

Synthesis, characterization, and electrochemistry of tetracarbonyl(6-ferrocenyl-2,2'-bipyridine)tungsten(0)

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Received 13 November 2006; received in revised form 29 December 2006; accepted 3 January 2007

Available online 14 January 2007

Abstract

6-Ferrocenyl-2,2'-bipyridine (fcbpy) was prepared by the reaction of lithiated ferrocene with bipyridine and employed as a bidentate ligand for the formation of tetracarbonyl(6-ferrocenyl-2,2'-bipyridine)tungsten(0). The labile complex pentacarbonyl[η^2 -bis(trimethylsilyl)ethyne]tungsten(0) reacts with fcbpy in CH_2Cl_2 to yield the disubstitution product, $\text{W}(\text{CO})_4(\text{fcbpy})$, which was isolated as analytically pure substance and characterized by elemental analysis, IR, UV–Vis, MS, ^1H and ^{13}C NMR spectroscopies. Electrochemistry of the fcbpy molecule and its complex $\text{W}(\text{CO})_4(\text{fcbpy})$ was studied by cyclic voltammetry and controlled potential electrolysis combined with UV–Vis spectrometer. In the cyclic voltammogram of both the fcbpy molecule and its complex, an irreversible reduction and a reversible oxidation are assigned to the bipyridine and ferrocene moieties, respectively. The $\text{W}(\text{CO})_4(\text{fcbpy})$ complex exhibits additionally two irreversible oxidations due to the tungsten centered electron transfer reactions.

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Keywords: Ferrocene; Bipyridine; Carbonyl; Tungsten; Electrochemistry; Synthesis

1. Introduction

Ferrocene [1] is a versatile building block for the preparation of compounds with tailor-made properties in many fields, such as organic synthesis, homogeneous catalysis, materials chemistry, and production of fine chemicals, due to its high stability and powerful electron-releasing ability and well-established methods for its incorporation into more complex structures [2]. Chemical stability and reversibility of the ferrocene/ferrocenium redox couple [3,4] have made ferrocene one of the most classical redox agents of organometallic chemistry [5]. Ferrocene has been used in the development of many new materials having interesting properties [6], including homogeneous catalysts [2], molecular sensors [7], molecular magnets [8], non-linear optic materials [9], and liquid crystals [10]. As part of an ongoing interest in transition metal compounds with electronically communicating metal centers linked by conju-

gated bridges, we thought that the Group 6 metal-carbonyl complexes of a ferrocene-functionalized imine ligand would be of interest to study the long-range metal–metal interactions. 2-Ferrocenylpyridine has been employed as such a ligand, however, none of the $\text{M}(\text{CO})_5(2\text{-ferrocenylpyridine})$ complexes ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) has been found to be stable because of the weak $\text{M} \rightarrow \text{N}$ backbonding [11]. Similar to the tetracarbonyl(ethylenediamine)tungsten(0) and tetracarbonyl(diimine)tungsten(0) complexes [12,13], 2,2'-bipyridine is known to form stable chelate complexes even with low valent transition metal ions [14–16]. Therefore, a bipyridine containing ferrocenyl moiety was considered to be convenient ligand forming stable chelate complexes with Group 6 metal carbonyls. 2,2'-Bipyridine consists of two planar pyridyl rings connected with covalent C–C bond and coordinates to metal with both nitrogens yielding the chelate ring [17,18]. The lone pair of nitrogen can form σ -bond with the central atom, while the aromatic system can take part in back-bonding. π -Electron density is delocalized over the chelate ring via the metal–diimine bonding. In the case

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of 6-ferrocenyl-2,2'-bipyridine complexes, an electronic communication is anticipated between two transition metal atoms through π -conjugation.

Here, we report the synthesis and characterization of 6-ferrocenyl-2,2'-bipyridine (fcbpy) and its tetracarbonyl-tungsten(0) complex, $W(CO)_4(fcbpy)$ for the first time. The ligand substitution reaction of pentacarbonyl(η^2 -bis(trimethyl)silylethyne)tungsten(0), $W(CO)_5(\eta^2\text{-btmse})$ [19] with 6-ferrocenyl-2,2'-bipyridine in dichloromethane yields the complex $W(CO)_4(fcbpy)$ which could be isolated from the solution as orange crystalline substance and characterized by elemental analysis, IR, UV-Vis, MS, 1H and ^{13}C NMR spectroscopies.

2. Experimental

2.1. Materials and methods

All reactions and manipulations were carried out either in vacuum or under a dry and O_2 free inert atmosphere (N_2 or Ar). Solvents were distilled after refluxing over Na or P_2O_5 for 3–4 days and stored under N_2 until used. Analytical grade and deuterated solvents, hexacarbonyl-tungsten(0), *n*-butyllithium (*n*BuLi, 2.5 M solution in *n*-hexane), bis(trimethyl)silylethyne (btmse), tetrabutylammonium tetrafluoroborate, and 2,2'-bipyridine were purchased from Aldrich and used without further purification. Ferrocene was obtained from Merck and used as received. Neutral aluminumoxide (Al_2O_3 , 70–230 mesh, Merck) was used for column chromatography in the purification of 6-ferrocenyl-2,2'-bipyridine and its complex. The thermal reactions and other treatments of metal carbonyl compounds such as purification and crystallization were followed by taking Infrared spectra from solutions on a Perkin-Elmer 16 PC FT-IR spectrometer. NMR spectra were recorded on a Bruker Advance DPX 400 spectrometer (400.1 MHz for 1H ; and 100.6 MHz for ^{13}C). TMS was used as internal reference for 1H and ^{13}C NMR chemical shifts. Mass spectra were taken on a Fisons VG Autospec with *m*-nitrobenzylalcohol as matrix at Colorado State University, Fort Collins, USA. Elemental analysis was carried out by using LECO CHNS-932 instrument at METU Central Laboratory. The UV-Vis spectra were taken from the dichloromethane solutions at room temperature by using Hewlett Packard 8453A Model Diode Array Spectrophotometer with UV-Visible ChemStation software. Electrochemical study was performed on A HEKA IEEE 488 model potentiostat under inert gas nitrogen atmosphere using anhydrous (*n*-Bu) $_4$ NBF $_4$ as electrolyte, Ag-wire or saturated calomel electrode (SCE) as the reference, platinum disc electrode as counter and platinum bead electrode as working electrode. The oxidation processes of 6-ferrocenyl-2,2'-bipyridine (fcbpy) and its complex $W(CO)_4(fcbpy)$ were carried out at 0 °C and at –21 °C, respectively, in their CH_2Cl_2 solutions at the peak potentials observed in cyclic voltammetry and followed by taking electronic absorption spectra at every 5 mC on a

Hewlett Packard 8453A Model Diode Array Spectrophotometer with UV-Visible ChemStation software.

Photochemical reactions were carried out in an immersion-well apparatus [20] (solidex glass, $\lambda > 280$ nm) using a Hanau TQ 150 high pressure mercury lamp, which was cooled by circulating H_2O or cold MeOH. Pentacarbonyl(η^2 -bis(trimethyl)silylethyne)tungsten(0), $W(CO)_5(\eta^2\text{-btmse})$ was prepared according to the literature procedure [19].

2.1.1. 6-Ferrocenyl-2,2'-bipyridine, fcbpy

This compound was prepared by using the literature procedure [21,22] as follows: in 10 mL tetrahydrofuran, 2.2 g (12 mmol) ferrocene was dissolved at 0 °C and 4.8 mL (12 mmol) of 2.5 M hexane solution of *t*-butyllithium was slowly added at 0 °C. After standing 15 min at 0 °C, the solution was warmed up to room temperature and the volatiles were removed in vacuum. The remaining solid was suspended in 30 mL diethyl ether and 1.87 g (12 mmol) of 2,2'-bipyridine was added to the solution cooled down to –70 °C under vigorous stirring. The reaction mixture was warmed up slowly to room temperature and stirred for three days before being hydrolyzed under aerobic conditions with 30 mL water. The organic layer was separated and the remaining solid in the water phase was further extracted with dichloromethane until the solution became almost colorless. The combined organic fraction was taken to dryness using rotary evaporator. The oily residue was transferred to a column (3 cm in diameter and 35 cm in height) packed with aluminum oxide in *n*-hexane. Ferrocene was first eluted with *n*-hexane and, then, a mixture of diethyl ether–dichloromethane (1:1) was used to elute the orange colored fraction containing 6-ferrocenyl-2,2'-bipyridine. After removing the solvents by using the rotary evaporator, the solid was crystallized from hexane:diethyl ether (4:1). (0.20 g, 26% yield). 1H NMR (δ in ppm, $CDCl_3$): 7.36 (d, 1H, $J_{4-5} = 7.8$ Hz, H-5), 7.65 (t, 1H, H-4), 8.14 (dd, 1H, $J_{3-4} = 7.7$ Hz, $J_{5-3} = 0.7$ Hz, H-3), 8.62 (d, 1H, $J_{6'-4'} = 1.7$ Hz, $J_{6'-3'} \approx 0$, H-6'), 7.24 (ddd, 1H, $J_{5'-6'} = 4.7$ Hz, $J_{5'-4'} = 7.8$ Hz, $J_{5'-3'} = 1.1$ Hz, H-5'), 7.78 (dt, 1H, H-4'), 8.51 (d, 1H, H-3'), 4.96 (t, 2H, $J_{\alpha-\beta} = 1.8$ Hz, α -C $_5$ H $_4$), 4.35 (t, 2H, β -C $_5$ H $_4$), 3.98 (s, 5H, unsub-C $_5$ H $_5$); ^{13}C NMR (δ in ppm, $CDCl_3$): 155.60, 154.272 (C-2, C-2'), 116.66 (C-3), 135.78, 135.76 (C-4, C-4'), 120.18 (C-3'), 119.01 (C-5), 122.52 (C-5'), 157.45 (C-6), 147.97 (C-6'), 68.78 (β -C $_5$ H $_4$), 66.44 (α -C $_5$ H $_4$), 83.13 (*i*-C $_5$ H $_4$), 68.58 (unsub. –C $_5$ H $_5$); UV-Vis (CH_2Cl_2): $\lambda(CT) = 234$ nm ($\epsilon = 3.3 \times 10^4$ L mol $^{-1}$ cm $^{-1}$), 286 nm ($\epsilon = 2.2 \times 10^4$ L mol $^{-1}$ cm $^{-1}$), $\lambda(d-d$ Fe(II)) = 354 nm ($\epsilon = 6.3 \times 10^3$ L mol $^{-1}$ cm $^{-1}$), 460 nm ($\epsilon = 2.9 \times 10^3$ L mol $^{-1}$ cm $^{-1}$); CV(CH_2Cl_2 , SCE): irrev. red. of bipyridine = –1.250 V, rev. ox. of ferrocenyl = 0.710 V.

2.1.2. Tetracarbonyl(6-ferrocenyl-2,2'-bipyridine)tungsten(0), $W(CO)_4(fcbpy)$ (I)

To a solution of 413 mg (0.835 mmol) $W(CO)_5(\eta^2\text{-btmse})$ in 15 mL dichloromethane at room temperature

was added 282 mg (0.835 mmol) fcbpy. The solution was stirred for 45 h at room temperature. The solvent was evaporated under vacuum. The dark red colored residue was dissolved in 1 ml dichloromethane and transferred onto a column (3 cm in diameter and 25 cm in height) packed with aluminum oxide in *n*-hexane. The unreacted fcbpy was first eluted with a 5:1 mixture of *n*-hexane and THF. Acetonitrile was used to elute the red fraction containing $W(CO)_4(fcbpy)$. The solvent was removed under vacuum (0.20 g, 38% yield). Anal. Calc. for $C_{24}H_{16}O_4N_2WFe$ ($M = 636.08$): C, 44.3; H, 2.83; N, 4.20. Found: C, 45.3; H, 2.54; N, 4.40%. MS $m/z = 636.0$ (M^+), 605.9 ($M^+ - CO$), 577.9 ($M^+ - 2CO$), 549.9 ($M^+ - 3CO$), 521.9 ($M^+ - 4CO$). IR(CH_2Cl_2): $\nu(CO) = 2005, 1884, 1870, 1823\text{ cm}^{-1}$; 1H NMR (δ in ppm, $CDCl_3$): 8.12 (d, 1H, $J_{3-4} = 8.1\text{ Hz}$, $J_{3-5} < 1.0\text{ Hz}$, H-3), 7.95 (t, 1H, $J_{4-5} = 7.5\text{ Hz}$,

H-4), 8.04 (d, 1H, H-5), 8.19 (dd, 1H, H-3'), 7.99 (dt, 1H, $J_{4'-3'} = 7.5\text{ Hz}$, H-4'), 7.42 (ddd, 1H, $J_{5'-4'} = 5.7\text{ Hz}$, $J_{5'-3'} = 1.8\text{ Hz}$, H-5'), 9.25 (dd, 1H, $J_{6'-5'} = 5.6\text{ Hz}$, $J_{6'-4'} < 1.0\text{ Hz}$, H-6'), 5.01 (t, 2H, $J_{\alpha-\beta} = 0.006\text{ Hz}$, α - C_5H_4), 4.60 (t, 2H, β - C_5H_4), 4.15 (s, 5H, unsub- C_5H_5); ^{13}C NMR (δ in ppm, $CDCl_3$): 216.44 (CO-2), $\delta = 212.08$ (CO-3), 202.77 (CO-1), 164.49 (C-6), 157.52 (C-2), 155.95 (C-2'), 153.08 (C-6'), 137.47 (C-4), 135.94 (C-4'), 129.20 (C-5), 125.58 (C-3), 123.30 (C-3'), 120.10 (C-5'), 88.80 (*i*- C_5H_4), 71.50 (β - C_5H_4), 69.90 (α - C_5H_4), 70.47 (unsub- C_5H_5); UV-Vis. (CH_2Cl_2): $\lambda(CT) = 230\text{ nm}$, 250 nm, $\lambda(d-d\text{ Fe(II)}) = 372\text{ nm}$, 468 nm; $\lambda(d-d\text{ W(0)}) = 308\text{ nm}$; CV(CH_2Cl_2 , SCE) rev. red. of bipyridine = -1.44 V , rev. ox. of bipyridine = -1.63 V , irrev. ox. ($W \rightarrow W^+$) = 0.58 V , irrev. ox. ($W^+ \rightarrow W^{2+}$) = 0.72 V , rev ox. of ferrocene = $0.82, 0.67\text{ V}$.

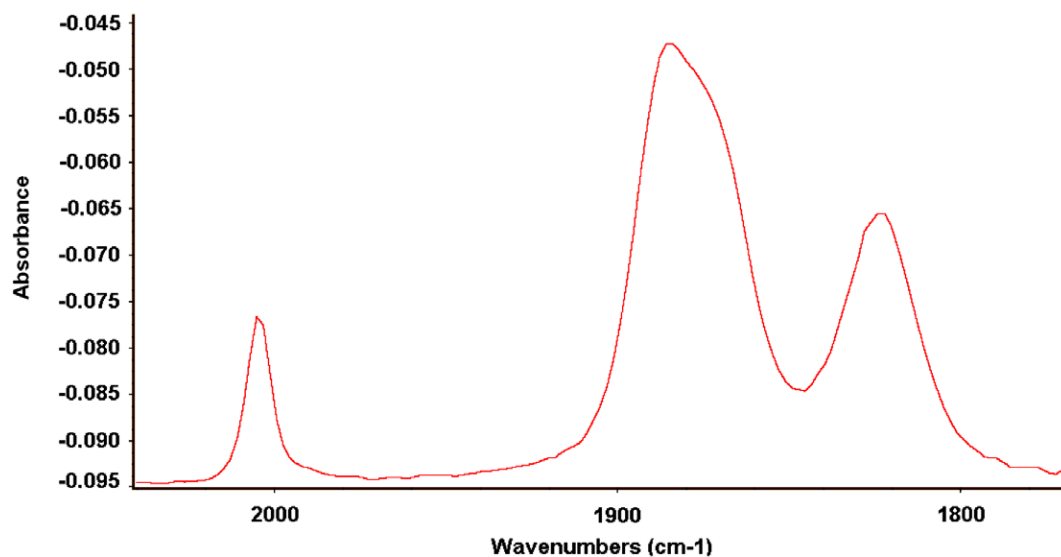


Fig. 1. Part of the IR spectrum of $W(CO)_4(fcbpy)$, recorded from CH_2Cl_2 solution, showing $\nu(CO)$ bands (2005, 1884, 1870, 1823 cm^{-1}).

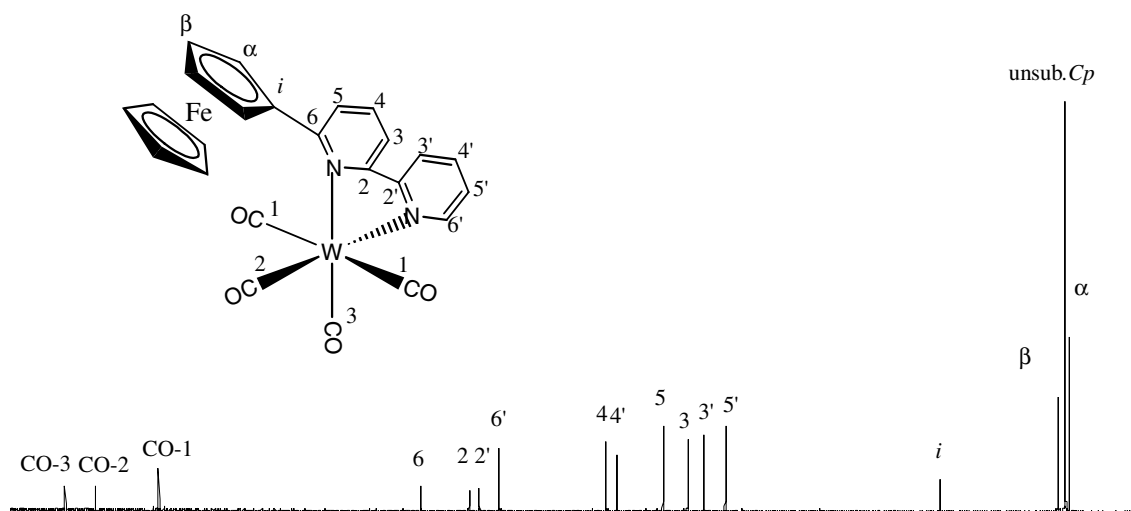


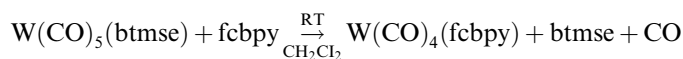
Fig. 2. $^{13}C\{-^1H\}$ NMR spectrum of $W(CO)_4(fcbpy)$ taken in CD_2Cl_2 solution.

3. Results and discussion

The reaction between bipyridine and lithiated ferrocene yields 6-ferrocenyl-2,2'-bipyridine as the major product which was isolated and identified by taking the ^1H NMR spectrum [23]. Furthermore, its ^{13}C NMR, UV–Vis electronic absorption spectroscopic properties and electrochemistry were studied. In line with the molecular structure of the compound, the ^{13}C NMR spectrum gives 14 signals which were assigned by using a two-dimensional heteronuclear correlation technique (HMQC) as given in Section 2. The UV–Vis electronic absorption spectrum of 6-ferrocenyl-2,2'-bipyridine in CH_2Cl_2 shows four absorption bands at 234 ($\epsilon = 3.3 \times 10^4$), 286 ($\epsilon = 2.2 \times 10^4$), 354 ($\epsilon = 6.3 \times 10^3$) and 460 nm ($\epsilon = 2.9 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$). By comparing with the spectrum of ferrocene [24], the first

two bands at 234 and 286 nm are assigned as charge transfer transitions whereas the other two at 354 and 460 nm are assigned as d–d transitions. In cyclic voltammogram, fcbpy exhibits an irreversible reduction peak at -1.25 V assigned to bipyridine moiety [25] and a reversible oxidation peak at 0.71 V due to the electron transfer from the ferrocenyl unit.

Thermal substitution reaction of $\text{W}(\text{CO})_5(\eta^2\text{-btmse})$ with 6-ferrocenyl-2,2'-bipyridine in dichloromethane solution at room temperature yields tetracarbonyl(6-ferrocenyl-2,2'-bipyridine)tungsten(0) as followed by IR spectroscopy



The reaction involves the replacement of the btmse ligand and one CO ligand by fcbpy, most probably stepwise. The question whether a CO or alkyne substitution

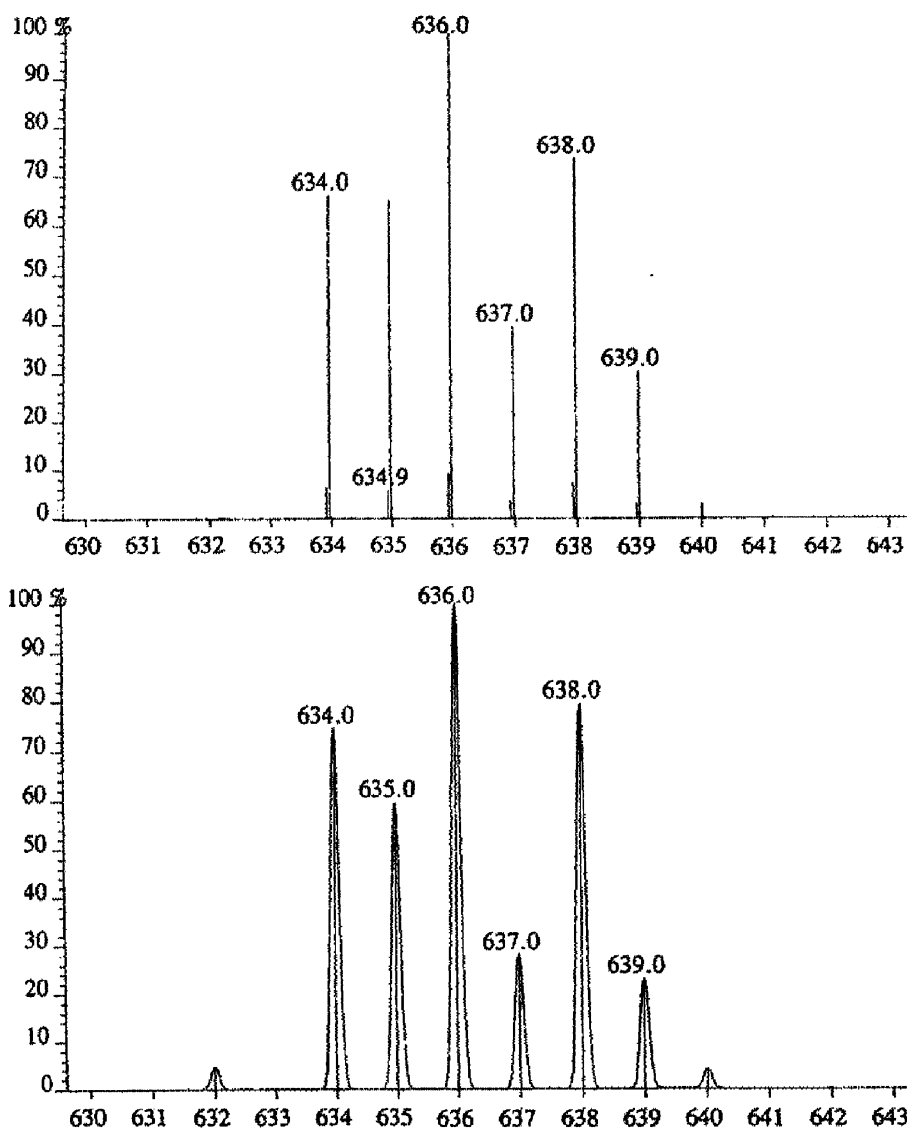
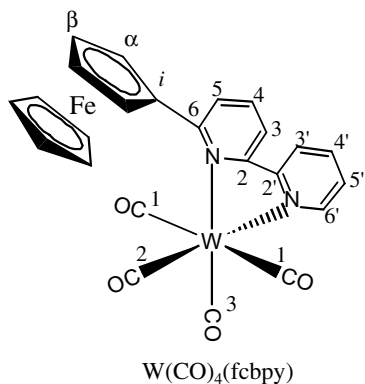


Fig. 3. (Top) Experimentally recorded positive ion FAB-MS spectrum of the complex $\text{W}(\text{CO})_4(\text{fcbpy})$ revealing the molecular peak with the characteristic isotopic distribution pattern. (Bottom) Simulated spectrum for $\text{W}(\text{CO})_4(\text{fcbpy})$. Note the excellent match of the top (experimental) and bottom (simulated) spectra.

occurs first remains unclear. In either case, the fcbpy molecule attacks the vacant site at the metal centre and, then, ring-closure reaction occurs with the concomitant displacement of the second ligand. The resulting complex $W(CO)_4(fcbpy)$ could be isolated from the reaction mixture as analytically pure substance and characterized by elemental analysis, IR, UV–Vis, MS, 1H and ^{13}C NMR spectroscopies. Despite of all the attempts using various solvent and crystallization procedures we couldn't obtain single crystals of $W(CO)_4(fcbpy)$ suitable for structure determination by X-ray diffraction.



The FT-IR spectrum of $W(CO)_4(fcbpy)$ in CH_2Cl_2 exhibits four absorption bands at 2005, 1884, 1870, 1823 cm^{-1} for the CO stretching (Fig. 1). This $\nu(CO)$ pattern resembles to the one observed for $W(CO)_4(2,2'$ -bipyridine) [26,27] and indicates a local C_{2v} symmetry for the $W(CO)_4$ moiety in the complex. Thus, the complex molecule has four vibrational modes of $2A_1$, B_1 , B_2 for the CO stretching [28].

The 1H NMR spectrum of $W(CO)_4(fcbpy)$ in CD_2Cl_2 shows a pattern similar to that of the free fcbpy molecule. However, all peaks are shifted to lower magnetic field upon coordination indicating that the fcbpy molecule acts mainly as σ donor ligand. The ^{13}C NMR spectrum of $W(CO)_4(fcbpy)$ in CD_2Cl_2 (Fig. 2) shows three signals at 216.44, 212.48 and 202.77 ppm with a relative intensity ratio of 1:1:2 for the carbonyl carbon atoms. Ten signals of the carbon atoms on the bipyridine moiety are shifted to lower field upon coordination to tungsten center, to an extent depending on the closeness to the ligating nitrogen atoms, similar to those observed for $W(CO)_4(2,2'$ -bipyridine) [29]. The three plus one signals of the cyclopentadienyl carbons show only slight changes upon coordination.

The positive ion FAB-MS spectrum of the complex $W(CO)_4(fcbpy)$ gives not only a molecular peak with the characteristic isotopic distribution pattern which could be nicely simulated (Fig. 3), but also peaks corresponding to the sequential CO loss products.

The cyclic voltammogram of $W(CO)_4(fcbpy)$ in CH_2Cl_2 solution (Fig. 4) shows a reversible reduction at -1.63 V readily assigned to the bipyridine moiety. Two irreversible

oxidations at 0.58 V and 0.72 V are due to the tungsten metal centered electron transfer reactions. These assignments are based on the comparison with the cyclic voltammogram of a similar complex $W(CO)_4(bpy)$ which has two irreversible oxidations at 0.53 V and 1.02 V due to the tungsten metal center and a reversible peak at -1.58 V for bipyridine moiety [25]. The irreversibility of these oxidations was supported by the cyclic voltammogram taken

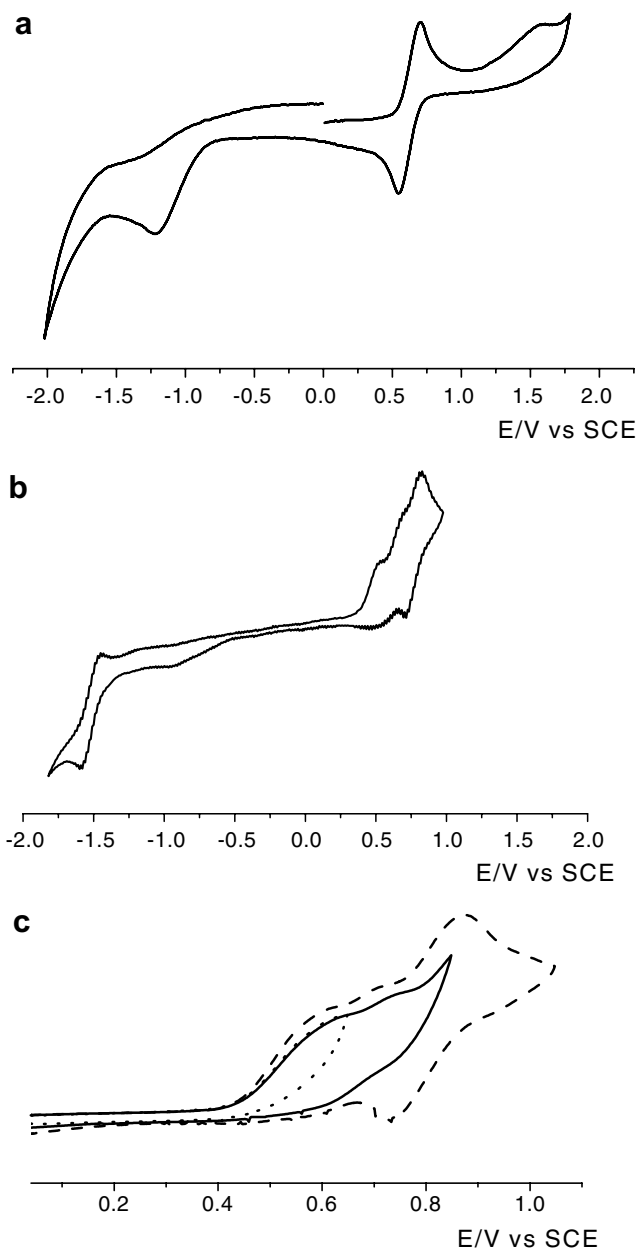


Fig. 4. (a) Cyclic voltammogram of fcbpy in the potential range of -2 and 2 V. (b) Cyclic voltammogram of $W(CO)_4(fcbpy)$ in the potential range of -2 and 2 V. (c) Stepwise cyclic voltammogram of $W(CO)_4(fcbpy)$ with the dotted line for peak clipping at 0.65 V, solid line for peak clipping at 0.85 V and dashed line for peak clipping at 1.05 V. Tetrabutylammonium tetrafluoroborate was used as electrolyte and SCE was used as reference electrode for taking the cyclic voltammograms of both molecules in CH_2Cl_2 solution.

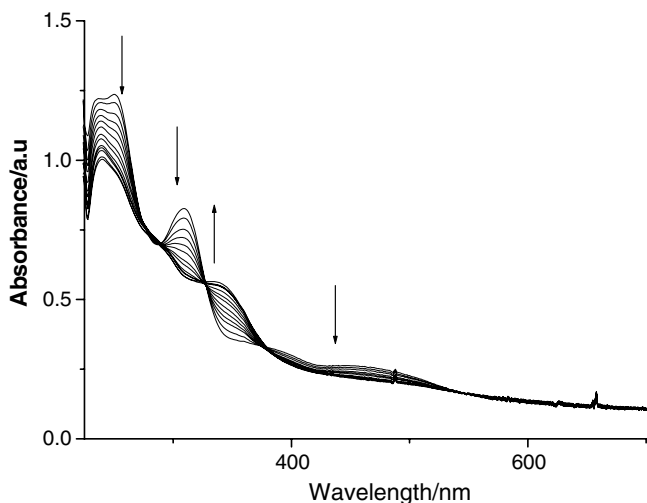


Fig. 5. UV-Vis electronic absorption spectra recorded during the electrolysis of 1.0×10^{-4} M $W(CO)_4(fcbpy)$ in dichloromethane with 5 mC increment for three electron transfer.

stepwise from the same solution by peak clipping at 0.65 V (the dotted line) and 0.85 V (solid line) as shown in Fig. 4c. The oxidation peak at 0.87 V was shown to be reversible (Fig. 4c, dashed line for peak clipping at 1.05 V) and assigned to the iron center in the ferrocenyl group, similar to that of the free fcbpy molecule. The electrochemical oxidation of $W(CO)_4(fcbpy)$ was carried out in CH_2Cl_2 solution at $-21^\circ C$ and followed by monitoring the UV-Vis absorption spectra (Fig. 5). The observation of nice isosbestic points indicates the straightforward conversion of the complex to the products. During the electrolysis, the potential was set to the 0.75 V until the passage of two electrons per mole of complex was completed and then increased to 1.1 V and kept constant at this voltage until the end of third electron passage.

The UV-Vis electronic absorption spectrum of $W(CO)_4(fcbpy)$ in CH_2Cl_2 shows four absorption bands at 230, 250, 372 and 468 nm related to the 6-ferrocenyl-2,2'-bipyridine ligand (slightly shifted compared to those of the free fcbpy molecule) and one absorption band at 308 nm due to the d-d transition of W(0) center. Since the same d-d transition for $W(CO)_4(2,2'$ -bipyridine) has been observed at 364 nm [26], the ferrocenyl moiety causes a significant increase in the d orbital splitting energy of tungsten center in $W(CO)_4(fcbpy)$ compared to that of $W(CO)_4(2,2'$ -bipyridine).

Compared to $W(CO)_5(2$ -ferrocenyl pyridine) [11], the $W(CO)_4(fcbpy)$ complex appears to be more stable obviously due to the delocalization of π -electron density over the chelate ring via the metal-diimine bonding. However, the attempt to prepare the analogous chromium complex, $Cr(CO)_4(fcbpy)$, failed. The formation of $Cr(CO)_4(fcbpy)$ from the reaction of $Cr(CO)_5(THF)$ and fcbpy in THF could be suggested by solution IR spectrum giving four absorption bands at 2006, 1893, 1879, and 1828 cm^{-1} for CO stretching.

4. Conclusions

6-Ferrocenyl-2,2'-bipyridine (fcbpy) was prepared from the reaction of lithiated ferrocene with bipyridine and employed as a bidentate ligand for the formation of a relatively stable complex $W(CO)_4(fcbpy)$. Although this complex has the ferrocenyl group linked to the tungsten center, the electrochemical study shows no electronic communication between the two transition metal centers. The actual interaction between two metal centers by conjugation depends on the conformation of the molecule which is not known. However, two metal centers exhibit separately their unique oxidation behavior in the cyclic voltammogram. This can be attributed to the insignificant π conjugation between two centers, may be, due to the mainly σ -bonding character of ferrocenyl-bipyridine attachment.

Acknowledgements

The partial support of this work by Scientific and Technical Research Council of Turkey (TUBITAK, TBAG-2320) and Turkish Academy of Sciences is gratefully acknowledged.

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