



Crystal structures of $(\eta^5\text{-C}_5\text{H}_4\text{COC}_6\text{H}_5)\text{Cr}(\text{NO})_2(\text{X})$ ($\text{X} = \text{Cl}, \text{I}$), and unequivocal assignments of C(2,5) and C(3,4) on the cyclopentadienyl ring of dicarbonyl(η^5 -cyclopentadienyl)nitrosylchromium, (η^5 -cyclopentadienyl)halodinitrosylchromium (halo = Cl, Br, I), bis(η^5 -cyclopentadienyl)iron, and tricarbonyl(η^5 -cyclopentadienyl)methyltungsten bearing a carbonyl substituent in ^{13}C NMR spectra

Yu-Pin Wang^{*}, Wei-Der Tang, Jin-Mei Hwu, Jia-Chwen Wu, Hsiu-Yao Cheng, Tso-Shen Lin

Department of Chemistry, Tunghai University, Taichung 407, Taiwan, ROC

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ABSTRACT

Metallocenyl ketones $(\eta^5\text{-C}_5\text{H}_4\text{COC}_6\text{H}_5)\text{Cr}(\text{NO})_2(\text{X})$ ($\text{X} = \text{Cl}$, **3b**; $\text{X} = \text{I}$, **5b**), $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}[(\eta^5\text{-C}_5\text{H}_4)\text{CO}(\eta^5\text{-C}_5\text{H}_5)]\text{Cr}(\text{NO})_2(\text{X})$ ($\text{X} = \text{Cl}$, **3c**; $\text{X} = \text{I}$, **5c**), and $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}[(\eta^5\text{-C}_5\text{H}_4)\text{CO}(\eta^5\text{-C}_5\text{H}_5)]\text{W}(\text{CO})_3(\text{CH}_3)$ **6c** are synthesized. The structures of **3b** and **5b** are determined by X-ray diffraction studies. The exocyclic carbon of **5b** bends toward the Cr atom with a θ value of 3.46° . The correlation between the magnitudes of nonplanarity of Cp-exocyclic carbon to π -acceptor carbonyl substituents and the twist angle of NO to Cp-exocyclic carbon are discussed. Based on the 2D HETCOR, C(2,5) resonating at a lower field than C(3,4) on the Cp(Cr) ring whereas C(3,4) resonating at a lower field than C(2,5) on the Cp(Fe) and the Cp(W) ring are revealed. The hypothesis to elucidate these data assignments has been proposed. The electron density distribution in the cyclopentadienyl ring has been discussed on the basis of ^{13}C NMR data and compared with calculations using the density functional B3LYP exchange–correlation method for those with X-ray diffraction studies.

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1. Introduction

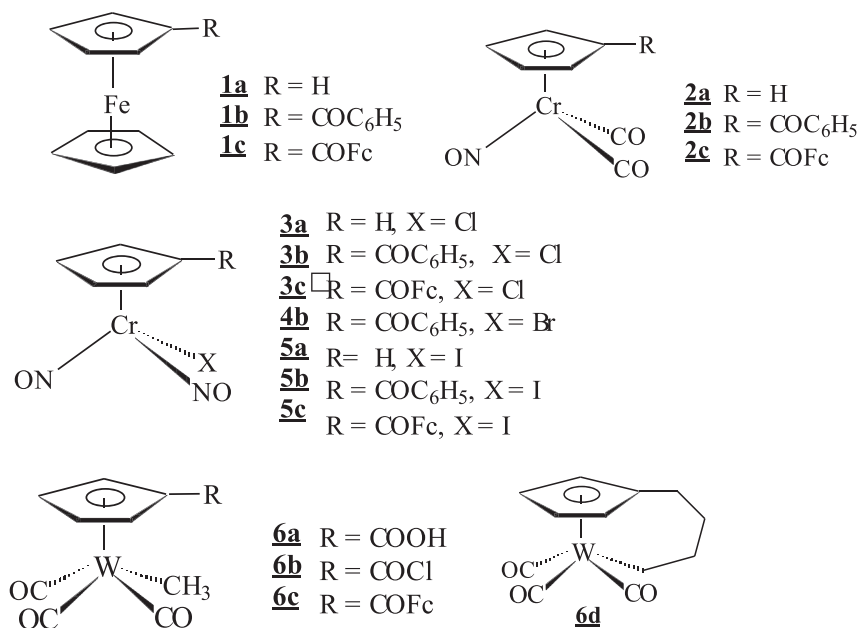
Heterobimetallic complexes have become increasingly important in view of their potential applications in a variety of fields, such as catalysis [1] and drug design [2]. Previously, we attempted to decipher [3] the mystery of the negative correlation of the assignments of C(2,5) and C(3,4) on the Cp ring, in the ^{13}C NMR spectra, between ferrocene **1a** and dicarbonyl(η^5 -cyclopentadienyl)nitrosyl chromium **2a** derivatives bearing electron-withdrawing substituents. To further confirm the hypothesis and their potential applications, complexes containing both Cp(Cr) and Fc moieties, $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}[(\eta^5\text{-C}_5\text{H}_4)\text{CO}(\eta^5\text{-C}_5\text{H}_5)]\text{Cr}(\text{NO})_2(\text{Cl})$ **3c** and $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}[(\eta^5\text{-C}_5\text{H}_4)\text{CO}(\eta^5\text{-C}_5\text{H}_5)]\text{Cr}(\text{NO})_2(\text{I})$ **5c**, and $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}[(\eta^5\text{-C}_5\text{H}_4)\text{CO}(\eta^5\text{-C}_5\text{H}_5)]\text{W}(\text{CO})_3(\text{CH}_3)$ **6c** were synthesized and their ^{13}C NMR data have been examined. The opposite orientation between the

NO ligand and the π -donor or the π -acceptor substituent on the Cp ring of monosubstituted cymenylidene ($\text{CpCr}(\text{CO})_2(\text{NO})$) derivatives was also discovered earlier [4]. The nitrosyl group is located at the side toward the π -donor substituent, while trans oriented to the π -acceptor substituent [5]. The qualitative relationship of nonplanarity of Cp-exocyclic carbon to substituent π -donor and π -acceptor interactions has been addressed. The π -donor substituents and the ipso-carbon atoms to which they are attached are bent away from the $\text{Cr}(\text{CO})_2\text{NO}$ fragments while the π -acceptor substituents and the ipso-carbon atoms to which they are attached are approximately in the Cp plane or are bent toward the $\text{Cr}(\text{CO})_2\text{NO}$ fragments. The magnitudes and directions of these distortions of the Cp planarity appear to be due primarily to electronic effects [6,7]. In hopes of confirming those hypotheses and the validity of them to other Cp(Cr) derivatives, $(\eta^5\text{-C}_5\text{H}_4)\text{COC}_6\text{H}_5)\text{Cr}(\text{NO})_2(\text{X})$ ($\text{X} = \text{Cl}$, **3b**; Br, **4b**; I, **5b**)—having the chromium metal coordinated with electron-withdrawing ligands (NO, X) and the Cp(Cr) ring bearing a benzoyl substituent—were synthesized and

^{*} Corresponding author.

E-mail address: ypwang@thu.edu.tw (Y.-P. Wang).

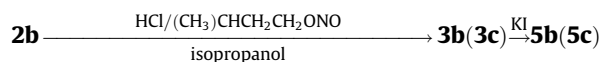
their X-ray structures were studied. Herein, we report the syntheses of new complexes **3b**, **5b**, **5c**, and **6c**, the results of spectral studies on complexes **1a–6a**, **1b–5b**, **1c–3c**, **5c** and **6c**, and the X-ray structural comparisons among complexes **2c**, **3b**, **4b**, and **5b**.



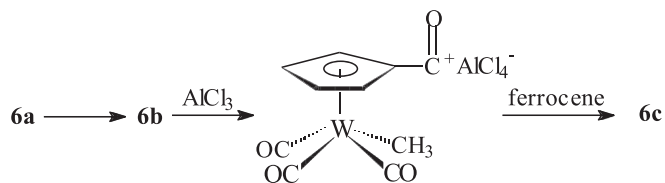
2. Results and discussion

2.1. Synthesis

Chlorination/nitrosylation of **2b** (η^5 -benzoylcyclopentadienyl) dicarbonylnitrosylchromium in isopropanol, a novel method of replacing dicarbonyl with (NO)Cl ligand [8], produced **3b** in 88% yield. By reacting with potassium iodide [9], complex **3b** was converted into iodo derivative **5b** in a yield of 86%. Accordingly, ferrocenyl substituent derivative **5c** (η^5 -C₅H₅)Fe[(η^5 -C₅H₄)CO(η^5 -C₅H₅)]Cr(NO)₂(I) was synthesized from **3c** with a yield of 59%.



By reacting with phosphorus pentachloride, (η^5 -carboxycyclopentadienyl)tricarbonylmethyltungsten **6a** [10] was transformed into the acid chloride **6b**, which formed the Perrier-type complex [11] with aluminum chloride afterwards and subsequently reacted with ferrocene to result in tricarbonyl(η^5 -ferrocenoylcyclopentadienyl)methyltungsten **6c** in 11% yield [12].

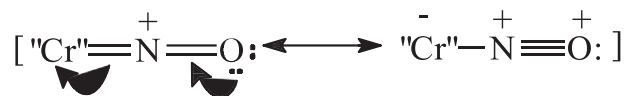


2.2. Characterization: IR

Table 1 [3,8,12–15] lists IR data in the CO and NO regions. All complexes **3b–5b**, **3c**, and **5c** exhibit two terminal nitrosyl

stretching bands, the symmetric mode occurring at 1816–1828 cm⁻¹, and the asymmetric mode at 1715–1739 cm⁻¹. Other functional groups showed their characteristic absorbances. It is interesting to compare the NO stretching frequency of the de-

rivatives of CpCr(CO)₂(NO) (**2b**, 1700; **2c**, 1710 cm⁻¹), CpCr(NO)₂(Cl) (**3b**, 1823, 1738; **3c**, 1818, 1718 cm⁻¹), and CpCr(NO)₂(I) (**5b**, 1821, 1735; **5c**, 1816, 1715 cm⁻¹) with the corresponding band(s) of each unsubstituted parent complex CpCr(CO)₂(NO) (**2a**, 1680 cm⁻¹), CpCr(NO)₂(Cl) (**3a**, 1823, 1715 cm⁻¹), and CpCr(NO)₂(I) (**5a**, 1808, 1709 cm⁻¹). The higher-frequency shift reflects the strong electron withdrawing property of the bridging carbonyl group. The data is consistent with the result found from the study of the ¹³C NMR spectra. The electron withdrawing substituent on Cp ring depletes the electron density of Cr, decreasing the tendency of π back-bonding from Cr to NO ligands, higher frequencies of NO result.



2.3. Characterization: ¹H NMR

The ¹H spectra are listed in Table 2 [3,8,12–15]. The ¹H NMR spectra of complexes **3b**, **5b**, **5c**, and **6c** are consistent with their assigned structures and are similar to other metallocenyl systems [11,16–18]. The ¹H NMR spectrum of **5c** (Fig. 1) exhibits an A₂B₂ pattern for each of the Cp(Cr) and the Cp¹(Fe) ring related to the observed triplets. One pair of triplets resonate at δ = 4.96 and 4.67 ppm corresponding to the protons H(2,5) and H(3,4) of Cp¹(Fe), and the other pair of triplets at δ = 6.42 and 5.90 ppm corresponding to protons of H(2,5) and H(3,4) of Cp(Cr). The downfield triplet can be assigned to the H(2,5) protons of the Cp. This assignment is made on the basis of the fact that the carbonyl group would exert a diamagnetic anisotropic effect. As expected, H(2,5) would be deshielded to a greater extent than the protons on the more remote 3- and 4-positions. Accordingly, the assignments were made. Similarly, chemical shifts of the H(2–5) of Cp(M) for

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