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Synthesis of $(Cl)(NO)_2Cr(\eta^5\text{-}C_5H_4)C(O)(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$. An unexpected product from the Friedel–Crafts acylation of $(CO)_2(NO)Cr(\eta^5\text{-}C_5H_4)C(O)(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$ with $(CO)_2(NO)Cr[(\eta^5\text{-}C_5H_4)C(O)Cl]$

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Abstract

Chlorination/nitrosylation of [η^5-(ferrocenoyl)cyclopentadienyl]dicarbonylnitrosylchromium (3) with hydrogen chloride/isoamyl nitrite gives chloro[η^5-(ferrocenoyl)cyclopentadienyl]dinitrosylchromium 6 which is also obtained by an unexpected Friedel–Crafts acylation of 3 with [η^5-(chloroformyl)cyclopentadienyl]dicarbonylnitrosylchromium (5).

Introduction

Metallocenyl ketones containing two metalloaromatic substituents are well known, for example, diferrocenyl ketone, **1** [1,2], ferrocenyl ruthenocenyl ketone, **2** [1,3], dicymantrenyl ketone [4], cymantrenyl ferrocenyl ketone [4] and cynichrodenyl ferrocenyl ketone **3** * [5]. Metallocenyl ketones which contain three metallo-aromatic substituents are very rare, except for 1,1′-dicymantrenoyl ferrocene **4**. It was of interest to synthesize an analogous trimetallocenyl ketone, 1,1′-dicynichrodenoyl ferrocene [6] by Friedel–Crafts acylation of **3** with cynichrodenoyl chloride **5**. Unexpectedly, a new dimetallocenyl ketone chloro[η^5-(ferrocenoyl)cyclopentadienyl]dinitrosylchromium **6** was obtained. Complex **6** to be the first example of a functionally-substituted-Cp derivative of the $(Cl)(Cp)(NO)_2Cr$ type.

Complex **6** has also been prepared by chlorination/nitrosylation of **3** with hydrogen chloride/isoamylnitrite, a novel method of replacing dicarbonyl with (NO)Cl ligands. The same method can also be used to synthesize chlorocyclopentadienyldinitrosylchromium **7** from cynichrodene **8**.

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* 3 = [η^5-(ferrocenoyl)cyclopentadienyl]dicarbonylnitrosylchromium.

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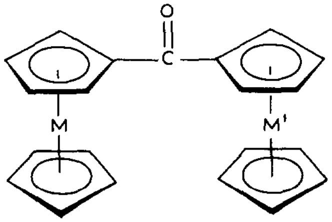
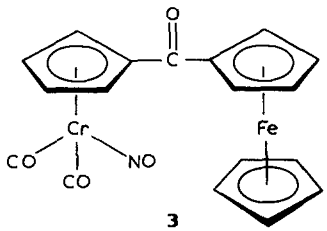


1 M = M' = Fe
2 M = Fe, M' = Ru



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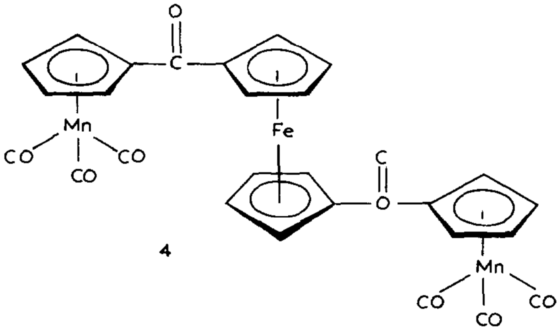

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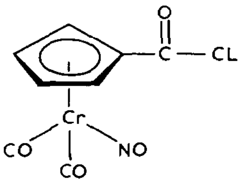

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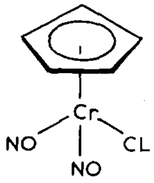

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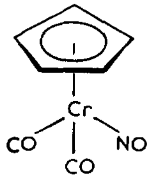

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Experimental

All operations were carried out under nitrogen by use of Schlenk techniques. Traces of oxygen in the nitrogen were removed with BASF catalyst and the deoxygenated nitrogen was dried over molecular sieves 3Å and P_2O_5. Hexane, pentane, benzene and dichloromethane were dried over calcium hydride and freshly distilled under argon from calcium hydride. Diethyl ether was dried over sodium and redistilled under argon from sodium benzophenone ketyl. All the other solvents were used as commercially obtained.

Column chromatography was carried out under nitrogen with Merck Kiesel-gel 60. The silica gel was heated with a heat gun during mixing in a rotary evaporator attached to a vacuum pump for 2 h to remove water and oxygen, and was kept under nitrogen. Cynichrodenylferrocenyl ketone **3** and cynichrodenoic acid **9** were prepared as previously described [5,7].

^{1}H and ^{13}C NMR were recorded on Bruker AM-300-WB or Am-400 spectrometers. Chemical shifts were referenced to tetramethylsilane. Infrared spectra were recorded with a Perkin–Elmer 682 spectrophotometer. Microanalyses were carried out by the Microanalytic Laboratory of the National Taiwan University.

Preparation of chloro[η^5-(ferrocenoyl)cyclopentadienyl]dinitrosylchromium, **6**

Method I. Cynichrodenoic acid **9** (0.30 g, 1.21 mmol) was stirred with phosphorus pentachloride (0.25 g, 1.2 mmol) in 30 ml of dry methylene chloride for 30 min at 0 ° C. Then aluminum chloride (0.32 g, 2.4 mmol) was added and the mixture was stirred for another 2 h at room temperature. The solution was filtered to remove $AlCl_3$ and the filtrate was added dropwise to a solution of **3** (0.5 g, 1.2 mmol) in 50 ml methylene chloride at 0 ° C. After complete addition, the reaction mixture was stirred at room temperature for 12 h. No reaction was detected from TLC analysis. The reaction mixture was then refluxed for 26 h, cooled to 0 ° C and slowly hydrolyzed with 50 ml ice-water in the presence of 3 drops of concentrated hydrochloric acid. The aqueous and organic layers were separated and the aqueous layer was extracted twice with methylene chloride. The combined organic portion was washed five times with water, once with a sodium bicarbonate solution, again with water, and dried with anhydrous magnesium sulfate. The solution was filtered, concentrated to 25 ml under aspirator vacuum. Then silica gel (2 g) was added and the remaining solvent was removed under vacuum. The residue was added to a dry-packed column (2 cm × 35 cm) of silica gel. Elution of the column with benzene/ether (8 : 1) gave a brown band which upon removal of the solvent under vacuum gave **6**, 0.22 g (42%). An analytical sample, mp. 149 ° C(dec), was obtained as dark brown red crystals by recrystallization from methylene chloride/pentane (1/4).

Analysis: Found: C, 45.37; H, 3.21; N, 6.34. $C_{16}H_{13}ClN_2O_3CrFe$ calcd.: C, 45.26; H, 3.09; N, 6.60%. ^{1}H NMR ($CDCl_3$): δ (relative intensity, multiplicity, assignment): 4.25 (5H, s, Cp^2(Fe) unsubstituted ring protons); 4.63 (2H, t, Cp^1(Fe) H(3,4)); 4.96 (2H, t, Cp^1(Fe) H(2,5)); 5.80 (2H, t, Cp(Cr) H(3,4)); 6.28 (2H, t, Cp(Cr) H(2,5)). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (assignment): 70.41 (Cp^2(Fe)); 70.84 (Cp^1(Fe), C(2,5)); 73.21 (Cp^1(Fe), C(3,4)); 77.98 (Cp^1(Fe), C^1); 102.67 (Cp(Cr), C(3,4)); 106.57 (Cp(Cr), C(2,5)); 111.94 (Cp(Cr), C(1)); 190.27 (-C(O)-). IR spectrum ($CDCl_3$): cm^{-1} (intensity): 1818 (vs), 1718 (vs), 1628 (w). Mass spectrum: $m/e = 424.5$ (M^+).

Method II. Through a solution of **3** (0.3 g, 0.72 mmol) in 100 ml of isopropanol and 10 ml of methylene chloride, was bubbled hydrogen chloride for 5 min. After cooling to 0–10 ° C, isoamyl nitrite (0.15 ml, 1.13 mmol) was added slowly and the reaction mixture was stirred for 30 min. Then the solvent was removed under vacuum and the residue was extracted with 100 ml methylene chloride, washed several times with water, and dried with magnesium sulfate. The solution was filtered, silica gel (2 g) was added and the solvent removed under vacuum. The residue was added to a dry-packed column (2.5 × 15 cm) of silica gel. Elution of the column with benzene/ether (8 : 1) solvent gave **6**, 0.21 g (68%), as a dark brown-solid.

Preparation of chloro(η^5-cyclopentadienyl)dinitrosylchromium, 7

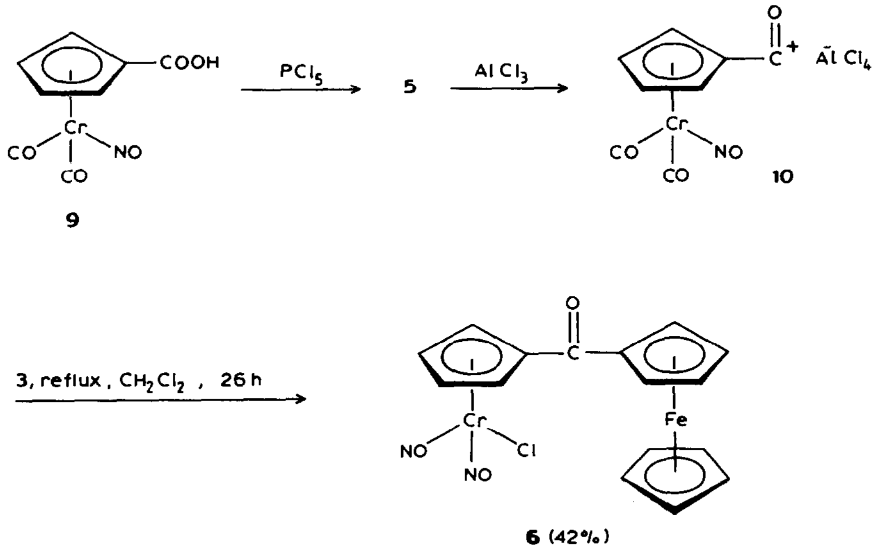
Through a solution of cynichrodene **8** (1.0 g, 4.93 mmol) in 10 ml of isopropanol, was bubbled hydrogen chloride for 5 min. After cooling to 0–10 ° C, isoamyl nitrite (1.0 ml, 7.44 mmol) was added slowly and the reaction mixture was stirred for 30 min. The solvent was removed, the residue was extracted with 100 ml methylene chloride. The extracts were washed several times with water and dried with magnesium sulfate, and the solvent was removed to give a greenish-yellow solid. Methylene chloride (15 ml) was added to dissolve the solid, and 3 g of silica gel was added. After filtration the solvent was removed under vacuum. The residue was added to a dry-packed column (1.8 × 9 cm) of silica gel. Elution of the column with benzene/hexane (3/1) gave a brown-green band which upon removal of solvent under vacuum gave 7, 0.85 g (81%), as a dark-green solid, mp. 136–138 ° C. ^{1}H NMR ($CDCl_3$): δ (multiplicity) 5.73 (s). ^{13}C NMR ($CDCl_3$): δ 103.02. IR spectrum ($CDCl_3$) cm^{-1}: (intensity) 1820 (vs), 1710 (vs). Mass spectrum: $m/e = 212$ (M^+). The data are in consistent with published data for the compound [8].

Results and discussion

The complex, [carboxy-(η^5-cyclopentadienyl](dicarbonyl)(nitrosyl)chromium (**9**), [7] was treated with phosphorus pentachloride to give the acid chloride **5**. The Perrier-type complex **10** [9], which was obtained from the reaction of **5** with aluminum chloride, was allowed to react with **3** under reflux for 26 h to give the only isolable product, [η^5-(ferrocenoyl)cyclopentadienyl](chloro)(dinitrosyl)chromium, **6**, in 42% yield.

Complex **6** can also be prepared by chlorination/nitrosylation of **3** with HCl/isoamylnitrite in 68% yield. The same method was applied to convert **8** and **7** in 81% yield.

$$3 \xrightarrow[\text{isopropanol}/CH_2Cl_2]{HCl/(CH_3)_2CHCH_2CH_2ONO} 6\ (68\%)$$



The infrared spectrum of **6** exhibits two nitrosyl stretching bands, a symmetric mode at 1818 cm^{-1} and an asymmetric mode at 1718 cm^{-1} [9]. Delocalization of the π electrons of the C=O group from both sides reduces the double bond character of the C=O causing absorption at a lower wave number (1628 cm^{-1}) than that of the normal C=O stretching frequency.

The ^{1}H NMR spectrum of **6** exhibits an AA′XX′ pattern for each of Cp(Cr) and Cp^1(Fe), consisting of two pairs of apparent triplets [10]. One pair of triplets resonate at δ 4.63 and 4.96 corresponding to the protons H(3,4) and H(2,5) of Cp^1(Fe) and the other pair of triplets at δ 5.80 and 6.28 corresponding to protons H(3,4) and H(2,5) of Cp(Cr). In each pair, the downfield and the upfield triplets were assigned to H(2,5) and H(3,4) respectively. These assignments were made on the assumption that the protons near the electron-withdrawing carbonyl group are expected to be deshielded to a greater extent than the protons on the more distant 3- and 4-position as compared with similarly arranged cyclopentadienyl ring protons in many other metallo-aromatic systems [9,11,12]. The ^{1}H NMR spectrum of **6** shows that the chemical shifts of protons on both Cp^1(Fe) and Cp(Cr) occur at a lower field than those of the corresponding protons of ferrocene (δ 4.18) and chlorocyclopentadienyldinitrosylchromium, **7**, (δ 5.73). This reflects the strong electron-withdrawing effects of the bridging $>$C=O groups.

The assignments of ^{13}C NMR spectrum for compound **6** are based on: (i) standard ^{13}C NMR correlations [13]; (ii) 2D-HetCOR; and (iii) DEPT techniques. Three less intense signals at δ 190.27, 111.94 and 77.98 correspond to the organic carbonyl carbon, C(1) of Cp(Cr) and C(1) of Cp^1(Fe), respectively. Carbons of Cp^2(Fe) resonate at δ 70.41. The lines for C(2-5) of Cp(Cr) and of Cp^1(Fe) were assigned on the basis of 2D-HetCOR (Fig. 1). Chemical shifts at δ 102.67 and 106.57 were assigned to C(3,4) and C(2,5) of the Cp(Cr) ring, respectively. Chemical shifts at δ 70.84 and 73.21 were assigned to C(2,5) and C(3,4) of Cp^1(Fe) ring, respectively. The assignment of highfield and lowfield chemical shifts to C(2,5) and C(3,4) of Cp^1(Fe) ring, respectively, is analogous to the assignments for ferrocene derivatives bearing an electron-withdrawing substituent [14]. However, the opposite assignment in which the downfield shift and upfield shift are assigned to C(2,5) and C(3,4) of Cp(Cr) ring, respectively, is analogous to the assignments for cynichrodene derivatives bearing an electron-withdrawing substituent [5,15].

Complex **6** has been identified crystallographically [16].

Two types of reactions can be considered for the Perrier adduct **10** under Friedel–Crafts conditions: (a) **10** acts as an electrophile to attack the strong nucleophile to give usual Friedel–Crafts products such as in the preparation of compound **3** [5]. (b) **10** decomposes at high temperature to liberate

$$\mathbf{10} + (C_5H_5)Fe(C_5H_5) \rightarrow \mathbf{3}$$

nitrosyl chloride, which displaces the carbonyl ligand from cynichrodene **8** to give chlorocyclopentadienyldinitrosylchromium [17].

$$\underset{\mathbf{8}}{(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)} + NOCl \xrightarrow{CH_2Cl_2} \underset{\mathbf{7}}{(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl} + 2CO$$

When the weak nucleophile **3** was exposed to the Perrier compound **10** at low temperature, no acylation was observed. When the temperature is raised **10** decom-

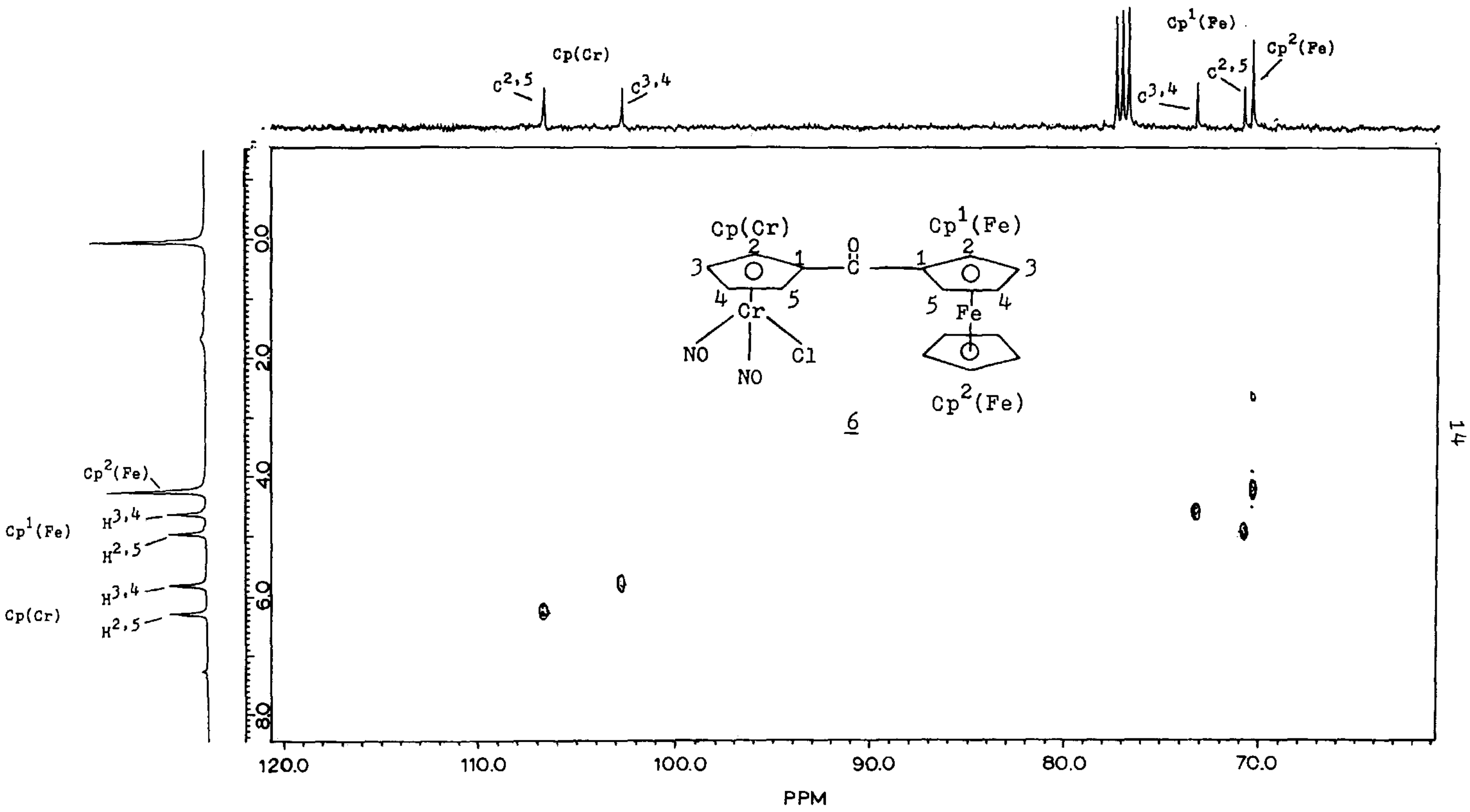


Fig. 1. 2D-HetCOR NMR spectrum of **6**.

poses and releases NOCl, which then reacts with the cynichrodenyl fragment of **3** to give **6**.

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