ELSEVIER

Journal of Organometallic Chemistry 637–639 (2001) 209–215

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Synthesis, structures and electrochemical properties of Group 6 metal carbonyl complexes containing ferrocenylpyrazole ligands

Liang-Fu Tang *, Wen-Li Jia, Zhi-Hong Wang, Jian-Fang Chai, Ji-Tao Wang

Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, People's Republic of China

Received 28 December 2000; received in revised form 19 February 2001; accepted 26 March 2001

Abstract

A series of carbonylchromium, molybdenum and tungsten complexes containing ferrocenylpyrazole ligands, ($M(CO)_5L$) ($M = Cr$, Mo or W; L represents ferrocenyl pyrazole), have been prepared by the photochemical reactions of ferrocenylpyrazole ligands with $M(CO)_6$. Their electrochemical behaviors have also been investigated by cyclic voltammetry, indicating that chromium complexes exhibit two one-electron reversible or quasi-reversible couples, while molybdenum and tungsten complexes have one reversible couple corresponding to the ferrocenyl group and one irreversible oxidation process for the molybdenum or tungsten center. The crystal structures of 3-ferrocenylpyrazole pentacarbonyltungsten (**3**) and 3-methyl-5-ferrocenylpyrazole pentacarbonyltungsten (**6**) are determined by X-ray diffraction method, indicating that both 3(5)-ferrocenylpyrazole and 3(5)-methyl-5(3)-ferrocenylpyrazole act as a monodentate ligand, and the central metal of W is six-coordinate with a quasi-octahedral coordination geometry in both complexes. Complex **3** is linked into a one-dimensional chain in solid through intermolecular hydrogen bonds formed by metal carbonyl as hydrogen bond acceptors, while complex **6** forms a dimer by similar intermolecular hydrogen bond interactions. The N–H···O distances in complexes **3** and **6** are 2.932(11) and 2.900 Å, respectively. All new compounds have been characterized by elemental analyses, IR, ^{1}H-NMR. ^{13}C-NMR spectra of molybdenum and tungsten complexes have also been determined.

Keywords: Ferrocenylpyrazole; Metal carbonyl complexes; Cyclic voltammetry; Crystal structures

1. Introduction

Due to its high stability and reversible redox characteristics, ferrocence has been extensively used as starting materials in the synthesis of versatile ferrocenyl derivatives [1]. For example, ferrocenyl derivatives are very important electron-transfer systems for molecular electronics owing to its characteristic redox behaviors [2], and they could also be expected to play a key role of an electron chemical probe of the electron-transfer process in biological molecules [3]. The aromatic heterocyclic systems covalently linked to ferrocenyl fragment have shown some interesting electrochemical behaviors, which allows electronic communication between ferrocene and another coordinated metal center through the π-conjugated systems [4–11]. Ferrocenylpyrazole is one of above systems. Recently, there has been increasing interest in the use of ferrocenylpyrazole ligands to produce polymetallic species owing to their versatile coordination possibility [11–19]. In these complexes, ferrocenylpyrazoles can act as mono-, bi- and polydentate ligands. In this paper, we report the photochemical reaction of ferrocenylpyrazole ligands with $M(CO)_6$ to yield novel $M(CO)_5L$ complexes ($M = Cr$, Mo or W; L represents ferrocenylpyrazole ligands). The single crystal X-ray analysis shows that substituents on the pyrazole ring affect significantly the solid structures of complexes. The electrochemical properties of $M(CO)_5L$ complexes have also been investigated by cyclic voltammetry.

2. Experimental

All reactions were carried out under an oxygen-free atmosphere. Solvents were dried by standard methods and distilled prior to use. NMR spectra were recorded

---

* Corresponding author Fax: + 86-22-2350-2458.
E-mail address: tanglf@eyou.com (L.-F. Tang).

0022-328X/01/$ - see front matter © 2001 Elsevier Science B.V. All rights reserved.
PII: S0022-328X(01)00907-X

on BRUKER AC-P-200 spectrometer using $CDCl_3$ as solvent unless otherwise noted, and chemical shifts were referenced to Me_4Si for ^{1}H- and ^{13}C-NMR spectra. IR spectral data were obtained from a Bio-Rad FTS 135 spectrometer in KBr pellets. Elemental analyses were carried out on a Perkin–Elmer 240C analyzer. 3(5)-Ferrocenylpyrazole (L_1) [18], 3(5)-methyl-5(3)-ferrocenylpyrazole (L_2) and 3(5)-phenyl-5(3)-ferrocenyl pyrazole (L_3) [20] were prepared according to the literature methods.

2.1. Reaction of ferrocenylpyrazoles with $M(CO)_6$ ($M = Cr$, Mo and W)

As all the reactions are similar, a general procedure is described as follows. The solution of $M(CO)_6$ (1 mmol) and ferrocenylpyrazole (1 mmol) dissolved in THF (20 ml) was irradiated with a 400 W high-pressure mercury lamp for 6–12 h at room temperature (r.t.). The reaction mixture was monitored by TLC. After the reaction completed, the solvent was removed in vacuo, and the residual was purified by column chromatography on silica using $CH_3CO_2C_2H_5$:hexane (v:v = 1:4) as eluent. The yellow eluent was concentrated to dryness under a reduced pressure. The residue was recrystallized from CH_2Cl_2–hexane to give a yellow crystalline solid.

2.1.1. 3-Ferrocenylpyrazole pentacarbonylchromium (**1**)

^{1}H-NMR: δ 4.11 (s, 5H, C_5H_5), 4.36, 4.51 (s, s, 2H, 2H, C_5H_4), 6.25 (br, s, 1H, H^4 of pyrazole), 7.37 (br, s, 1H, H^5 of pyrazole), 9.35 (br, s, 1H, NH). IR: $\nu_{NH} =$ 3446.2 (s); $\nu_{CO} = 2068.2$ (m), 1981.2 (m), 1949.4 (vs), 1898.9 (vs), 1873.4 (vs); $\nu_{pyrazole\ ring} = 1593.8$ (m) cm^{-1}. Anal. Calc. for $C_{18}H_{12}CrFeN_2O_5$: C, 48.65; H, 2.70; N, 6.31. Found: C, 49.04; H, 2.45; N, 6.39%.

2.1.2. 3-Ferrocenylpyrazole pentacarbonylmolybdenum (**2**)

^{1}H-NMR: δ 4.09 (s, 5H, C_5H_5), 4.39, 4.57 (s, s, 2H, 2H, C_5H_4), 6.65 (d, 1H, H^4 of pyrazole), 8.13 (d, 1H, H^5 of pyrazole), 9.34 (br, s, 1H, NH). ^{13}C-NMR: δ 66.6, 69.4, 71.6 (C_5H_4), 69.7 (C_5H_5), 104.2 (C^4 of pyrazole), 145.0 (C^5 of pyrazole), 154.2 (C^3 of pyrazole), 204.0, 210.5 (CO). IR: $\nu_{NH} = 3384.7$ (m); $\nu_{CO} = 2074.0$ (w), 1974.5 (sh), 1948.0 (vs), 1928.1 (s), 1857.8 (vs), 1827.3 (vs); $\nu_{pyrazole\ ring} = 1596.0$ (m) cm^{-1}. Anal. Calc. for $C_{18}H_{12}FeMoN_2O_5$: C, 44.26; H, 2.46; N, 5.74. Found: C, 44.44; H, 2.92; N, 6.29%.

2.1.3. 3-Ferrocenylpyrazole pentacarbonyltungsten (**3**)

^{1}H-NMR: δ 4.14 (s, 5H, C_5H_5), 4.39, 4.56 (s, s, 2H, 2H, C_5H_4), 6.24 (d, 1H, H^4 of pyrazole), 7.58 (d, 1H, H^5 of pyrazole), 9.54 (br, s, 1H, NH). ^{13}C-NMR: δ 66.8, 69.6, 70.9 (C_5H_4), 69.9 ($C_5H_4 + C_5H_5$), 104.8 (C^4 of pyrazole), 146.1 (C^5 of pyrazole), 148.5 (C^3 of pyrazole), 197.9, 201.8 (CO). IR: $\nu_{NH} = 3384.4$ (s); $\nu_{CO} =$ 2074.2 (m), 1976.2 (sh), 1923.8 (vs), 1858.2 (vs), 1827.6 (vs) (CO); $\nu_{pyrazole\ ring} = 1596.1$ (m) cm^{-1}. Anal. Calc. for $C_{18}H_{12}FeN_2O_5W$: C, 37.50; H, 2.08; N, 4.86. Found: C, 37.35; H, 2.12; N, 5.00%.

2.1.4. 3-Methyl-5-ferrocenylpyrazole pentacarbonylchromium (**4**)

^{1}H-NMR: δ 2.26 (s, 3H, CH_3), 4.13 (br, 9H, $C_5H_5 + C_5H_4$), 6.00 (s, 1H, H^4 of pyrazole), 9.09 (br, s, 1H, NH). IR: $\nu_{NH} = 3446.7$ (s), 3426.3 (sh); $\nu_{CO} = 2068.3$ (m), 1981.2 (m), 1947.2 (vs), 1900.4 (vs), 1842.0 (m), 1873.5 (vs); $\nu_{pyrazole\ ring} = 1594.2$ (m) cm^{-1}. Anal. Calc. for $C_{19}H_{14}CrFeN_2O_5$: C, 49.78; H, 3.06; N, 6.11. Found: C, 49.64; H, 2.97; N, 6.60%.

2.1.5. 3-Methyl-5-ferrocenylpyrazole pentacarbonylmolybdenum (**5**)

^{1}H-NMR: δ 2.32 (s, 3H, CH_3), 4.14 (s, 5H, C_5H_5), 4.36, 4.51 (m, m, 2H, 2H,C_5H_4), 6.12 (s, 1H, H^4 of pyrazole), 9.15 (br, s, 1H, NH). ^{13}C-NMR: δ 15.5 (CH_3), 66.7, 69.5, 71.6 (C_5H_4), 69.7 ($C_5H_4 + C_5H_5$), 104.2 (C^4 of pyrazole), 145.0 (C^5 of pyrazole), 154.3 (C^3 of pyrazole), 204.0, 210.2 (CO). IR: $\nu_{NH} = 3407.9$ (m), 3386.3 (m); $\nu_{CO} = 2075.7$ (m), 1994.8 (m), 1932.1 (vs), 1892.8 (vs), 1870.5 (vs), 1843.6 (vs); $\nu_{pyrazole\ ring} = 1599.1$ (m) cm^{-1}. Anal. Calc. for $C_{19}H_{14}FeMoN_2O_5$: C, 45.42; H, 2.79; N, 5.58. Found: C, 45.30; H, 3.20; N, 6.02%.

2.1.6. 3-Methyl-5-ferrocenylpyrazole pentacarbonyltungsten (**6**)

^{1}H-NMR: δ 2.34 (s, 3H, CH_3), 4.14 (s, 5H, C_5H_5), 4.37, 4.52 (m, m, 2H, 2H, C_5H_4), 6.08 (s, 1H, H^4 of pyrazole), 9.18 (br, s, 1H, NH). ^{13}C-NMR: δ 16.4 (CH_3), 66.8, 69.7, 71.3 (C_5H_4), 69.9 ($C_5H_4 + C_5H_5$), 104.2 (C^4 of pyrazole), 145.8 (C^5 of pyrazole), 155.3 (C^3 of pyrazole), 197.8, 201.7 (CO). IR: $\nu_{NH} = 3390.7$ (m), 3363.9 (m); $\nu_{CO} = 2073.1$ (m), 1985.2 (m), 1921.4 (vs), 1867.5 (vs), 1829.2 (vs); $\nu_{pyrazole\ ring} = 1598.8$ (m) cm^{-1}. Anal. Calc. for $C_{19}H_{14}FeN_2O_5W$: C, 38.64; H, 2.37; N, 4.75. Found: C, 38.70; H, 1.95; N, 5.05%.

2.1.7. 3-Phenyl-5-ferrocenylpyrazole pentacarbonyltungsten (**7**)

Two conformational isomers (an analog is shown in Fig. 3) were obtained. The relative ratio of isomers is ca. 44:56 calculated from the integration of H^4 signals of the pyrazole ring in ^{1}H-NMR spectrum. ^{1}H-NMR of the mixtures: δ 4.18, 4.20 (s, s, C_5H_5), 4.41, 4.59, 4.64 (m, m, m, C_5H_4), 6.32, 6.72 (s, s, H^4 of pyrazole), 7.47–7.55 (m, C_6H_5), 9.44, 9.64 (s, s, NH). ^{13}C-NMR: δ 66.8, 68.2, 69.0, 69.4, 70.6, 70.9 (C_5H_4), 69.8, 69.9 (C_5H_5), 104.4, 106.2 (C^4 of pyrazole), 125.8, 126.9, 128.3, 128.7, 129.3, 129.5, 129.9, 132.8 (C_6H_5), 145.3, 145.9 (C^5 of pyrazole), 158.4, 159.6 (C^3 of pyrazole), 197.6, 197.8, 201.5 (CO). IR: $\nu_{NH} = 3394.3$ (sh), 3383.6 (m); $\nu_{CO} = 2072.5$ (m), 1976.5 (m), 1924.9 (vs), 1856.6

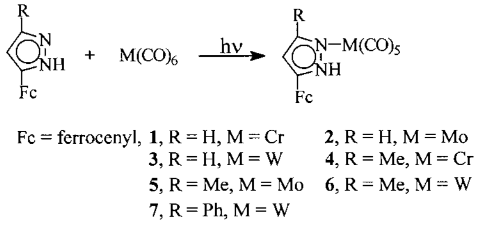
(vs), 1825.0 (vs); $\nu_{\text{pyrazole ring}} = 1591.7, 1571.6$ (w) cm^{-1}. Anal. Calc. for $C_{24}H_{16}FeN_2O_5W$: C, 44.17; H, 2.45; N, 4.29. Found: C, 44.20; H, 2.67; N, 4.37%.

2.2. Electrochemical experimental

Cyclic voltammetric experiments were performed on a BAS-100B electrochemical analyser equipped with a three-electrode assembly with 0.1 M Bu_4NPF_6 as support electrolyte and CH_3CN as solvent. The working electrode was a platinum disk ($\phi = 1$ mm). The reference electrode was 0.1 M $AgNO_3$ | Ag prepared in a 0.1 M Bu_4NPF_6–CH_3CN solution. A Pt filament was used as an auxiliary electrode. The ferrocenium ferrocene redox couple was taken as an internal standard. $E_{1/2}$ values were determined as $(E_{pa} + E_{pc})/2$.

Table 1
Crystal data and structure refinement parameters for complexes **3** and **6**

	3	**6**
Empirical formula	$C_{18}H_{12}FeN_2O_5W$	$C_{19}H_{14}FeN_2O_5W$
Formula weigh	576.00	590.02
Crystal size (mm)	0.30 × 0.30 × 0.25	0.20 × 0.20 × 0.30
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell dimensions		
a (Å)	7.0910(10)	9.787(2)
b (Å)	23.129(5)	21.459(4)
c (Å)	11.192(2)	18.749(4
β (°)	98.89(3)	92.84(3)
V (Å^3)	1813.5(6)	3932.8(14)
D_{calc} (g cm^{-3})	2.110	1.993
Absorption coefficient (mm^{-1})	7.170	6.615
Z	4	8
F(000)	1096	2256
Reflections collected	3357	7101
Independent reflections (R_{int})	3184 (0.0604)	6882 (0.0367)
No. of parameters	245	505
R, R_w [$I > 2\sigma(I)$]	0.0555, 0.1503	0.0335, 0.0805
Goodness-of-fit on F^2	0.993	0.929



Scheme 1. Fc = ferrocenyl; **1**, R = H, M = Cr; **2**, R = H, M = Mo; **3**, R = H, M = W; **4**, R = Me, M = Cr; **5**, R = Me, M = Mo; **6**, R = Me, M = W; **7**, R = Ph, M = W.

2.3. Crystal structures determination

Crystals of complexes **3** and **6** suitable for X-ray analysis were grown from CH_2Cl_2–hexane at 4 °C. All intensity data were collected at r.t. with an Enraf-Nonius CAD4 diffractometer using graphite monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å). The correction for empirical absorption was applied to intensity data, structures were resolved by direct method and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. All calculations were performed on a PDP11/44 computer using SDP-PLUS program system. A summary of the fundamental crystal data for complexes **3** and **6** is listed in Table 1.

3. Results and discussion

3.1. Synthesis and characterization of the complexes

The photochemical reactions of ferrocenylpyrazoles with $M(CO)_6$ (M = Cr, Mo and W) in the molar ratio 1:1 or 2:1 (ligand:metal) at room temperature yielded $M(CO)_5L$ complexes (L = ferrocenylpyrazole) as the major products (Scheme 1). However, the reaction of 3(5)-phenyl-5(3)-ferrocenylpyrazole with $Cr(CO)_6$ or $Mo(CO)_6$ did not take place in this reaction conditions, possibly owing to bulky steric hindrance of substituents on the pyrazole ring decreasing the donor ability of this ligand. Some $M(CO)_4L_2$ complexes were also obtained during the reactions, but their stability was poor, and no pure products were isolated. The stability of monosubstituted complexes is in the order Cr(0) ~ W(0) > Mo(0), which is similar with the order of Cr(0) ~ W(0) > Mo(0) in $M(CO)_5L$ complexes of L = pyrimidine or triazine [21], but remarkably different from the stability order of W(0) > Mo(0) > > Cr(0) in $M(CO)_5L$ complexes of pyrazine [22]. All complexes are soluble in chlorinated solvents, and they are slightly air-sensitive in solution.

The IR spectra of complexes **1**–**3** show the characteristic absorption peak of N–H stretching band nearby 3446 and 3384 cm^{-1}. However, two N–H bands are observed in complexes **4**–**7**, which is consistent with the existence of two conformational isomers in these solid complexes (Fig. 3). Two N–H bonds of conformational isomers in complexes **4**–**7** are remarkably different owing to only one N–H bond forming N–H···O hydrogen bond. The carbonyl spectra are also interesting. Five to six ν_{CO} bands are observed in all complexes, which is different from other monosubstituted Group 6 metal carbonyl complexes [23–26]. This is probably due to a superposition of the absorption of the two different $W(CO)_5$ fragments.

Table 2
Electrochemical data for ligands and complexes **1**–**7**

Compound	v (mV s^{-1})	E_{pa} (mV)	E_{pc} (mV)	$E_{1/2}$ (mV)
L_1	100	62	−30	16
L_2	100	40	−30	5
L_3	100	120	−27	47
1	100	184	83	133
		442	335	388
	200	181	92	136
		440	340	390
2	100	197	96	146
		739		
	200	192	77	134
		736		
3	100	182	92	137
		750		
	200	183	87	135
		744		
4	100	178	98	138
		435	346	390
	200	180	95	137
		425	334	379
5	100	182	104	143
		767		
6	100	181	100	140
		724		
7	100	199	87	143
		735		

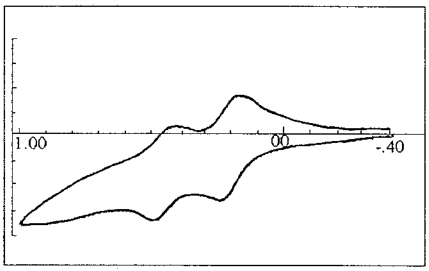


Fig. 1. Cyclic voltammogram at a potential sweep rate of 200 mV s^{-1} for complex **4**.

The ^{1}H-NMR spectra of all the complexes indicate expected the signals of pyrazole protons. These pyrazole protons in the complexes are shifted downfield compared with those of the free ligands. Although X-ray analyses show that complexes **4**–**6** have two conformational isomers in solid, only one set of signals of pyrazole ligand are observed in solution, which can be easily understood possibly owing to the rapid conformational conversion existing in solution. The ^{13}C-NMR spectra of complexes **2**, **3**, **5** and **6** exhibit two signals of the carbonyl carbon atoms with ca. a 1:4 intensity ratio, which is consistent with the formula $M(CO)_5L$ [24]. It is also noteworthy that the ^{1}H- and ^{13}C-NMR spectra of complex **7** clearly show a mixture of two isomers compared with the conformational isomers of complex **6** (Fig. 3). Two sets of signals for the protons of the pyrazole ring and ferrocenyl group, respectively, are observed in the ^{1}H-NMR spectrum at room temperature. The ratio of the isomers is ca. 44:56, determined by integration of H^4 signals of the pyrazole ring. The ^{13}C-NMR spectrum of complex **7** also shows two sets of signals for the carbon atoms of ferrocenyl group and pyrazole ring, but only three signals for the carbonyl carbon atoms from two isomers are observed, this may be the result of low contents of one isomer. The bulky steric hindrance of phenyl and ferrocenyl groups on pyrazole ring should be responsible for the two sets of signals for ^{1}H and ^{13}C resonances, which slows down the conformational conversion between the two isomers of complex **7**. The time-averaging signal of two isomers on the NMR time scale was not appeared. However, attempts to separate the two isomers at room temperature were not successful.

3.2. Electrochemical properties of the complexes

The electrochemical properties of the complexes were investigated by cyclic voltammetry at room temperature in CH_3CN solution. The voltammetric data are listed in Table 2. A typical CV curve of complex **4** is illustrated in Fig. 1. The electrochemical behaviors of $M(CO)_5$ fragments are significantly different from those of $M(CO)_4$ fragments (M = Cr, Mo and W). One reversible or quasi-reversible one-electron oxidation process is observed in complexes N–NM(CO)$_4$ (N–N represents bis(pyrazol-1-yl)alkanes) [27]. However, in the present work, chromium complexes exhibit two pairs of reversible or quasi-reversible redox peaks, one is attributed to the ferrocenyl group and the other to the chromium center, respectively. A reversible one-electron oxidation process for ferrocenyl group and an irreversible oxidation for the other metal center are observed in molybdenum and tungsten complexes. The irreversible oxidation process of molybdenum and tungsten center was also observed in many other systems containing $M(CO)_5$ fragments [28,29]. The poor chemical stability of the oxidation products of molybdenum and tungsten complexes at room temperature may be responsible for the irreversible oxidation of the metal centers. The peak potential ($E_{1/2}$) of the ferrocenyl groups in the complexes lies in the range of 133–147 mV, which varies only slightly with different metals in complexes indicating that there may be no electronic communication between ligands with metal centers. This is possibly owing to bulky steric hindrance leading to relatively weak conjugation effects of ferrocenyl group with pyrazole plane in the oxidation products especially to complexes **4**–**7** (Fig. 3) [4]. Large positive shifts compared with free ligands are observed, and we suggest that inductive effects may be the major factors owing to the electron-withdrawing effect of $M(CO)_5$ fragments [23,24].

3.3. Crystal structures of complexes **3** and **6**

The molecular structures of complexes **3** and **6** were confirmed by single crystal X-ray diffraction analyses. Selected bonds distances and angles for complexes **3** and **6** are listed in Tables 3 and 4, respectively.

The crystal structure of complex **3** is shown in Fig. 2. It clearly shows that ferrocenylpyrazole ligand acts as a monodentate ligand, which coordinates to tungsten center through the nitrogen atom away from bulky ferrocenyl group, in order to avoid the steric repulsion of ferrocenyl group. The tungsten atom is six-coordinate with a quasi-octahedral coordination geometry. The W–N distance is 2.204(8) Å, which is comparable to those found in other octahedral W(0) complexes with pyrazole ligands (such as average 2.255 Å in $CH_2(3,5\text{-}Me_2\text{-}4\text{-}ClPz)_2W(CO)_4$ [27] and 2.275 Å in $(CH_2)_2(3,5\text{-}Me_2Pz)_2W(CO)_4$ [30], respectively, Pz = pyrazole). It is noteworthy that the W–C distance *trans* to the pyrazole ligand is 1.947(11) Å, and shorter than the other four W–C distances, while the C(1)–O(1) distance is 1.147(16) Å, and is longer than other four C–O distances. It is also interesting that C(4)O(4) carbonyl bends toward pyrazole ligand with the W(1)–C(4)–O(4) angle of 176.1(12)°.

It is well-known that the interactions of hydrogen bonds play a key role in self-assembly of metal complexes into supramolecular architectures. Hydrogen bonds formed by metal carbonyl as hydrogen bond acceptors have been observed in several systems [31–34]. The crystal packing of complex **3** shows that the molecules are linked into a one-dimensional chain via intermolecular hydrogen bonds interactions between the N–H groups and the oxygen atoms of metal carbonyls *trans* to pyrazole ligands in different adjacent molecules. The hydrogen bond N···O distance is 2.932(11) Å, and the angle N–H···O is ∠166.6°.

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

Bond lengths			
W(1)–C(2)	1.947(11)	C(1)–O(1)	1.147(16)
W(1)–C(1)	1.969(17)	C(2)–O(2)	1.128(13)
W(1)–C(5)	2.016(13)	C(3)–O(3)	1.112(13)
W(1)–C(3)	2.025(14)	C(4)–O(4)	1.086(14)
W(1)–C(4)	2.036(12)	C(5)–O(5)	1.093(14)
W(1)–N(1)	2.204(8)	C(8)–C(11)	1.444(13)
N(2)···O(2)[a]	2.932(11)		
Bond angles			
C(2)–W(1)–C(1)	90.9(5)	C(3)–W(1)–N(1)	90.4(4)
C(2)–W(1)–C(5)	89.1(5)	C(4)–W(1)–N(1)	89.2(4)
C(1)–W(1)–C(5)	93.2(6)	O(1)–C(1)–W(1)	178.8(10)
C(2)–W(1)–C(3)	89.3(5)	O(2)–C(2)–W(1)	178.2(10)
C(1)–W(1)–C(3)	179.6(5)	O(3)–C(3)–W(1)	175.9(10)
C(5)–W(1)–C(3)	87.1(6)	O(4)–C(4)–W(1)	176.1(12)
C(2)–W(1)–C(4)	90.7(5)	O(5)–C(5)–W(1)	173.2(10)
C(1)–W(1)–C(4)	86.0(5)	C(7)–C(8)–C(11)	133.1(9)
C(5)–W(1)–C(4)	179.2(5)	N(2)–C(8)–C(11)	122.3(8)
C(3)–W(1)–C(4)	93.7(5)	C(6)–N(1)–W(1)	130.6(7)
C(2)–W(1)–N(1)	179.6(4)	N(2)–N(1)–W(1)	125.1(5)
C(1)–W(1)–N(1)	89.5(4)	C(15)–C(11)–C(8)	129.3(8)
C(5)–W(1)–N(1)	91.0(3)	C(12)–C(11)–C(8)	127.2(9)
N(2)–H···O(2)[a]	166.6		

[a] $x+1/2$, $-y+1/2$, $z+1/2$.

Table 4
Selected bond lengths (Å) and bond angles (°) for complex **6**

A		**B**	
Bond lengths			
W(1)–C(4)	1.940(9)	W(2)–C(6)	1.950(8)
W(1)–C(2)	1.992(12)	W(2)–C(10)	2.011(11)
W(1)–C(5)	2.014(9)	W(2)–C(9)	2.031(9)
W(1)–C(1)	2.030(8)	W(2)–C(8)	2.039(10)
W(1)–C(3)	2.050(11)	W(2)–C(7)	2.044(8)
W(1)–N(25)	2.258(6)	W(2)–N(45)	2.249(6)
C(1)–O(1)	1.139(9)	C(6)–O(6)	1.161(10)
C(2)–O(2)	1.171(12)	C(7)–O(7)	1.127(9)
C(3)–O(3)	1.138(11)	C(8)–O(8)	1.130(10)
C(4)–O(4)	1.161(10)	C(9)–O(9)	1.136(10)
C(5)–O(5)	1.159(11)	C(10)–O(10)	1.167(12)
C(13)–C(23)	1.464(11)	C(43)–C(51)	1.440(10)
N44...O4	2.900		
Bond angles			
C(4)–W(1)–C(2)	86.6(4)	C(6)–W(2)–C(10)	89.5(4)
C(4)–W(1)–C(5)	89.6(4)	C(6)–W(2)–C(9)	89.0(3)
C(2)–W(1)–C(5)	89.9(5)	C(10)–W(2)–C(9)	89.8(4)
C(4)–W(1)–C(1)	86.0(3)	C(6)–W(2)–C(8)	85.4(3)
C(2)–W(1)–C(1)	89.3(4)	C(10)–W(2)–C(8)	174.8(4)
C(5)–W(1)–C(1)	175.5(3)	C(9)–W(2)–C(8)	90.9(4)
C(4)–W(1)–C(3)	85.8(4)	C(6)–W(2)–C(7)	89.2(3)
C(2)–W(1)–C(3)	172.3(4)	C(10)–W(2)–C(7)	85.8(3)
C(5)–W(1)–C(3)	88.9(4)	C(9)–W(2)–C(7)	175.3(4)
C(1)–W(1)–C(3)	91.3(3)	C(8)–W(2)–C(7)	93.3(3)
C(4)–W(1)–N(25)	177.5(3)	C(6)–W(2)–N(45)	174.8(3)
C(2)–W(1)–N(25)	92.9(3)	C(10)–W(2)–N(45)	95.7(3)
C(5)–W(1)–N(25)	92.9(3)	C(9)–W(2)–N(45)	90.5(3)
C(1)–W(1)–N(25)	91.6(3)	C(8)–W(2)–N(45)	89.5(3)
C(3)–W(1)–N(25)	94.7(3)	C(7)–W(2)–N(45)	91.7(3)
O(1)–C(1)–W(1)	174.7(7)	O(6)–C(6)–W(2)	176.8(8)
O(2)–C(2)–W(1)	176.2(10)	O(7)–C(7)–W(2)	176.0(7)
O(3)–C(3)–W(1)	172.4(9)	O(8)–C(8)–W(2)	173.5(8)
O(4)–C(4)–W(1)	179.0(7)	O(9)–C(9)–W(2)	175.9(9)
O(5)–C(5)–W(1)	175.8(9)	O(10)–C(10)–W(2)	174.6(10)

The X-ray crystal structure of complex **6** is presented in Fig. 3, which consists of two crystallographically independent molecules (**A** and **B**). The two molecules are essentially the same, and similar to complex **3**. The main difference between them is the dihedral angles formed by cyclopentadienyl rings and pyrazole planes. The dihedral angle between the C_5H_5 and C_5H_4 rings in molecule **A** (Fig. 3) is 1.6°, similar to that in molecule **B** (1.5°), but slightly lower than that in complex **3** (2.6°). The dihedral angle between the C_5H_4 ring and the pyrazole plane in molecule **B** is 40.1°, considerably larger than those in molecule **A** (19.2°) and complex **3** (3.4°), respectively. The significantly different dihedral angles between the C_5H_4 rings and pyrazole planes in

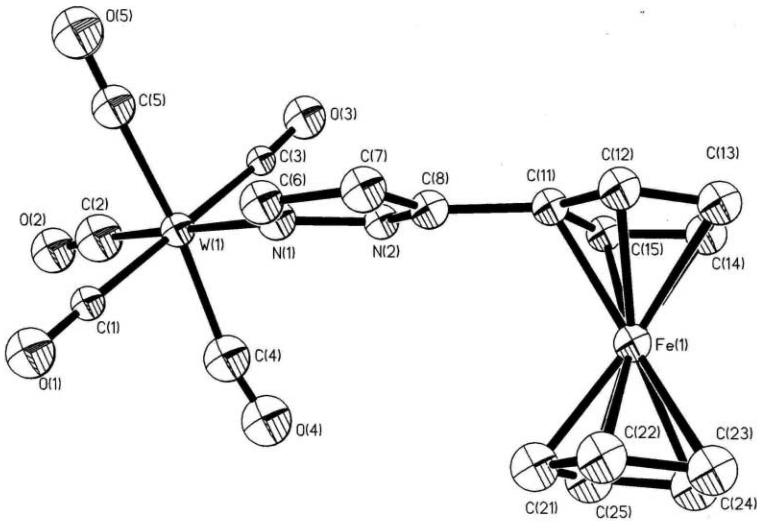


Fig. 2. The molecular structure of complex **3**.

these molecules obviously came from the results of the different steric effects in ferrocenylpyrazole ligands. The W(1)–N(25) distance (2.258(6) Å) in molecule **A** is similar to the W(2)–N(45) distance (2.249(6) Å) in molecule **B**, slightly longer than the W–N distance in complex **3** (2.204(8) Å). The four carbonyls *cis* to the pyrazole ligands in molecules **A** and **B** deviate from linearity, and bend away from the pyrazole ligands. In addition, hydrogen bonds formed by metal carbonyl as hydrogen bond acceptors still exist in complex **6**, but no one-dimensional chain via intermolecular hydrogen bonds is formed in complex **6**, possibly owing to more steric hindrance in complex **6** due to a methyl group adjacent to the coordinated nitrogen atom. Molecules **A** and **B**, through hydrogen bond, only form a dimer. The hydrogen bond N44···O4 distance is 2.900 Å.

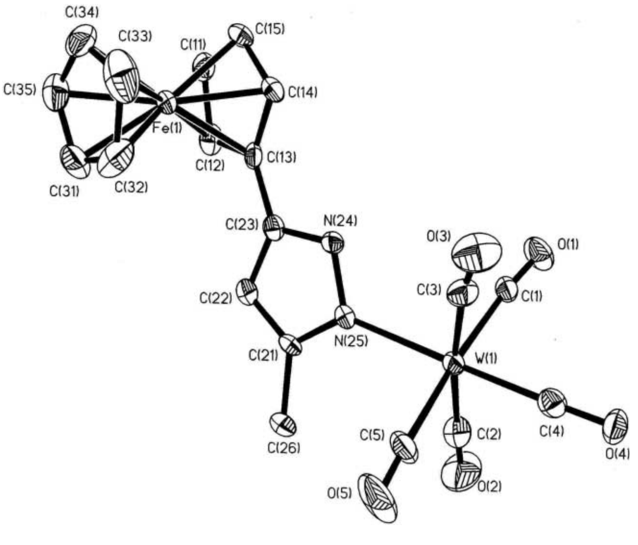


Fig. 3. The molecular structure of complex **6**.

In conclusion, a series of Group 6 metal carbonyl complexes containing ferrocenylpyrazole ligands have been synthesized successfully by photochemical reactions. Their electrochemical behaviors have also been investigated by cyclic voltammetry. Hydrogen bonds, formed by metal carbonyl as hydrogen bond acceptors, have also been found in these complexes. Complex **3** shows a one-dimensional chain structure in the solid state by this kind of hydrogen bond interactions. It is also shown that the substituents of pyrazole ring affect significantly the conformations of complexes.

4. Supplementary information

Crystallographic data (CIF files) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 154098 for complex **3** and CCDC no. 154099 for complex **6**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work is supported by the National Natural Science Foundation of China (no. 29902002) and Visiting Scholar Foundation of Key Lab. In University.

References

[1] A. Togni, T. Hayashi (Eds.), Ferrocenes, VCH, Weinheim, 1995.
[2] D. Astruc, Acc. Chem. Res. 30 (1997) 383.

[3] P.D. Beer, Acc. Chem. Res. 31 (1998) 71.
[4] T.L. Rose, A.B. Kon, Inorg. Chem. 32 (1993) 781.
[5] B. Farlow, T.A. Nile, J.L. Walsh, A.T. McPhail, Polyhedron 12 (1993) 2891.
[6] I.R. Butler, Organometallics 11 (1992) 74.
[7] U. Siemeling, U. Vorfeld, B. Neumann, H.G. Stammler, Chem. Ber. 128 (1995) 481.
[8] I.R. Butler, S.J. McDonald, M. Hursthouse, K.M. Abdul Malik, Polyhedron 14 (1995) 529.
[9] A.M. Santos, F.E. Kühn, W.M. Xue, E. Herdtweck, J. Chem. Soc. Dalton Trans. (2000) 3570.
[10] J.D. Carr, S.J. Coles, M.B. Hursthouse, M.E. Light, E.L. Munro, J.H.R. Tucker, J. Westwood, Organometallics 19 (2000) 3312.
[11] W.R. Thiel, T. Priermeier, D.A. Fiedler, A.M. Bond, M.R. Mattner, J. Organomet. Chem. 514 (1996) 137.
[12] J.A. Campo, M. Cano, J.V. Heras, E. Pinilla, M.R. Bermejo, R. Torres, J. Organomet. Chem. 582 (1999) 173.
[13] N. Chabert-Couchouron, C. Marzin, G. Tarrago, New J. Chem. 21 (1997) 355.
[14] A. Schnyder, A. Togni, U. Wiesli, Organometallics 16 (1997) 255.
[15] R.J. Less, J.L.M. Wicks, N.P. Chatterton, M.J. Dewey, N.L. Cromhout, M.A. Halcrow, J.E. davies, J. Chem. Soc. Dalton Trans. (1996) 4055.
[16] N. Chabert, L. Jacquet, C. Marzin, G. Tarrago, New J. Chem. 19 (1995) 443.
[17] C. Lopez, R.M. Claramunt, S. Trofimenko, J. Elguero, Can. J. Chem. 71 (1993) 678.
[18] K. Niedenzu, J. Serwatowski, S. Trofimenko, Inorg. Chem. 30 (1991) 524.
[19] L.F. Tang, Z.H. Wang, Y.M. Xu, J.T. Wang, Synth. React. Inorg. Met.-Org. Chem. 30 (2000) 1129.
[20] C.R. Hauser, J.K. Lindsay, J. Org. Chem. 22 (1957) 482.
[21] T.W. Stringfield, R.E. Shepherd, Inorg. Chim. Acta 292 (1999) 225.
[22] T.W. Stringfield, Y. Chen, R.E. Shepherd, Inorg. Chim. Acta 285 (1999) 157.
[23] F.A. Cotton, C.S. Kraihanzel, J. Am. Chem. Soc. 84 (1962) 4432.
[24] C.S. Kraihanzel, F.A. Cotton, Inorg. Chem. 2 (1963) 533.
[25] M.A. Reynolds, I.A. Guzei, B.C. Logsdon, L.M. Thomas, R.A. Jacobson, R.J. Angelici, Organometallics 18 (1999) 4075.
[26] E. Peris, J.A. Mata, V. Moliner, J. Chem. Soc. Dalton Trans. (1999) 3893.
[27] L.F. Tang, Z.H. Wang, Y.M. Xu, J.T. Wang, H.G. Wang, X.K. Yao, Polyhedron 18 (1999) 2383.
[28] W.Y. Wong, S.H. Cheung, S.M. Lee, S.Y. Leung, J. Organomet. Chem. 596 (2000) 36.
[29] F.E. Kühn, I.S. Goncalves, A.D. Lopes, J.P. Lopes, C.C. Romão, W. Wachter, J. Mink, L. Hajba, A.J. Parola, F. Pina, J. Sotomayor, Eur. J. Inorg. Chem. (1999) 295.
[30] L.F. Tang, Z.H. Wang, Y.M. Xu, J.T. Wang, H.G. Wang, X.K. Yao, Transition Met. Chem. 24 (1999) 708.
[31] S. Camiolo, S.J. Coles, P.A. Gale, M.B. Hursthouse, T.A. Mayer, M.A. Paver, J. Chem. Soc. Chem. Commun. (2000) 275.
[32] P.Y. Yang, F.C. Chang, M.C. Suen, J.D. Chen, T.C. Keng, J.C. Wang, J. Organomet. Chem. 596 (2000) 226.
[33] S.E. Kabir, E. Rosenberg, Organometallics 14 (1995) 721.
[34] C.P. Casey, A.J. Shusterman, N.W. Vollendorf, K.J. Haller, J. Am. Chem. Soc. 104 (1982) 2417.