complex **3** and the free bfeda molecule.

In the ^{1}H NMR spectrum of **4** two signals are observed for the imine protons, one (8.51 ppm) for the coordinated and one (8.16 ppm) for the uncoordinated imine group. All the other signals were assigned by comparing them with the signals of the complex **3** and the free bfeda molecule.



The electronic absorption spectrum of bfeda consists of four absorption bands at 234, 267, 346 and 460 nm. The first two bands are assigned to charge transfer transitions while the latter two to d–d transitions in comparison with the spectrum of ferrocene [22]. The electronic absorption spectral data of the complexes **1**, **2**, **3** and the free bfeda molecule are listed in Table 4. The complexes show essentially the same absorption pattern for the bfeda ligand plus one additional absorption due to charge transfer transition on the central metal atom. However, in the spectrum of **1**, a d–d transition on the chromium is not observed, while the **2** and **3** give one more absorption due to the d–d transition on the iron center. The bands at 304 and 306 nm are assigned to the d–d transition of Mo(0) and W(0) by

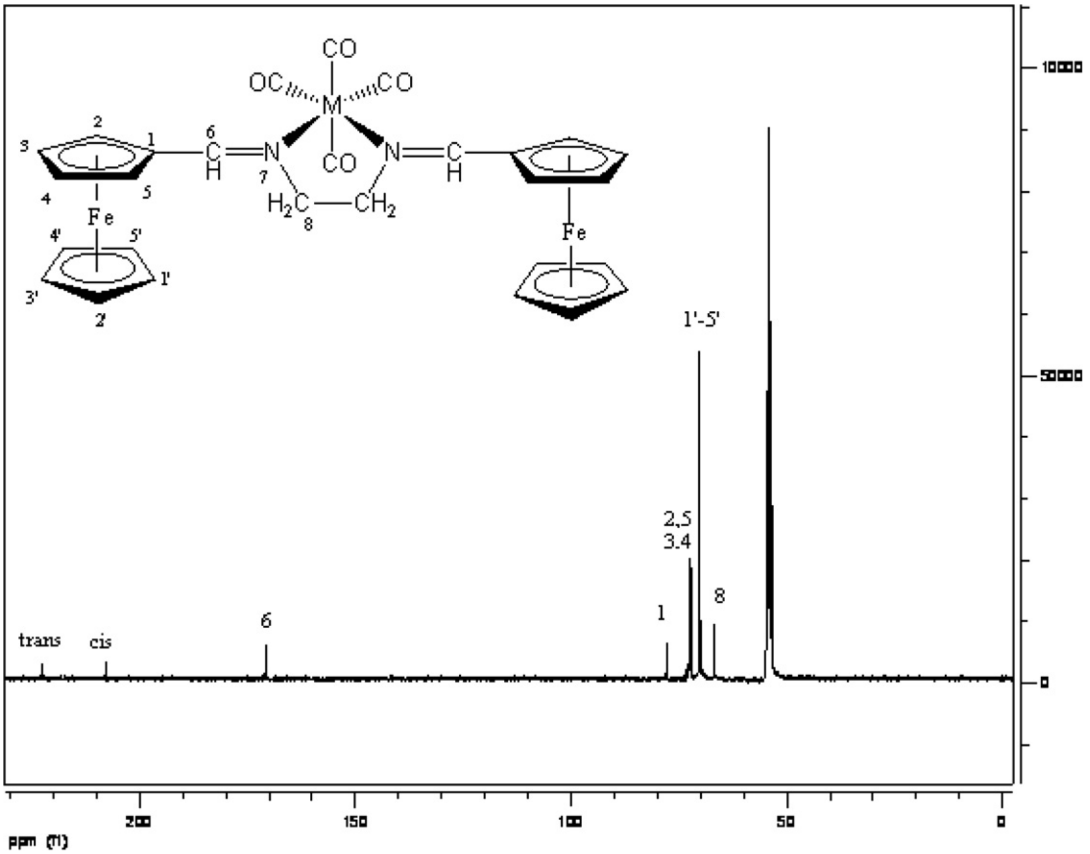


Fig. 1. The ^{13}C–{^{1}H}-spectrum of $Mo(CO)_4$(bfeda) in CD_2Cl_2.

Table 2
^{13}C NMR chemical shifts (δ, in ppm) of bfeda and $M(CO)_4$(bfeda) complexes

Compound	C1	C2, C5	C3, C4	C1′–C5′	C6	C8	CO(*trans*)	CO(*cis*)
bfeda	80.9	70.7	68.7	69.4	162.7	62.7	–	–
$Cr(CO)_4$(bfeda) (**1**)	78.3 (−2.6)	72.5 (1.8)	72.3 (3.5)	70.1 (0.4)	171.1 (8.4)	66.1 (3.5)	228.5	217.3
$Mo(CO)_4$(bfeda) (**2**)	77.7 (−3.2)	72.6 (1.9)	72.3 (3.5)	70.1 (0.4)	170.8 (8.1)	66.6 (4.0)	222.5	207.9
$W(CO)_4$(bfeda) (**3**)	77.2 (−3.7)	72.6 (1.9)	72.4 (3.6)	69.8 (0.1)	170.6 (7.9)	67.5 (4.9)	214.1	204.9

The coordination shifts ($\Delta\delta$, in ppm) are also given for the complexes in parentheses with respect to the free bfeda molecule.

Table 3
^{1}H NMR chemical shifts of bfeda and $M(CO)_4$(bfeda) (M = Cr, Mo, W) complexes

Compound	H2, H5	H3, H4	H1′–H5′	H6	H8
bfeda	4.72	4.33	4.10	8.11	3.74
$Cr(CO)_4$(bfeda) (**1**)	5.09 (0.37)	4.59 (0.26)	4.26 (0.16)	8.50 (0.39)	3.67 (−0.07)
$Mo(CO)_4$(bfeda) (**2**)	5.15 (0.43)	4.61 (0.28)	4.27 (0.17)	8.44 (0.33)	3.76 (0.02)
$W(CO)_4$(bfeda) (**3**)	5.16 (0.44)	4.64 (0.31)	4.27 (0.17)	8.43 (0.32)	3.84 (0.1)

comparing with the reported values of similar complexes [23]. The complex **3** exhibits one more absorption due to charge transfer transition of the ferrocenyl units.

4. Electrochemical studies

Fig. 3a gives the CVs of the complexes **1**, **2** and **3** and the bfeda molecule in dichloromethane solution. A reversible oxidation/reduction is observed at 0.803 and 0.574 mV, respectively, in the CV of bfeda taken at 200 mV/s scan rate. The ratio of cathodic peak current to anodic peak current, I_a/I_c, is almost unity at all scan rates which is a compelling evidence for the reversibility of electron transfer reaction. In line with the presence of two ferrocenyl subunits, the controlled potential coulometry showed that oxidation was completed after the passage of 2 F per mole of bfeda. Hence, the bfeda molecule can be considered as a two-electron reservoir.

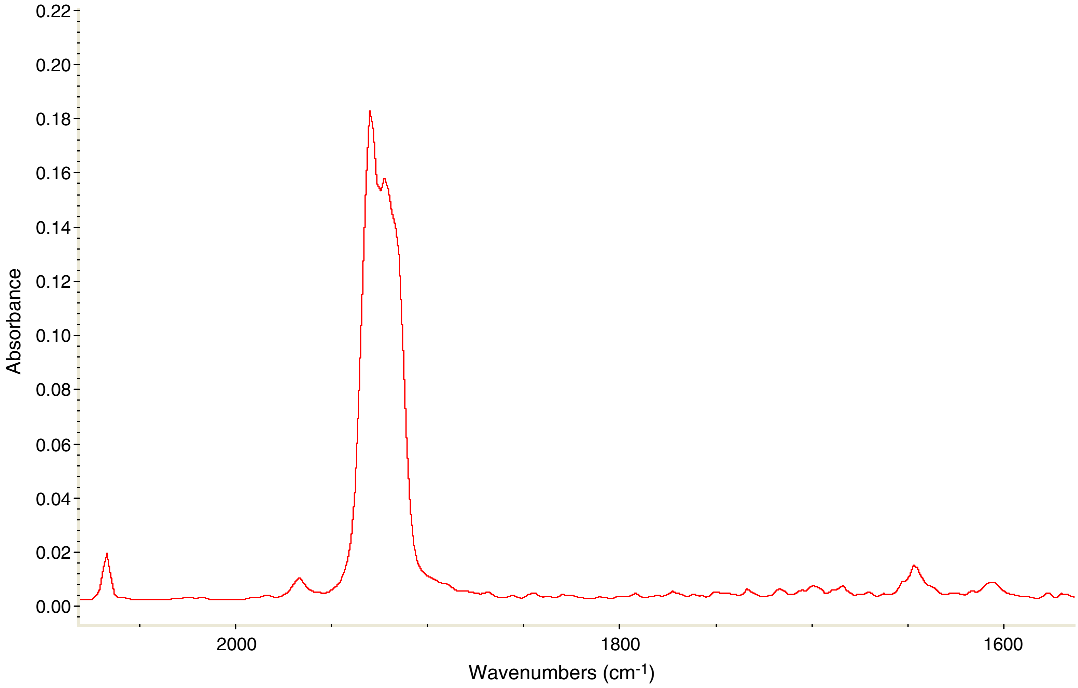


Fig. 2. Part of the IR spectrum of $W(CO)_5(bfeda)$ (**4**), recorded from *n*-hexane solution, showing $\nu(CO)$ bands at 2067 s, 1966 vw, 1960 vs, 1922 s, 1915 sh cm^{-1}; and $\nu(C{=}N)$ bands at 1652, 1605 cm^{-1}.

Table 4
The electronic absorption spectral data of bfeda and $M(CO)_4(bfeda)$ (M = Cr, Mo, W) complexes in dichloromethane at room temperature

Compound	λ (nm) CT	λ (nm) CT	λ (nm) d–d transition on central metal	λ (nm) d–d transition on iron center
bfeda	234	267	–	346, 460
$Cr(CO)_4(bfeda)$ (**1**)	233	269	–	340
$Mo(CO)_4(bfeda)$ (**2**)	236	259	304	348, 480
$W\ (CO)_4(bfeda)$ (**3**)	237	250, 277	306	351, 477

Four oxidation peaks are observable in the CV of the complexes **1**, **2** and **3** (Fig. 3a). The first and fourth oxidations belong to the central metal fragment while the second and third oxidations are assigned to sequential oxidations of Fe(II) centers of two ferrocenyl groups. The first oxidation peak of $Cr(CO)_4(bfeda)$ is reversible whereas the corresponding peaks of the Mo and W analogues are irreversible in agreement with the literature [24]. The oxidation potential of ferrocenyl units in bfeda increases by about 20–100 mV upon coordination. This shift is readily attributed to the electron donation from bfeda to the $M(CO)_4$ group making iron centers slightly more difficult to oxidize than that of free bfeda. The two equivalent ferrocenyl groups are no longer independent of each other in the $M(CO)_4(bfeda)$ complexes; rather, they are electronically communicating through the central metal atom, leading to two distinct reversible oxidation processes, which are not fully resolved. However, the separation between the two ferrocenyl oxidation peaks increases in the order Cr < Mo < W as seen more easily by differential pulse voltammograms (Fig. 3b).

In order to investigate the origins of electron transfer reactions, constant potential electrolysis of the complexes was carried out successively at their peak potentials at 0 °C in their CH_2Cl_2 solution and the electrolysis was followed by in situ recording the electronic absorption spectra in every 5 mC. The constant potential electrolysis of **1** differs from **2**, **3** in a way that the central Cr(0) metal atom is oxidized first and electrolysis continues with oxidations of two ferrocenyl groups until the end of totally three moles of electron passage per mole of complex. The molybdenum and tungsten complexes show a different behavior in electrolysis as illustrated in Fig. 4a for the complex **3**. During the constant potential electrolysis of **3** at its first oxidation potential, the absorption bands at 237 and 277 nm decrease in intensity and shift to 245 and 269 nm, respectively, while the d–d transition band of tungsten center at 306 nm gradually gains intensity and shifts to 298 nm. One of the d–d transition bands due to Fe centers also loses intensity and undergoes a red shift from 354 to 372 nm, while the lower energy d–d transition band at 477 nm gradually gains intensity and shifts to 510 nm. The observation of two isosbestic points at 280 and 330 nm indicates a straightforward conversion.

When the one-electron transfer is over, the potential was increased to the second peak potential and electrolysis continued at this potential until two-electron transfer is over. Similar changes are observed in the electronic absorption spectra during this period. Upon further electrolysis at the third oxidation potential and then fourth oxidation

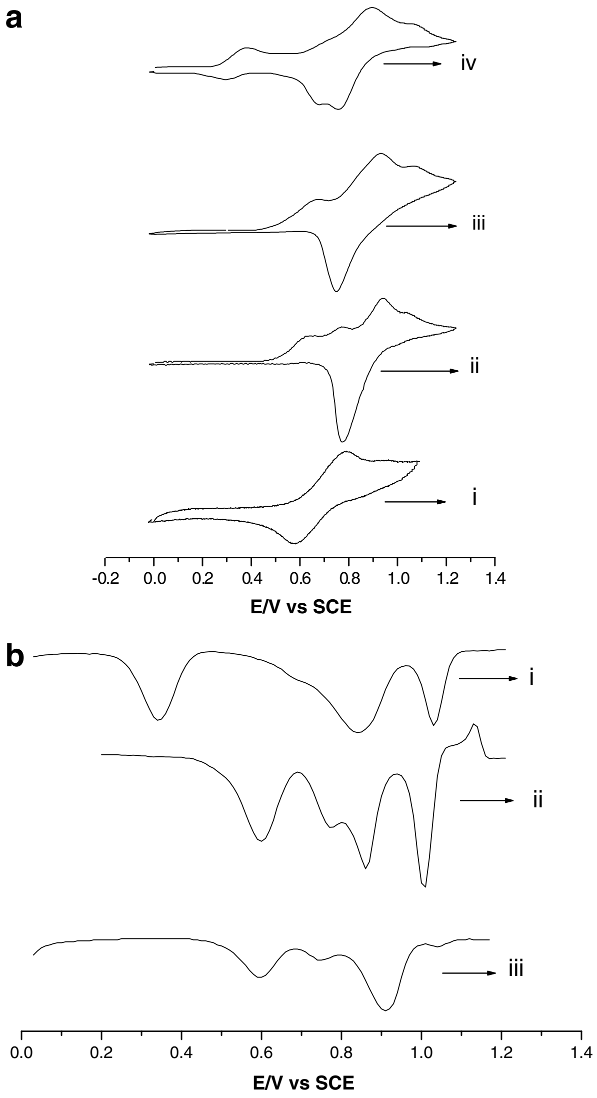


Fig. 3. (a) CV of bfeda (i), $W(CO)_4$(bfeda) (ii), $Mo(CO)_4$(bfeda) (iii), and $Cr(CO)_4$(bfeda) (iv) taken at a scan rate of 200 mV/s in dichloromethane solution. (b) DPV of $Cr(CO)_4$(bfeda) (i), $Mo(CO)_4$(bfeda) (ii), and $W(CO)_4$(bfeda) (iii) measured in dichloromethane solution.

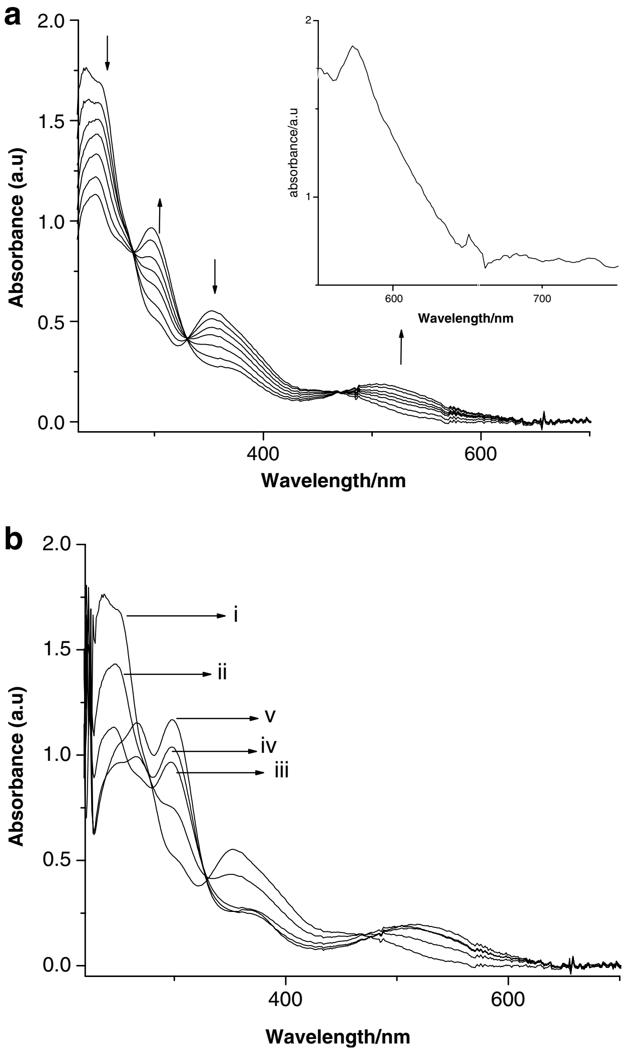


Fig. 4. The changes in the electronic absorption spectrum of 5×10^{-5} M $W(CO)_4$(bfeda) solution in dichloromethane during electro-oxidation: (a) during the first two moles of electron passage. The inset: electronic absorption spectrum of 5×10^{-3} M $W(CO)_4$(bfeda) solution in dichloromethane, after two-electron transfer. (b) Before electrolysis (i), after one-electron transfer (ii), after two-electron transfer (iii), after three-electron transfer (iv), and after four-electron transfer (v).

potential, the shoulder at 276 nm starts to gain intensity forming a well defined absorption band. On the other hand, two lower energy bands, due to d–d transitions of Fe center, almost maintain their intensity until the third and fourth electron transfers are completed. The isosbestic points become ill defined during this period. These observations indicate that the electrode reactions are similar during the first two-electron transfer and that the first two oxidations are related to the iron centers in the bfeda ligand. In other words the spectral changes in the first two oxidations are ligand based. However, the CV and DPV data indicates that the first oxidation is related to the central metal. This implies on an electronic interaction of iron centers and tungsten metal atom. Further support for the electronic interaction between two metal centers comes from changes in the electronic absorption spectra recorded during the electrolysis of a concentrated solution of the complex **3** (the inset in Fig. 4a). A broad absorption band at about 576 nm grows in during the first two-electron transfer, which can be attributed to the formation of ferrocenium ion. This absorption is characteristic for the ferrocenium species [25] and is also observed at about 574 nm during the in situ electrooxidation of bfeda.

Taking together all the findings of CV, DPV and constant potential electrolysis we propose that the first oxidation of $W(CO)_4$(bfeda) ocurs on the tungsten center forming a short-lived species which undergoes an intramolecular one-electron transfer and is reduced back to W(0) while one of the ferrocene uits is oxidized to the ferrocenium cation at the same time. Oxidation mechanism of the $W(CO)_4$(bfeda) is outlined as follows: (i) First oxidation of tungsten from W^0 to W^+ and then self reduction of tungsten(+1) to tungsten(0) by intramolecular electron transfer from iron(+2) centers which is then oxidized to iron(+3). (ii) Oxidation of second ferrocene moiety, changing the oxidation state of iron center from (+2) to (+3). (iii) Oxidation of tungsten center, changing the oxidation state of tungsten from (0) to (+1). (iv) Oxidation of tungsten center, changing the oxidation state of tungsten from (+1) to (+2).

5. Conclusions

$M(CO)_4$(bfeda) (M = Cr, Mo, W) complexes are readily accessible by substitution reaction of appropriate labile starting materials with *N*,*N*′-bis(ferrocenylmethylene)ethylenediamine (bfeda). They could be isolated from the reaction solution as analytically pure solids and characterized by elemental analysis, MS, UV–Vis, IR, ^{1}H NMR, and ^{13}C NMR spectroscopies. Although the free bfeda molecule has two isolated ferrocene units, two iron centers in the $M(CO)_4$(bfeda) complexes are in interaction with each other through the Group 6 metal atom. Thus, readily oxidizable ferrocene unit can provide electron for the central metal atom. In other words, the bfeda ligand acts as an electron reservoir. This feature makes the complexes favorable for electrocatalysis.

Acknowledgements

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References

[1] Gmelin Handbook of Inorganic and Organometallic Chemistry, eighth ed., Fe Organic Compounds, vol. A10, Springer, Berlin, 1991.
[2] A. Togni, T. Hayashi, Ferrocenes – Homogeneous Catalysis, Organic Synthesis, Materials Science, VCH, Weinheim, 1995.
[3] P.D. Beer, D.K. Smith, Prog. Inorg. Chem. 46 (1997) 1.
[4] J.S. Miller, A.J. Epstein, Angew. Chem., Int. Ed. Engl. 33 (1994) 385.
[5] N.J. Long, Angew. Chem., Int. Ed. Engl. 34 (1995) 21.
[6] H.J. Coles, S. Meyer, P. Lehmann, R. Deschenaux, I. Juaslin, J. Mater. Chem. 9 (1999) 1085.
[7] C. Ganter, C. Kaulen, U. Englert, Organometallics 18 (1999) 5444.
[8] H.Y. Zhang, J. Lei, Y. Chen, L. Lin, Q. Wu, H.Q. Zhang, Synth. React. Inorg. Met.-Org. Chem. 31 (2001) 1053.
[9] K.S. Coleman, S. Turberville, S.I. Pascu, M.L.H. Green, J. Organomet. Chem. 689 (2004) 770.
[10] B. Bildstein, M. Malaun, H. Kopacka, K. Wurst, M. Mitterboeck, K.H. Ongania, G. Opromolla, P. Zanello, Organometallics 18 (1999) 4325.
[11] B. Bildstein, M. Malaun, H. Kopacka, M. Fontani, P. Zanello, Inorg. Chim. Acta 300–302 (2000) 16.
[12] R. Bosque, C. Lopez, J. Sales, X. Solans, M. Font-Bardia, J. Chem. Soc., Dalton Trans. (1994) 735.
[13] Z. Petrovski, S.S. Braga, S.S. Rodrigues, C.C.L. Pereira, I.S. Goncalves, M. Pillinger, C. Freire, C.C. Romao, New J. Chem. 29 (2005) 347–354.
[14] M. Kotzian, C.G. Kreiter, S. Özkar, J. Organomet. Chem. 229 (1982) 29.
[15] H. Werner, R. Prinz, Chem. Ber. 100 (1967) 265.
[16] F.W. Grevels, J. Jacke, R. Goddard, C.W. Lehmann, S. Özkar, S. Saldamli, Organometallics 24 (2005) 4613.
[17] A. Benito, J. Cano, R. Martinez-Manez, J. Soto, J. Paya, F. Lloret, M. Julve, J. Faus, D.M. Marcos, Inorg. Chem. 32 (1993) 1197.
[18] P.S. Braterman, Metal Carbonyl Spectra, Academic Press, London, 1975.
[19] J. Briyanga, J. Mol. Struct. 570 (2001) 109.
[20] For the metal–carbonyl complexes containing donor ligands, the *trans* carbonyl carbon is more deshielded than the *cis* one. G.E. Bodner, M.P. May, L.E. McKinney, Inorg. Chem. 19 (1980) 1951.
[21] T.E. Pickett, C.J. Richards, Tetrahedron Lett. 40 (1999) 5251.
[22] M.M. Rohmer, A. Veillard, M.H. Wood, Chem. Phys. Lett. 29 (1974) 466.
[23] (a) A.F. Schreiner, G.E. Ober, Inorg. Chem. 21 (1982) 3575;
(b) K.A. Rawling, A.J. Lees, Inorg. Chem. 28 (1989) 2154;
(c) A.J. Lees, J. Am. Chem. Soc. 104 (1982) 2038;
(d) P.C. Servaas, H.K. Van Dijk, T.L. Snoeck, D.J. Stufkens, A. Oskam, Inorg. Chem. 24 (1985) 4494.
[24] (a) W.Y. Wong, S.H. Cheung, S.M. Lee, S.Y. Leung, J. Organomet. Chem. 596 (2000) 36;
(b) F.E. Kühn, I.S. Goncalves, A.D. Lopes, J.P. Lopes, C.C. Romao, W. Wachter, J. Mink, L. Hajba, A.J. Parola, F. Pina, J. Sotomayor, Eur. J. Inorg. Chem. (1999) 295;
(c) R.J. Crutchley, A.B.P. Lever, Inorg. Chem. 21 (1982) 2276.
[25] Y.S. Sohn, D.N. Hendrickson, H.B. Gray, J. Am. Chem. Soc. 93 (1971) 3603.