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Synthesis and reactivity impact from electron-withdrawing substituent on the cyclopentadienyl ligand of cobalt(I)–(III) complexes

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Abstract

Cobaltocene [$\eta^5\text{-C}_5\text{H}_4\text{COOC}(\text{CH}_3)=\text{CH}_2$]₂Co (**1**) was synthesized from $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ at -30°C . **1** showed two reversible redox potentials at -0.335 and -1.418 V, respectively. It was found that the electron-withdrawing substituent on the cyclopentadienyl ligand facilitated the formation of cobaltocene quantitatively. ($\eta^5\text{-C}_5\text{H}_4\text{COOCH}_3$)Co(C_8H_{12}) (**2**) was synthesized from **1** at -50°C under sodium amalgam and the structure of **2** was determined by single-crystal X-ray diffraction. The change of the electron-withdrawing group from the carboisopropenyloxy to the carbomethoxy group on the cyclopentadienyl ligand is also discussed.

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1. Introduction

Recent studies on coordination chemistry have shown considerable interest in the use of so-called hemilabile ligand [1]. The cyclopentadienyl group is one of the most important ligands that can stabilize transition metals in low and high oxidation states. During the last decade, the introduction of a pendant functional group to the cyclopentadienyl ligand of the metal complexes has become an interesting tool to sometimes modify drastically the chemical and physical properties of the compounds [2]. Such pendant functional group on the cyclopentadienyl ligand can temporarily block a vacant coordination site on metal, therefore it is possible to stabilize highly reactive intermediates and find applications in catalytic processes [3]. The interaction between the pendant functional group and the metal center has also become a central topic in inorganic and organometallic chemistry. In a proper case, the pendant functional group will react with the metal center to form a chelate,

even when the functional group is a weak donation group such as butenyl on the cyclopentadienyl ligand [4]. Okuda and his coworkers had successfully separated such weakly chelated compound with butenyl cyclopentadienyl ligand [5]. It was reported that chelated cobalt(I) compound can be prepared from cobalt(III) chloride via reduction under sodium amalgam [6]. We had synthesized some cobalt(I) carbonyl and cobalt(III) iodide compound with similar hemilabile group of weak donating ability on their cyclopentadienyl ligand and try to make chelates via the reduction under sodium amalgam [7]. We found some interesting physical and chemical properties of these compounds during preparation and reduction and would like to report here.

2. Experimental

2.1. General procedures

All reactions were carried out by standard Schlenk techniques under an inert atmosphere of dinitrogen. Solvents were deoxygenated and dried by standard methods and distilled under dinitrogen before use [8].

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Co(III) compounds of $(\eta^5\text{-C}_5\text{H}_4\text{COOC}(\text{CH}_3)=\text{CH}_2)\text{Co}(\text{PPh}_3)_2$, $(\eta^5\text{-C}_5\text{H}_4\text{COOC}(\text{CH}_3)=\text{CH}_2)\text{Co}(\text{CO})\text{I}_2$, $(\eta^5\text{-C}_5\text{H}_4\text{COOCH}_2\text{C}_6\text{H}_5)\text{Co}(\text{PPh}_3)_2$ and $(\eta^5\text{-C}_5\text{H}_4\text{COOCH}_2\text{C}_6\text{H}_5)\text{Co}(\text{CO})\text{I}_2$ were prepared and characterized according to the literature methods [9]. Elemental analyses were performed on a rapid CHN–O 240C analyzer (Heraeus, Germany) at the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. IR spectra were recorded on a Nicolet AVATAR-360IR spectrophotometer in KBr pellets. $^1\text{H-NMR}$ spectra were recorded on a Bruker MSL-300 NMR spectrometer and chemical shifts are reported in ppm referenced to deuterated solvent. UV–vis spectra were recorded on a HP diode-array model 8453 spectrometer in CH_2Cl_2 . Mass spectra were recorded on HP 5989A spectrometer with EI source.

Cyclic voltammetry (CV) was carried out in dry CH_2Cl_2 containing 0.2 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte, using a CHI660A electrochemical workstation. The electrochemical cell was a three-electrode system, with a Teflon cap assembled by a platinum disk electrode ($\Phi = 2$ mm) as working electrode, a platinum wire served as an auxiliary electrode and silver/silver acetate (saturated in CH_2Cl_2) separated by a salt bridge employed as a reference electrode. The potentials were reported vs. the ferrocenium/ferrocene (Fc^+/Fc) reference couple (+0.4 V vs. SCE) as recommended by IUPAC [10]. The experimental reference electrode was calibrated with an internal standard at the termination of each experiment.

The crystal structure was determined on an ENRAF–Nonius CAD4 X-ray diffractometer equipped with a graphite monochromator. Data collection was performed with Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å) using the ω – 2θ scan technique to a maximum 2θ value of 30.17° at the room temperature of 20 ± 1 °C. The structure of the crystal was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically with full-matrix least-squares. Hydrogen atoms were not included in refinement. The final agreement factors are $R_1 = 0.400$ and $wR_2 = 0.1042$ for observed reflections. All calculations were performed on a PC computer using SHELX-97 (Sheldrick, 1997).

2.2. Preparation of $\text{Na}(\eta^5\text{-C}_5\text{H}_4\text{COOC}(\text{CH}_3)=\text{CH}_2)$

Sodium sand (0.95g, 41.3 mmol) was reacted with excess freshly distilled cyclopentadiene in 15 ml of THF under an ice water bath. When sodium sand disappeared, the solvent was evaporated under vacuum. The residue was re-dissolved in 100 ml of THF and cooled to -60 °C. 4.5 ml (41.3 mmol) of $\text{ClCOOC}(\text{CH}_3)=\text{CH}_2$ was added slowly. After 5 h stirring under that temperature, 2.80 g (41.1 mmol) sodium ethoxide in 10

ml of THF solution was added. The reaction mixture was continuously stirred for 3 h. The color of the solution turned orange after warmed to room temperature (r.t.). Evaporating all the solvent, the residue was washed with hexane several times to give 6.3 g of pale yellow solid. Yield 85%. δ_{H} ($\text{DMSO-}d_6$): 6.11 (m, 2H, Cp), 5.54 (t, 2H, Cp, $J = 2.8$ Hz), 4.44 (s, 1H, $=\text{CH}_2$, trans), 4.41 (s, 1H, $=\text{CH}_2$, cis), 1.84 (s, 3H, $-\text{CH}_3$)

2.3. Preparation of $[\eta^5\text{-C}_5\text{H}_4\text{COOC}(\text{CH}_3)=\text{CH}_2]_2\text{Co}$ (1)

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.458 g, 1.92 mmol) was dissolved in 2 ml of absolute ethanol in a 100 ml Schlenk flask under stirring, and then 20 ml of THF was added. The violet red solution was cooled to -30 °C and then added slowly 20 ml of THF solution containing $\text{Na}(\eta^5\text{-C}_5\text{H}_4\text{COOC}(\text{CH}_3)=\text{CH}_2)$ (0.376 g, 2.21 mmol). The reaction mixture was allowed to warm to r.t. after stirring 4 h under -30 °C and then left overnight. The deep red turbid solution was evaporated to dryness in vacuo and the residue was extracted with 100 ml of ether. After filtration, the filtrate was cooled to -78 °C to give deep red solid. The solid was washed with 2×5 ml of cold ether and dried in vacuo. Yield 57% (0.39 g). Anal. Calc. for: $\text{C}_{18}\text{H}_{18}\text{O}_4\text{Co}$ (357.27 g mol^{-1}): C, 60.50; H, 5.08. Found: C, 59.83; H, 5.26%. IR (KBr pallet), $\nu_{\text{max}}/\text{cm}^{-1}$: 3114, 3095($=\text{CH}$ of C_5H_4 ring), 2955($-\text{CH}$ aliphatic), 2919, 1688 (C=O), 1459 (C–C), 1366, 1278, 1116. UV–vis $\lambda_{\text{max}}/\text{nm}$ (CH_2Cl_2): 229 ($\epsilon/\text{dm}^3 \text{mol}^{-1}$ 1.20×10^4), 263 (0.58×10^4), 269 (0.69×10^4), 337 (0.23×10^4). Mass spectrum (EI) m/e : 357 (100, M^+), 317 (13.76, $\text{C}_5\text{H}_4\text{COOC}(\text{CH}_3)=\text{CH}_2\text{CoC}_5\text{H}_4\text{COOH}^+$), 300 (6.86, $\text{C}_5\text{H}_4\text{COOC}(\text{CH}_3)=\text{CH}_2\text{CoC}_5\text{H}_4\text{CO}^+$), 277 (28.57, $\text{C}_5\text{H}_4\text{COOHCOC}_5\text{H}_4\text{COOH}^+$), 188 (5.79, $\text{C}_5\text{H}_5\text{CoC}_5\text{H}_4^+$). $E_{1/2}$ (V, CH_2Cl_2): -0.335 , -1.418 .

2.4. Preparation of $(\eta^5\text{-C}_5\text{H}_4\text{COOCH}_3)\text{Co}(\text{C}_8\text{H}_{12})$ (2)

To a $[\eta^5\text{-C}_5\text{H}_4\text{COOC}(\text{CH}_3)=\text{CH}_2]_2\text{Co}$ (0.1436 g, 0.40 mmol) THF solution (20 ml) was added 0.22 ml of freshly distilled C_8H_{12} (COD) dropwise. The reaction mixture was cooled to -50 °C, needle transferred to a flask containing sodium amalgam (56.0 mg Na, 2.43 mmol, 0.96% Na–Hg) while stirring. The reaction mixture was kept at -25 °C for 4 h and then allowed to warm to r.t. The turbid reaction mixture was filtered through a pad of celite, evaporating in vacuo. The resulting orange–yellow oil was dissolved in 10 ml of THF, loaded on 2 g of alumina, transferred on an alumina column and rinsed with hexane. The yellow band was collected to give 34.8 mg orange–yellow solid, yield 30%. Anal. Calc. for: $\text{C}_{15}\text{H}_{19}\text{O}_2\text{Co}$ (290.25 g mol^{-1}) C, 62.07; H, 6.60. Found: C, 62.20; H, 6.60%. IR (KBr pallet), $\nu_{\text{max}}/\text{cm}^{-1}$: 3115($=\text{CH}$ of C_5H_4 ring),

2978, 2933 (–CH aliphatic), 2865, 2825, 1695 (C=O), 1477 (C–C), 1321, 1022, 853, 803, 1455, 1382, 1282, 1190. δ_{H} (CDCl₃): 5.13 (t, 2H, Cp, $J=2.2$ Hz), 4.43 (t, 2H, Cp, $J=2.2$ Hz), 3.89 (s, 3H, –OCH₃), 3.58 (br, 4H, COD, vinylic), 2.36 (m, 4H, CH₂ of COD), 1.62 (m, 4H, CH₂ of COD). The red crystals suitable for X-ray crystallographic analysis were obtained by crystallization from hexane and cooled under –28 °C. The crystal data and structure refinement parameters are given in Tables 1 and 2.

2.5. The reduction of (η^5 -C₅H₄COOC(CH₃)=CH₂)Co(PPh₃)I₂ and (η^5 -C₅H₄COOC(CH₃)=CH₂)Co(CO)I₂ by sodium amalgam

A solution of (η^5 -C₅H₄COOC(CH₃)=CH₂)Co(PPh₃)I₂ (0.22 g, 0.304 mmol) in THF (40 ml) was cooled to –60 °C, needle transferred to a sodium amalgam (22.0 mg Na, 0.956 mmol, 1% Na–Hg) under that temperature. The reaction mixture was allowed to warm slowly. When the temperature reached to –38 °C, the deep blue reaction mixture turned quickly to deep red. After half an hours stirring under –38 °C, the reaction mixture was filtered through a pad of celite and

Table 1
Crystal data and structure refinement for (η^5 -C₅H₄COOC(CH₃)Co(COD) (2)

Empirical formula	C ₁₅ H ₁₉ CoO ₂
Formula weight	290.23
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	<i>P</i> 1
Unit cell dimensions	
<i>a</i> (Å)	7.071(2)
<i>b</i> (Å)	8.066(3)
<i>c</i> (Å)	12.768(2)
α (°)	100.07(2)
β (°)	101.240(10)
γ (°)	106.40(3)
<i>V</i> (Å ³)	664.4(3)
<i>Z</i>	2
<i>D</i> _{calc} (Mg m ^{–3})	1.451
Absorption coefficient (mm ^{–1})	1.282
<i>F</i> (000)	2520
Crystal size (mm ³)	0.35 × 0.35 × 0.15
Theta range for data collection (°)	1.68–30.17
Index ranges	–9 ≤ <i>h</i> ≤ 9, 0 ≤ <i>k</i> ≤ 11, –18 ≤ <i>l</i> ≤ 17
Reflections collected/unique	4182/3923 [<i>R</i> _{int} = 0.0200]
Completeness to 2 θ = 30.17 (%)	100.0
Absorption correction	Empirical
Max. and min. transmission	0.8309 and 0.6625
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	3923/0/164
Goodness-of-fit on <i>F</i> ²	1.051
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0400, <i>wR</i> ₂ = 0.1042
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0881, <i>wR</i> ₂ = 0.1224
Largest difference peak and hole (e Å ^{–3})	0.649 and –0.427

Table 2
Selected bond lengths (Å) and bond angles (°) for (η^5 -C₅H₄COOC(CH₃)Co(COD) (2)

Bond lengths			
Co(1)–C(9)	2.012(3)	C(3)–C(4)	1.389(5)
Co(1)–C(12)	2.019(3)	C(4)–C(5)	1.412(5)
Co(1)–C(8)	2.025(3)	C(6)–O(1)	1.207(4)
Co(1)–C(13)	2.032(3)	C(6)–O(2)	1.335(4)
Co(1)–C(5)	2.065(3)	O(2)–C(7)	1.438(5)
Co(1)–C(2)	2.065(3)	C(8)–C(9)	1.384(5)
Co(1)–C(1)	2.073(3)	C(8)–C(15)	1.502(4)
Co(1)–C(3)	2.120(3)	C(9)–C(10)	1.504(6)
Co(1)–C(4)	2.121(3)	C(10)–C(11)	1.470(6)
C(1)–C(2)	1.418(4)	C(11)–C(12)	1.515(5)
C(1)–C(5)	1.421(4)	C(12)–C(13)	1.390(5)
C(1)–C(6)	1.455(4)	C(13)–C(14)	1.502(4)
C(2)–C(3)	1.412(5)	C(14)–C(15)	1.475(5)
Bond angles			
C(9)–Co(1)–C(12)	84.9(1)	C(4)–C(3)–C(2)	108.5(3)
C(9)–Co(1)–C(8)	40.1(1)	C(4)–C(5)–C(1)	108.9(3)
C(12)–Co(1)–C(13)	40.1(1)	O(1)–C(6)–C(1)	124.9(3)
C(8)–Co(1)–C(13)	84.1(1)	O(2)–C(6)–C(1)	111.9(3)
C(9)–Co(1)–C(1)	108.3(1)	C(9)–C(8)–C(15)	124.3(3)
C(12)–Co(1)–C(1)	110.2(1)	C(14)–C(15)–C(8)	114.0(2)
C(8)–Co(1)–C(3)	100.9(1)	C(8)–C(9)–C(10)	125.0(3)
C(13)–Co(1)–C(4)	98.9(1)	C(11)–C(10)–C(9)	114.0(3)
C(2)–C(1)–C(6)	124.7(3)	C(10)–C(11)–C(12)	114.1(3)
C(5)–C(1)–C(6)	129.0(3)	C(12)–C(13)–C(14)	124.8(3)
C(3)–C(2)–C(1)	108.5(3)	C(15)–C(14)–C(13)	114.3(3)
C(3)–C(4)–C(5)	107.8(3)		

evaporated in vacuo. The residue was dissolved in a small amount of methylene chloride and loaded on a column of alumina, rinsed with a mixed solvent of methylene chloride and petroleum ether in 1 to 5 ratios under –25 °C. The red band was collected and evaporated in vacuo under –30 °C. The residue was recrystallized in a mixed solvent of methylene chloride and petroleum ether to give 54 mg of rufous red solid. Yield 49.5%. IR (KBr pallet), ν_{max} /cm^{–1}: 1703 (C=O), 1675 (C=C), 1462 (C–C), 1362, 1278, 1122. Mass spectrum (EI): 356 (100, M⁺), 316 (39.72, C₅H₄COOC(CH₃)=CH₂CoC₅H₄COO⁺), 276 (95.82, C₅H₄COOHCOC₅H₄COO⁺), 208 (9.2, C₅H₄COOC(CH₃)=CH₂Co⁺), 187 (15.44, C₅H₄CoC₅H₄⁺), 151 (17.73, C₅H₄COC₅H₄⁺). UV–vis (λ_{max} /nm, CH₂Cl₂): 227 (ϵ /dm³ mol^{–1} 1.3 × 10⁴), 273 (1.4 × 10⁴), 330 (0.46 × 10⁴), 457 (0.22 × 10⁴), 512 (0.30 × 10⁴). E_{1/2} (V, CH₂Cl₂): –0.352.

A similar reaction was carried out with (η^5 -C₅H₄COOC(CH₃)=CH₂)Co(CO)I₂ (0.310 g, 0.633 mmol) in THF (50 ml) and freshly prepared sodium amalgam (39.0 mg Na, 1.70 mmol, 0.96% Na–Hg) under –70 °C. The deep blue color of the reaction mixture turned to deep red when reaching –45 °C. After half an hours stirring, the reaction mixture was filtered and evaporated under –40 °C. The residue was dissolved in a small amount of methylene chloride and loaded on an alumina column, rinsed with a mixed

solvent of methylene chloride, ethyl ether and petroleum ether in 1 to 2 to 5 ratios under -25°C . The red band was collected and evaporated. The residue was re-crystallized in a mixed solvent of methylene chloride and petroleum ether. 113 mg of rufous red solid was obtained. Yield 50%. IR (KBr pallet), $\nu_{\text{max}}/\text{cm}^{-1}$: 1701 (C=O), 1674 (C=C), 1460(C-C), 1361, 1278, 1120. Mass spectrum (EI): 356 (100, M^+), 276 (2.9, $\text{C}_5\text{H}_4\text{COOHCOC}_5\text{H}_4\text{COO}^+$), 188 (1.52, $\text{C}_5\text{H}_5\text{CoC}_5\text{H}_4^+$). UV-vis ($\lambda_{\text{max}}/\text{nm}$, CH_2Cl_2): 228 ($\epsilon/\text{dm}^3 \text{mol}^{-1}$ 1.3×10^4), 273 (1.5×10^4), 332 (0.46×10^4), 465 (0.22×10^4), 512 (0.30×10^4). $E_{1/2}$ (V, CH_2Cl_2): -0.336 .

2.6. The reduction of (η^5 - $\text{C}_5\text{H}_4\text{COOCH}_2\text{C}_6\text{H}_5$)Co(PPh_3) $_2$ and (η^5 - $\text{C}_5\text{H}_4\text{COOCH}_2\text{C}_6\text{H}_5$)Co(CO) $_2$ by sodium amalgam

The reaction was carried out with 0.290 g (0.375 mmol) of (η^5 - $\text{C}_5\text{H}_4\text{COOCH}_2\text{C}_6\text{H}_5$)Co(PPh_3) $_2$ in 50 ml of THF and freshly prepared sodium amalgam (25.8 mg Na, 1.01 mmol, 0.99% Na-Hg) under -50°C . The color of the reaction mixture changed gradually from deep blue to green blue, then yellow brown and finally to deep red when the temperature reached -35°C . After half an hour, the reaction mixture was filtered and evaporated under -30°C . The residue was dissolved in a small amount of methylene chloride and loaded on an alumina column, rinsed with a mixed solvent of methylene chloride, ethyl ether and petroleum ether in 1 to 4 to 2 ratios under -25°C . The red band was collected, evaporated and the residue was re-crystallized in a mixed solvent of methylene chloride and petroleum ether. Rufous red solid (82 mg) was obtained. Yield 48%. IR (KBr pallet), $\nu_{\text{max}}/\text{cm}^{-1}$: 1731 (C=O), 1497 (C=C), 1469 (C-C), 1384, 1272, 1131. Mass spectrum (EI): 457(100, M^+), 366 (0.93, $\text{C}_5\text{H}_4\text{COOCH}_2\text{C}_6\text{H}_5\text{-CoC}_5\text{H}_4\text{COO}^+$), 323 (2.44, $\text{C}_5\text{H}_4\text{COOCH}_2\text{C}_6\text{H}_5\text{-CoC}_5\text{H}_5^+$), 277 (12.84, $\text{C}_5\text{H}_4\text{COOHCOC}_5\text{H}_4\text{C}_5\text{H}_4\text{-COOH}^+$), 188 (2.99, $\text{C}_5\text{H}_5\text{CoC}_5\text{H}_4^+$). UV-vis ($\lambda_{\text{max}}/\text{nm}$, CH_2Cl_2): 226 ($\epsilon/\text{dm}^3 \text{mol}^{-1}$ 1.29×10^4), 271 (2.40×10^4), 326 (0.52×10^4), 450 (0.20×10^4), 502 (0.22×10^4). $E_{1/2}$ (V, CH_2Cl_2): -0.388 .

The same reaction was carried out with 0.280 g (0.518 mmol) of (η^5 - $\text{C}_5\text{H}_4\text{COOCH}_2\text{C}_6\text{H}_5$)Co(CO) $_2$ in 60 ml of THF with freshly prepared sodium amalgam (35.8 mg Na, 1.56 mmol, 0.99% Na-Hg) under -60°C . The color of the reaction mixture changed gradually from deep purple to deep red when the temperature reached -42°C . After half an hours stirring, the reaction mixture was filtered and evaporated under -25°C . The residue was dissolved in a small amount of methylene chloride and loaded on an alumina column, rinsed with a mixed solvent of methylene chloride, ethyl ether and petroleum ether in 1 to 1 to 4 ratios under -25°C . The red band was collected, evaporated and the residue was re-crystallized in a mixed solvent of

methylene chloride and petroleum ether. Rufous red solid (119 mg) was obtained. Yield 48%. IR (KBr pallet), $\nu_{\text{max}}/\text{cm}^{-1}$: 1730 (C=O), 1495 (C=C), 1467 (C-C), 1385, 1270, 1129. Mass spectrum (EI): 457(97.8, M^+). UV-vis ($\lambda_{\text{max}}/\text{nm}$, CH_2Cl_2): 228 ($\epsilon/\text{dm}^3 \text{mol}^{-1}$ 1.12×10^4), 272 (1.51×10^4), 326 (0.36×10^4), 458 (0.20×10^4), 503 (0.26×10^4). $E_{1/2}$ (V, CH_2Cl_2): -0.389 .

3. Results and discussion

It is known that sodium cyclopentadienide reacts with CoCl_2 affords cobaltocene Cp_2Co at room temperature [11], sometimes give better yield if reflux in THF [12]. But at a lower temperature, typically under -30°C , it gives chloro-bridged metal dimer $[\text{CpCoCl}]_2$ [13]. It seems that chloro-bridged structure has limited strength and it is easily broken under higher temperature. In our experiments, we treated sodium allyloxocarbonyl cyclopentadienide, $\text{Na}(\eta^5\text{-C}_5\text{H}_4\text{COOCH}_2\text{CH}=\text{CH}_2)$, with CoCl_2 under the temperature of -30°C . Cobaltocene **1** was obtained as the mature product (57% of yield), not the expected chloro-bridged metal dimer with substituted cyclopentadienyl ligands. If our calculation was based on the sodium salt, the yield was almost 100%. It was suggested that the cobaltocene is more thermally stable especially when there is electron-withdrawing group on the cyclopentadienyl ring. The chloro-bridged metal dimer $[\text{Cp}^*\text{CoCl}]_2$, probably being the reaction intermediate, can easily transfer to the structure of cobaltocene even under the temperature as low as -30°C . Since the electron density on the metal was withdrawn towards the cyclopentadienyl ring, not enough electron density on the metal can hold the chloro-bridged structure. Furthermore, the pendant functional side chain can quickly block the vacant coordination site on the metal to make chelated compound and activated another Co-Cl bond [14]. Since the cyclopentadienide is a stronger electrophilic reagent, cobaltocene is then formed easily. The effect of the electron-withdrawing group on the cyclopentadienyl ring is also shown by the reducing reaction of Co(III) compounds which consists of a cyclopentadienyl ligand with electron-withdrawing group. It was found that (η^5 - $\text{C}_5\text{H}_4\text{COOC}(\text{CH}_3\text{H}_2)\text{Co}(\text{PPh}_3)_2$ and (η^5 - $\text{C}_5\text{H}_4\text{COOC}(\text{CH}_3)=\text{CH}_2$)Co(CO) $_2$ gave the same product, $[\eta^5\text{-C}_5\text{H}_4\text{COOC}(\text{CH}_3)=\text{CH}_2]_2\text{Co}$, when reduced by amalgam under -60°C . Same reactions happened to (η^5 - $\text{C}_5\text{H}_4\text{COOCH}_2\text{C}_6\text{H}_5$)Co(PPh_3) $_2$ and (η^5 - $\text{C}_5\text{H}_4\text{COOCH}_2\text{C}_6\text{H}_5$)Co(CO) $_2$. They gave the same product, $[\eta^5\text{-C}_5\text{H}_4\text{COOCH}_2\text{C}_6\text{H}_5]_2\text{Co}$, also under -60°C , when treated with sodium amalgam. It was found that carbonyl compounds were more reactive since the color of their solution changed to red under lower temperature than their triphenyl phosphine analogues when reacted with sodium amalgam. The ele-

mental analysis agrees to the products of substituted cobaltocene from the reduction containing some solvent CH_2Cl_2 . It is possible since the product was obtained from the solvent of methylene chloride. Further more the IR, Mass spectra and CV measurements of the products demonstrated clearly that the carbonyl and triphenyl phosphine analogues gave the same substituted cobaltocene. And it was also found that all the transformation from mono cyclopentadienyl cobalt compounds to the corresponding cobaltocene was quantitative. Schore reported that as much as 85% of the carbomethoxy cyclopentadienyl dicarbonyl cobalt release carbomethoxy cyclopentadienide anion when treated with sodium amalgam [15]. Our experimental results supported the Schore's argument. It was suggested by the results of these reductions that the formation of a chloro-bridged metal dimer needs contribution of electron density from their metal center. A ligand of cyclopentadienyl with electron-withdrawing group on it disperses more electron density from the metal to the cyclopentadienyl ring, therefore, decreases the stability of the chloro-bridged structure. All the reported chloro-bridged cyclopentadienyl metal dimer contain electron-donating substituent on their Cp rings [16,6], their chloro-bridged structure should be benefited from their relatively electron rich ligands of Cp ring. The electron-withdrawing substituent on the Cp rings make against the formation of chloro-bridged metal dimer but facilitates the formation of cobaltocene is understandable. The possible reaction mechanism is presented by Scheme 1.

The impact of the electron-withdrawing substituent on the Cp ring to thermostability of the cobaltocene was demonstrated by the cyclic voltammetry experiment. CV analysis of **1** gave two redox potentials at -0.335 and -1.418 V, respectively, separated by 1.083 V (Fig. 1). This is the first example of two one-electron redox peaks of a cobaltocene observed. The redox potential of Cp_2Co and $[\text{C}_5(\text{CH}_3)_5]_2\text{Co}$ were reported at -0.91 V [17] and -1.47 V [18], respectively. The tremendous electronic effect of the substituted group on the cyclopentadienyl ring from electron-withdrawing to electron-

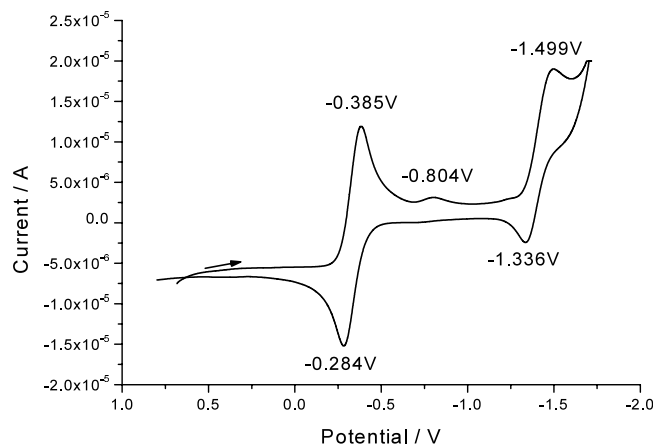
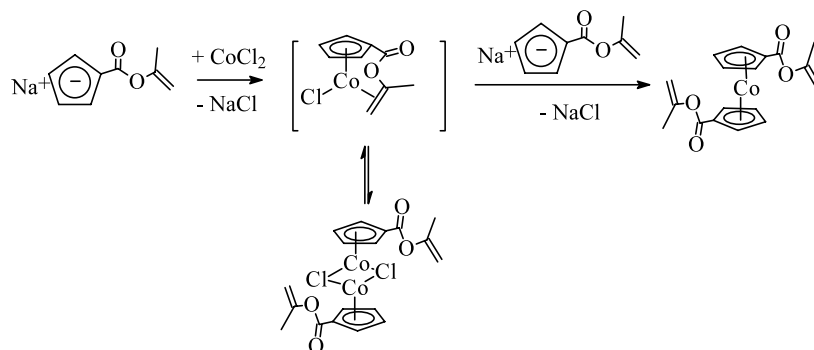


Fig. 1. Cyclic voltammogram of $[\eta^5\text{-C}_5\text{H}_4\text{COOC}(\text{CH}_3)=\text{CH}_2]_2\text{Co}$ (**1**) in methylene chloride with 0.2 M TBAP, showing the two reversible redox peaks.

donating in nature can be seen. Such an effect from the substituents to the redox potential of cyclopentadienyl metal complex was also observed by Lau and coworkers [19]. To explain the result of CV analysis, a possible reason can be suggested, that is each allyloxycarbonyl group on cyclopentadienyl ring of this substituted cobaltocene can assist to disperse one electron. It was suggested by Cramer and Seiwel that the cyclopentadienyl ligand was able to transfer of an electron pair from metal during nucleophilic attack [20]. Basolo found that the electron-withdrawing group to the cyclopentadienyl ring can causing the ring to pull more electron density away from the metal in the ground state [21]. This process was named ring-slippage mechanism, which was confirmed by the crystallographic works of Schonberg, Nesmeyanov and Merola, respectively [22]. Based on the ring-slippage mechanism the electron-withdrawing allyloxycarbonyl group may have a greater tendency to accept electron density from the cobalt in the reaction intermediate therefore increase the stability of $[\eta^5\text{-C}_5\text{H}_4\text{COOC}(\text{CH}_3)=\text{CH}_2]_2\text{Co}$ during the reduction. The stability of the reaction intermediate may be ascribed to a resonance stabilization effect and the delocalization of the electron density away from the

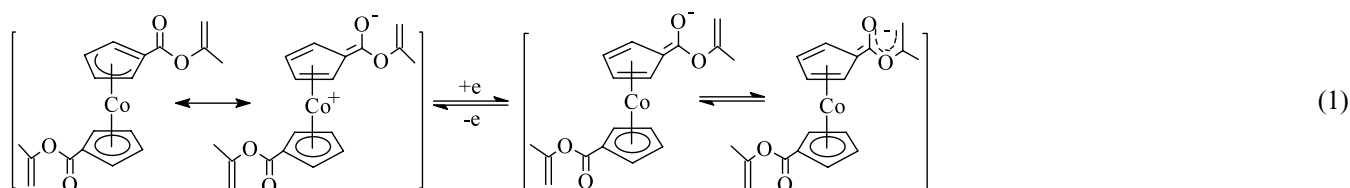


Scheme 1.

Cp ring owing to the presence of the electron-withdrawing allyloxycarbonyl group, which may be illustrated by the resonance structures and the equilibrium shown in Eq. (1).

The possible reaction mechanism is also illustrated by Scheme 2. Each reaction intermediate is stabilized by a possible resonance structure. Similar electron dispersion by the ring substituent was invoked to explain the dimerization of formyl(pentamethyl)cobaltocene [23].

Although the existence of electron-withdrawing group on the cyclopentadienyl ligand increases the stability of cobaltocene over chloro-bridged metal dimer, it decreases its stability towards reductive reagent. When Co(II) was reduced to Co(I) by sodium amalgam, one of the Cp ring in **1** was substituted by the neutral ligand cyclooctadiene (COD). Surprisingly, the product was $(\eta^5\text{-C}_5\text{H}_4\text{COOCH}_3)\text{Co}(\text{COD})$ (**2**), not the expected $(\eta^5\text{-C}_5\text{H}_4\text{COOC}(\text{CH}_3)\text{CH}_2)\text{Co}(\text{COD})$. The fact that the

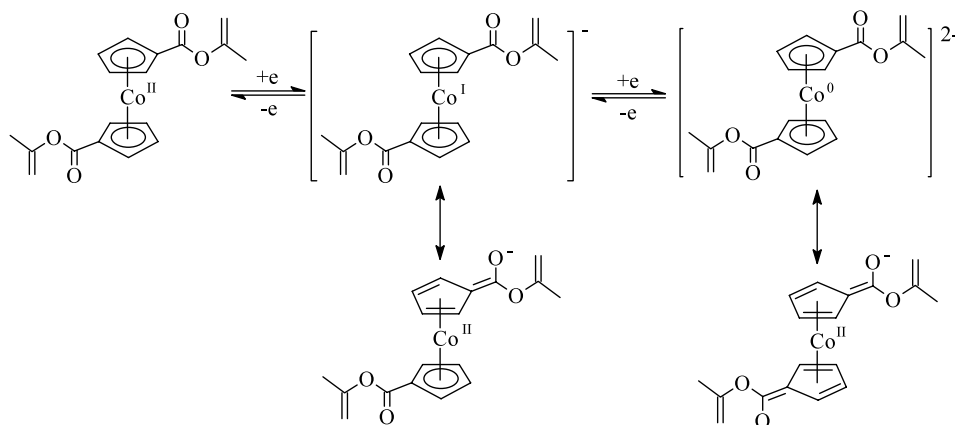


The stability of cyclopentadienyl cobalt complex during redox reaction by other electron-withdrawing ligand such as bipyridine was also reported in the literature [24].

$[\eta^5\text{-C}_5\text{H}_4\text{COOC}(\text{CH}_3)=\text{CH}_2]_2\text{Co}$ has a higher redox potential (-0.335V) than Cp_2Co and $[\text{C}_5(\text{CH}_3)_5]_2\text{Co}$ (-0.91 and -1.47V), can be ascribed to its electron-withdrawing ring substituents, which make it easier to accept electron during reduction. We can suspect that the second redox potential of Cp_2Co and $[\text{C}_5(\text{CH}_3)_5]_2\text{Co}$, if they do have, should be around -2.0 and -2.6V , respectively. Of course it is beyond the endurance of the solvent methylene chloride and could not be detected. But it is not seen that ferrocene has second redox potential even it has a d^6 metal compare to d^7 metal in cobaltocene. Since its redox potential is at 0.4V , the assumed second redox potential should fall into a range that the solvent can endure.

isopropenyl group attached to the carboxyl group changed to the methyl group cannot but was attributed to the reduction of excess sodium amalgam. The crystal structure of **2** is shown in Fig. 2.

The crystal structure **2** shows that the metal–carbon distances are in the normal range of $2.065(3)\text{--}2.120(3)\text{Å}$. Among them, $\text{Co}(1)\text{--C}(3)$ and $\text{Co}(1)\text{--C}(4)$ have longer bond length [$2.120(3)\text{Å}$], while $\text{Co}(1)\text{--C}(2)$ and $\text{Co}(1)\text{--C}(5)$ have shorter bond length [$2.065(3)\text{Å}$]. The distance of $\text{Co}(1)\text{--C}(1)$ [$2.073(3)\text{Å}$] is in between and the electron-withdrawing substituent is attached to the C(1). The cyclopentadienyl ring is in a slightly puckered form. The C–C bond lengths in the cyclopentadienyl ring are in the range of $1.389(5)\text{--}1.421(4)\text{Å}$. The C(3)–C(4) bond was found the furthest from the ring substituent and has the shortest bond length [$1.389(5)\text{Å}$] among the five ring C–C bonds, showing more double bond character. And it was also found that the



Scheme 2.

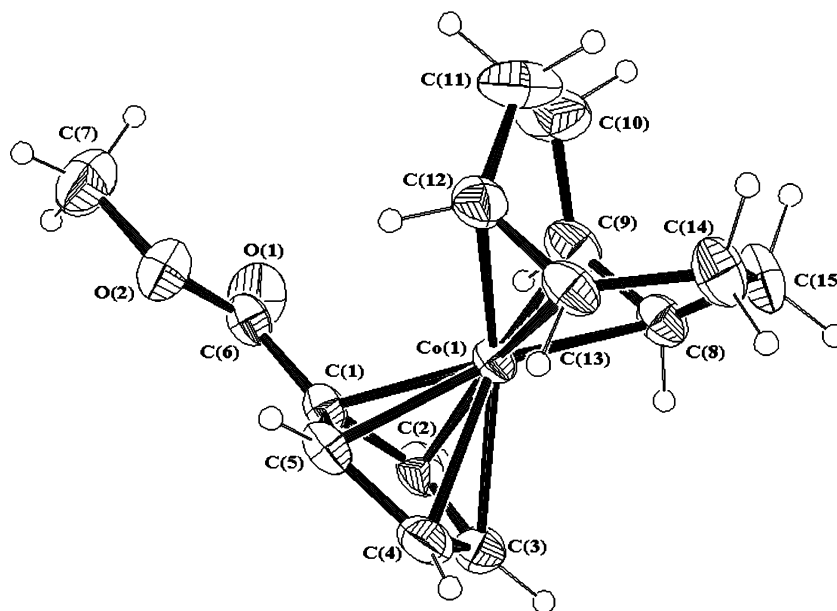


Fig. 2. Molecular structure of $(\eta^5\text{-C}_5\text{H}_4\text{COOCH}_3)\text{Co}(\text{COD})$ (**2**). Ellipsoids are drawn at 50% probability level.

closer to the ring substituent the longer the C–C bonds. Thus, the metal and cyclopentadienyl ring has a η^2, η^3 -bonding mode. The strong electron-withdrawing substituent of carbomethoxy group is linked to the center of the η^3 -bonding carbon that result in shorter metal-carbon distances compared to that of η^2 -bonding carbons. Hence we found that the cobalt atom is not on the central axis of the Cp ring, it deflects from C(3), C(4), and slightly towards C(1), C(2) and C(5) atoms. Similar bonding character was also found in the crystal structure of $(\eta^1:\eta^5\text{-C}_5\text{H}_4\text{COCH}_2\text{SCH}_3)\text{Mn}(\text{CO})_2$ where the shortest metal-ring carbon bond is linked to a strong electron-withdrawing substituent on the cyclopentadienyl ring and the ring carbons the furthest from the substituent have longer metal-carbon bond lengths [25]. In the crystal structure of a cobalt(III) compound, $(\eta^5\text{-C}_5\text{H}_4\text{COOCH}_2\text{C}_6\text{H}_5)\text{Co}(\text{PPh}_3)_2$ [26], the shortest metal-carbon bond is also linked to the strong electron-withdrawing substituent. The C–C bonds in the cyclopentadienyl ring become longer as they get closer to the carbon atom, which links the electron-withdrawing substituent.

The distances between cobalt atom and the coordinated carbon atoms of the double bonds in the COD ring of **2** are also not the same. The bond length of Co(1)–C(9) [2.012(3) Å] and Co(1)–C(12) [2.019(3) Å] are comparatively shorter than that of Co(1)–Co(8) [2.025(3) Å] and Co(1)–C(13) [2.032(3) Å], which can be explained by the strong *trans* effect of **2** compared to the longer Co(1)–C(3) and Co(1)–C(4) bond lengths and shorter Co(1)–C(2) and Co(1)–C(5) bond lengths across cobalt atom. But the bond lengths of C(8)–C(9) and C(12)–C(13) are 1.384(5) Å and 1.390(5) Å, respectively,

showing the normal characteristic of the coordinated double bond.

The crystal structure of **2** shows that the carbomethoxy group is coplanar with the cyclopentadienyl ring, hence the π conjugation system involving Cp ring and the carbomethoxy group. A better stability of this structure under reductive condition is expected.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 196051 for $(\eta^5\text{-C}_5\text{H}_4\text{COOCH}_3)\text{Co}(\text{COD})$. 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

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