Synthesis, reactivity and electrochemical properties of substituted cyclopentadienyl cobalt(III) complexes

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Cyclopentadienyl cobalt complexes (η^5-C_5H_4R)$CoLI_2$ [L = CO, R = -$COOCH_2CH=CH_2$ (3); L = PPh_3, R = -$COOCH_2$-$CH=CH_2$ (6); L = P(p-$C_6H_4CH_3$)$_3$, R = -$COOC(CH_3)=CH_2$ (7), -$COOCH_2C_6H_5$ (8), -$COOCH_2CH=CH_2$ (9)] were prepared and characterized by elemental analyses, ^{1}H NMR, IR and UV-vis spectra. The reaction of complexes (η^5-C_5H_4R)$CoLI_2$ [L = CO, R = -$COOC(CH_3)=CH_2$ (1), -$COOCH_2C_6H_5$ (2); L = PPh_3, R = -$COOC(CH_3)=CH_2$ (4), -$COOCH_2C_6H_5$ (5)] with Na-Hg resulted in the formation of their corresponding substituted cobaltocene (η^5-$C_5H_4R)_2Co$ [R = -$COOC(CH_3)=CH_2$ (10), -$COOCH_2C_6H_5$ (11)]. The electrochemical properties of these complexes 1—11 were studied by cyclic voltammetry. It was found that as the ligand (L) of the cobalt(III) complexes changing from CO to PPh_3 and P(*p*-tolyl)$_3$, their oxidation potentials increased gradually. The cyclic voltammetry of α,α′-substituted cobaltocene showed reversible oxidation of one electron process.

Keywords Cobalt, cyclopentadienyl derivatives, phosphine substituted compounds, cyclic voltammetry

Introduction

η^5-Cyclopentadienyl derivatives of cobalt metal have been intensively studied since the initial synthesis of cyclopentadienyl dicarbonyl cobalt in 1955.[1] Cycloaddition catalyzed by organocobalt complexes,[2,3] intramolecular cyclization and ring opening of epoxy derivatives catalyzed by carbonyl cobalt were reported.[4-6] The 16-electron cyclopentadienyl cobalt fragment CpCoL (Cp = η^5-C_5H_5; L = two-electron donor) has played an important role in the mechanistic elucidation of several fundamental organometallic transformations such as ligand substitution,[7] olefin insertion into a metal-alkyl band[8] and alkyne trimerization.[9] So, various kinds of structural modifications on the cyclopentadienyl ring have been made to improve its chemical and catalytical properties.[10] We are interested in the synthesis, reactivity and electrochemical properties of functionally substituted cyclopentadienyl cobalt complexes.[11] Here we report the synthesis, and structural characterization of some cobalt(III) complexes, and their reduction reaction and electrochemical behavior.

Experimental

General

All operations including column chromatography were carried out under purified nitrogen atmosphere using standard Schlenk techniques. The solvents employed hexane, tetrahydrofuran (THF), diethyl ether were predried over sodium wire and finally distilled under nitrogen atmosphere from sodium/benzophenone. Methylene chloride and petroleum ether were dried and distilled from calcium hydride. Methylene chloride for cyclic chromatography was fractionally distilled three times over

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calcium hydride. Neutral alumina was dried in an oven at 110℃ for several days, and then heated under reduced pressure in a rotary evaporator to remove residual water and oxygen. It was subsequently deactived with 5% (by weight) of degassed water. Triphenyl phosphine (PPh_3) was recrystallized from methanol prior to use. Tricyclohexyl phosphine (PCy_3) and tri-*p*-tolyl phosphine were obtained from Aldrich Chemicals and used without further purification.

The 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 measured on a Nicolet FT-IR-50-X spectrophotometer. ^1H NMR spectra were recorded on a Bruker MSL-300 NMR spectrometer and chemical shifts were reported in ppm relative to TMS as internal reference.

Electrochemical measurements were made with an m273A EG&G Princeton Applied Research Poteniostat. The electrochemical cell was a three-electrode system with a Teflon cap assembled by a platinum disc electrode ($\Phi = 2$ mm) as working electrode, a platinum wire as auxiliary electrode and a silver wire as pseudo-reference electrode. The oxidation and reduction potentials of the compounds were measured by cyclic voltammetry in dry CH_2Cl_2 containing 0.2 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte and were reported with the $[Fe(\eta^5\text{-}C_5H_5)_2]^{0/+}$ (Fc^0/Fc^+) couple ($E^{ox}_{1/2} = 0.4$ V versus SCE in CH_2Cl_2) as an internal reference.[12]

Complexes $(\eta^5\text{-}C_5H_4COOCH_2CH=CH_2)Co(CO)_2$, $(\eta^5\text{-}C_5H_4COOC(CH_3)=CH_2)Co(CO)I_2$ (**1**), $(\eta^5\text{-}C_5H_4COOCH_2C_6H_5)Co(CO)I_2$ (**2**), $(\eta^5\text{-}C_5H_4COOC(CH_3)=CH_2)Co\text{-}(PPh_3)I_2$ (**4**), and $(\eta^5\text{-}C_5H_4COOCH_2C_6H_5)Co(PPh_3)I_2$ (**5**) were prepared as previously reported,[11] and were confirmed by their IR and ^1H NMR spectra.

Synthesis of $(\eta^5\text{-}C_5H_4COOCH_2CH=CH_2)Co(CO)I_2$ (**3**)

To a solution of complex $(\eta^5\text{-}C_5H_4COOCH_2CH=CH_2)Co(CO)_2$ (0.58 g, 2.2 mmol) in ether (4 mL) was added dropwise a solution of iodine (0.59 g, 2.3 mmol) in ether (6 mL) at 0℃. The solution turned to purple immediately and gas evolved vigorously. After being stirred 2 h at 0℃, the reaction mixture was allowed to warm up to room temperature. The dark purple solution was filtered and the volatile was removed *in vacuo*. The residue was recrystallized from CH_2Cl_2/hexane in 1:5 ratio to give the complex **3** as black-purple crystals (0.91 g, 85%). mp 82℃. ν_{max}(KBr): 2073s(CO), 1728s(C=O), 1647m(C=C), 1472m, 1378m, 1284m, 1147m(C_5H_4) cm^{-1}. δ_H($CDCl_3$): 6.17(t, J = 2.1 Hz, 2H, Cp), 5.78(t, J = 2.1 Hz, 2H, Cp), 5.90—6.06(m, 1H, =CH), 5.47(d, J = 17.6 Hz, 1H, $=CH_2$-*trans*), 5.36(d, J = 9.8Hz, 1H, $=CH_2$-*cis*), 4.86(d, J = 5.0 Hz, 2H, OCH_2). Anal. $C_{10}H_9O_3CoI_2$. Calcd: C, 24.52; H, 1.85. Found: C, 24.60; H, 2.01.

Synthesis of $(\eta^5\text{-}C_5H_4COOCH_2CH=CH_2)Co(PPh_3)I_2$ (**6**)

Compound **3** (0.37 g, 0.75 mmol) was dissolved in ether (10 mL) at room temperature. To this solution triphenyl phosphine (0.20 g, 0.74 mmol) was added and gas evolution occurred immediately. After stirring for 6 h, a blue-green precipitate was formed in the solution. The precipitate was separated by a centrifuge and washed with ether and hexane. The precipitate was dried *in vacuo* to give a black solid (0.48 g, 89%). mp 126℃. ν_{max}(KBr): 1725s(C=O), 1628m(C=C), 1497w (C_6H_5), 1481m, 1378m, 1278m, 1156m (C_5H_4). δ_H($CDCl_3$): 5.93(t, J = 2.1 Hz, 2H, Cp), 4.23(t, J = 2.1 Hz, 2H, Cp), 6.10(1H, CH=), 5.51(d, J = 17.0 Hz, 1H, $=CH_2$-*trans*), 5.31(d, J = 10.9 Hz, 1H, $=CH_2$-*cis*), 4.93(d, J = 6.0 Hz, 2H, OCH_2), 7.51—7.84(m, 15H, PPh_3). Anal. $C_{27}H_{24}O_2CoPI_2$. Calcd: C, 44.76; H, 3.34. Found: C, 44.83; H, 3.36.

Synthesis of $(\eta^5\text{-}C_5H_4COOC(CH_3)=CH_2)CoP(p\text{-tolyl})_3I_2$ (**7**)

A similar procedure was used as that described for the preparation of compound **6** to afford a blue solid (Yield 92%). mp 140℃. ν_{max}(KBr): 1738s(C=O), 1675m(C=C), 1600w(C_6H_4Me), 1500w(C_6H_4Me), 1475m, 1375m, 1284m, 1140m(C_5H_4) cm^{-1}. δ_H($CDCl_3$): 7.95—6.91(m, 12H, tolyl), 5.98(t, J = 2.1 Hz, 2H, Cp), 4.15(t, J = 2.0 Hz, 2H, Cp), 4.99

(s, 1H, $=CH_2$-*trans*), 4.82(s, 1H, $=CH_2$-*cis*) 2.16(s, 3H, CH_3), 2.43(s, 9H, $C_6H_4CH_3$). Anal. $C_{30}H_{30}O_2CoPI_2$. Calcd: C, 47.02; H, 3.95. Found: C, 47.20; H, 4.03.

Synthesis of $(\eta^5\text{-}C_5H_4COOCH_2C_6H_5)CoP(p\text{-tolyl})I_2$ (**8**)

The same procedure as that described for compound **7** was used. A black solid was obtained (Yield 90%). mp 144℃. ν_{max}(KBr): 1725s(C=O), 1600w(C_6H_4-Me), 1497w(C_6H_4Me), 1475m, 1384m, 1278m, 1147m(C_5H_4) cm^{-1}. δ_H($CDCl_3$): 7.76—7.26(m, 17H, tolyl, Ph), 5.89(t, J=2.1 Hz, 2H, Cp), 4.21(t, J=2.1 Hz, 2H, Cp), 5.45(s, CH_2), 2.42 (s, 9H, $C_6H_4CH_3$). Anal. $C_{34}H_{32}O_2PCoI_2$. Calcd: C, 50.03; H, 3.95. Found: C, 50.37; H, 3.91.

Synthesis of $(\eta^5\text{-}C_5H_4COOCH_2CH=CH_2)CoP(p\text{-tolyl})_3I_2$ (**9**)

The same procedure as that described for compound **7** was used. A black-blue solid was obtained (Yield 89%). mp 142℃. ν_{max}(KBr): 1725s(C=O), 1625m (C=C), 1600w(C_6H_4Me), 1500w(C_6H_4Me), 1478m, 1378m, 1278m, 1153m(C_5H_4) cm^{-1}. δ_H($CDCl_3$): 5.91 (d, J=2.1 Hz, 2H, Cp), 4.92 (d, J=2.1 Hz, 2H, Cp), 6.16—6.03 (m, 1H, CH=), 5.43(d, J=17.9 Hz, 1H, $=CH_2$-*trans*), 5.39(d, J=10.7 Hz, 1H, $=CH_2$-*cis*), 4.19(s, 2H, OCH_2), 8.07—7.01(m, 12H, tolyl), 2.43(s, 9H, $C_6H_4CH_3$). Anal. $C_{30}H_{30}O_2PCoI_2$. Calcd: C, 47.02; H, 3.95. Found: C, 47.28; H, 3.85.

Reaction of $(\eta^5\text{-}C_5H_4COOC(CH_3)=CH_2)Co(CO)I_2$ (**1**) *with* Na-Hg

A solution of **1** (0.22 g, 0.45 mmol) in THF (60 mL) was mixed with Na-Hg (Na: 22 mg, 0.96 mmol, 1%) at −60℃. The reaction mixture was stirred and the reaction temperature was raised slowly. When the temperature reached −40℃, the color of the reaction mixture turned from blue to brown. The reaction mixture was then filtered at that temperature . The filtrate was evaporated to dryness and the residue was dissolved in a minimum amount of CH_2Cl_2. The solution was placed on an alumina-packed column and eluted with a mixture of CH_2Cl_2/petroleum ether (1/4) at −25℃. The red band was collected. After evaporation of the solvent, the residue was recrystallized from CH_2Cl_2/petroleum ether solution to give 54 mg of brown crystal **10** (Yield 33%). mp 108℃. λ_{max}(CH_2Cl_2): 227, 273, 330, 457, 512 nm. ν_{max}(KBr): 1703s(C=O), 1675m(C=C), 1462m, 1362m, 1278m, 1122m(C_5H_4) cm^{-1}. *m/z* (EI-MS): 356(M^+, 100). Anal. $C_{18}H_{18}O_4Co$. Calcd: C, 60.50; H, 5.04. Found: C, 59.29; H, 5.00.

Reaction of $(\eta^5\text{-}C_5H_4COOC(CH_3)=CH_2)Co(PPh_3)I_2$ (**4**) *with* Na-Hg

The reaction of **4** with Na-Hg was carried out according to the same method described above. Isolated brown solid was characterized as **10** (Yield 28%). mp 110℃. λ_{max}(CH_2Cl_2): 228, 273, 332, 465, 513 nm. ν_{max}(KBr): 1705s(C=O), 1678m(C=C), 1462m, 1365m, 1278m, 1120m(C_5H_4) cm^{-1}. *m/z* (EI-MS): 356(M^+, 100). Anal. $C_{18}H_{18}O_4Co$. Calcd: C, 60.50; H, 5.04. Found: C, 59.17; H, 5.02.

Reaction of $(\eta^5\text{-}C_5H_4COOCH_2C_6H_5)Co(CO)I_2$ (**2**) *with* Na-Hg

The reaction of **2** with Na-Hg was also carried out by the same method. The brown crystals were characterized as **11** (Yield 30%). mp 98℃. λ_{max}(CH_2Cl_2): 226, 271, 326, 450, 502nm. ν_{max}(KBr): 1731s(C=O), 1497w(C_6H_5), 1468m, 1382m, 1276m, 1120m (C_5H_4) cm^{-1}. *m/z* (EI-MS): 457(M^+, 100). Anal. $C_{26}H_{22}O_4Co$. Calcd: C, 68.27; H, 4.82. Found: C, 66.51; H, 4.80.

Reaction of $(\eta^5\text{-}C_5H_4COOCH_2C_6H_5)Co(PPh_3)I_2$ (**5**) *with* Na-Hg

The reaction of **5** with Na-Hg was carried out similar to the above method. The isolated brown solid was characterized as **11** (Yield 35%). mp 100℃. λ_{max} (CH_2Cl_2): 228, 272, 326, 458, 503 nm. ν_{max}(KBr): 1730s(C=O), 1497w(C_6H_5), 1465m, 1384m, 1254m, 1119m(C_5H_4) cm^{-1}. *m/z* (EI-MS): 457 (M^+, 100). Anal. $C_{26}H_{22}O_4Co$. Calcd: C, 68.27; H, 4.82. Found: C, 66.81; H, 4.70.

Results and discussion

Synthesis and characterization of cobalt(III) complexes

The reaction of $(\eta^5\text{-}C_5H_4R)Co(CO)_2$ with equimolar amount of iodine resulted in the isolation of $(\eta^5\text{-}C_5H_4R)Co(CO)I_2$ [R = -COOC(CH_3) = CH_2 (**1**), -$COOCH_2C_6H_5$ (**2**), -$COOCH_2CH$ = CH_2 (**3**) in good yields. However, attempt to synthesize the complex $(\eta^5\text{-}C_5H_4CH_2COOCH_2CH = CH_2)Co(CO)I_2$ by the similar reaction was unsuccessful. One of the carbonyl groups in complexes **1**—**3** was easily substituted by phosphine and the products were separated by crystallization.

The IR spectra of complexes **1**—**3** showed the same characteristic CO absorption at 2073 cm^{-1} in the ν_{CO} region, which indicated that the different substituents on the Cp ring of the complexes **1**—**3** exerted no influence on the CO vibration frequency. However, compared with $[(\eta^5\text{-}C_5H_5)Co(CO)I_2]$,[13] the absorption of metal carbonyl shifted to higher frequency due to their electron-withdrawing ring substitutents. The stretching frequency of the organic carbonyl ($\nu_{C=O}$ 1744, 1731, 1728 cm^{-1} for **1**—**3** respectively) in the substituents shifted to higher frequencies as the valence of center metal became higher.[11] For complexes **4**—**9**, the organic carbonyl stretching frequencies (which were in the range of 1738—1725 cm^{-1}) shifted slightly to lower frequencies due to carbonyl group replaced by phosphine.

In the ^1H NMR spectra of complexes **1**—**9**, the chemical shift of the protons of the cyclopentadienyl ring of the complexes showed a pair of typical pseudo triplets at δ = 6—4 for the substituted cyclopentadienyl. The split of chemical shift of the ring proton, $\Delta\delta$, in **1**, **2** and **3** is 0.43, 0.41 and 0.35 respectively. The splits were three times larger in complexes **4**—**9** than those in complexes **1**—**3**. The bulk phenyl groups might be attributed to the larger split owing to the disturbance from the phenyl group to the ring protons.

The electronic spectra of these complexes showed two strong absorption bands in ultraviolet region and a very weak absorption band in visible region (Table 1). The absorption band of higher energy in ultraviolet region around 260 nm was assigned to the $\pi \rightarrow \pi^*$ transition mainly occurring in Cp and the other strong band was assigned to ML charge transfer.[14] The weak band in visible region was due to d-d transition. Compared with the UV-vis spectrum data (221, 255, 538 nm) of $(\eta^5\text{-}C_5H_5)Co(CO)I_2$, all the absorption bands of the $\pi \rightarrow \pi^*$ transition (~ 257 nm), the ML charge transfer (~ 289 nm) and the d→d transition of the complexes **1**—**3** had red shifts. However, compared with the data (~ 260, ~ 300, ~ 425 nm) of their dicarbonyl parent complexes $(\eta^5\text{-}C_5H_4R)Co(CO)_2$, only the d→d transition of the complexes **1**—**3** shifted about 120 nm to longer wave length. King[15] reported that the UV-visible spectrum data of $(\eta^5\text{-}C_5H_5)Co(PPh_3)I_2$ in CH_2Cl_2 were 267, 589 nm. These data were consistent with those of complexes **5** and **6**. It was interesting that the $\pi \rightarrow \pi^*$ transition band was observed at ~ 230 nm in UV-vis spectra of complexes **4**, **7**—**9**. It is possible that the electron-withdrawing substituents of cyclopentadienyl ring have made the $\pi \rightarrow \pi^*$ transition easier and the transition shifted from ultra violet to violet range as we observed. This result indicated that the valence charge of the metal center might have more influence on the d→d transition and the substituents of cyclopentadienyl ring might have impact on the $\pi \rightarrow \pi^*$ transition.

Table 1 Data of UV-vis spectra

Compound	$\pi \rightarrow \pi^*$ transition	ML charge transfer	d → d transition
1	258	289	548
2	259	290	545
3	255	288	546
4	228	278	590
5		280	594
6		280	590
7	230	268	585
8	232	265	593
9	234	264	595

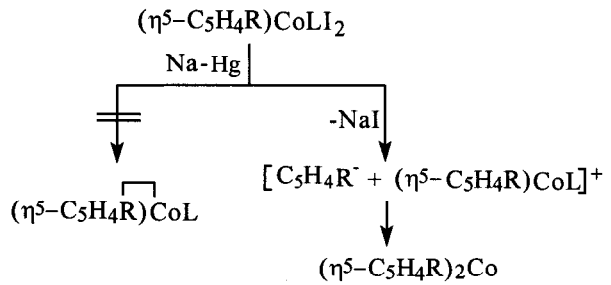
Reactivity of cobalt(III) complexes

Reduced by Na-Hg under −40℃ in THF solution, both cobalt (III) complexes $(\eta^5\text{-}C_5H_4COOC(CH_3) = CH_2)Co(CO)I_2$ (**1**) and $(\eta^5\text{-}C_5H_4COOC(CH_3) = CH_2)\text{-}Co(PPh_3)I_2$ (**4**) gave the same product $(\eta^5\text{-}C_5H_4COOC(CH_3) = CH_2)_2Co$ (**10**) which was obtained by column chromatography at −25℃. The expected chelated compound through the chain substituent on cyclopentadienyl ring with center metal cobalt has not been isolated in this reaction.[16] The IR, MS (EI), UV-vis spectra and elemental analyses of the two reaction products agreed to the

result that they might be the same complex (η^5-$C_5H_4COOC(CH_3)=CH_2)_2Co$ (**10**).

Since the substituted cyclopentadienyl anions could be generated[17] in the process of **1** or **4** reacting with Na-Hg, when NaI was produced and CO or PPh_3 were leaving from the complex, there was a great chance to form cobaltocene as it is illustrated by Scheme 1.

Scheme 1



L= CO, R = -$COOC(CH_3)=CH_2$ (**1**), -$COOCH_2C_6H_5$ (**2**);
L= PPh_3, R = -$COOC(CH_3)=CH_2$ (**4**), -$COOCH_2C_6H_5$ (**5**)

The same product was also isolated from the reduction of cobalt(III) complexes (η^5-$C_5H_4COOCH_2C_6H_5$)-$Co(CO)I_2$ (**2**) and (η^5-$C_5H_4COOCH_2C_6H_5$)$Co(PPh_3)I_2$ (**5**) with Na-Hg, which was confirmed as (η^5-$C_5H_4COOCH_2C_6H_5)_2Co$ (**11**) by their IR, MS and UV-vis spectra and elemental analyses. However, the cobalt(III) complexes (η^5-$C_5H_4COOCH_2CH=CH_2$)$Co(CO)I_2$ (**3**), (η^5-$C_5H_4COOCH_2CH=CH_2$)$Co(PPh_3)I_2$ (**6**) did not give the cobaltocene when it was treated with sodium amalgam.

Electrochemical properties

The redox properties of cobalt complexes were investigated by cyclic voltammetry. The decomposed products were strongly absorbed on the surface of the electrode. The electrode had to be well polished each time before the electrical scanning.

Carbonyl diiodocobalt complexes (**1—3**)

The features of the cyclic voltammogram of carbonyl diiodocobalt complexes **1—3** are very similar to each other. A typical cyclic voltammogram of **3** is presented as Fig.1. One redox couple (half-wave potential $E^{I}_{1/2}$ = 0.07 V, separation of peak potential ΔE = 312 mV) and two irreversible and partially overlapped oxidation waves at E^{II}_p = 0.39 V and E^{III}_p = 0.58 V were found in Fig.1. Increasing scan rate from 200 to 2000 mV/s, the redox couple I vanished gradually while oxidation waves II and III did not change. It seemed that the redox couple I was a partially reversible process and the oxidation process of II or III was electrochemically irreversibleprocess. In the range of 10—2000 mV/s a linear relationship was observed between the peak current i_p of I and the square root of the sweeping rate $\nu^{1/2}$, indicating that it was a diffusion controlled process.

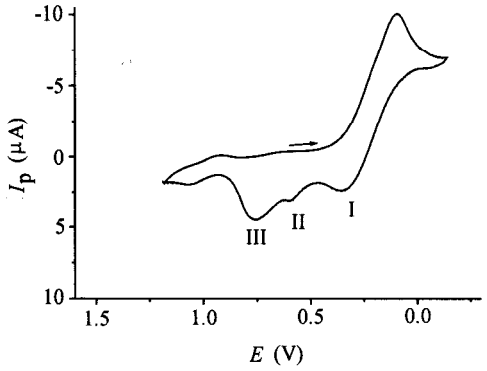
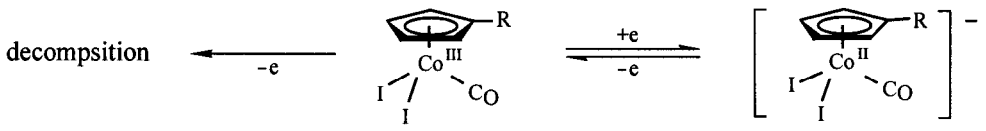


Fig. 1 Cyclic voltammogram of **3** in CH_2Cl_2, Pt electrode, 0.2M TBAP supporting electrolyte. V = 100 mV/s.

Thus, the rodox behavior of the substituted cyclopentadienyl carbonyl diiodocobalt on electrode might be described as that the cobalt(III) complex could reversibly gain one electron to form cobalt(II) intermediate which could be stabilized by pπ-dπ charge transfer of coordinated carbonyl group. But, when being oxidized, the cobalt(III) complexes decomposed (Scheme 2).

Scheme 2



Substituted cyclopentadienyl phosphine diiodocobalt complexes

The cyclic voltammograms of complexes **4**—**9** revealed similar behavior to **1**—**3** in oxidation scan less than 1.0 V. But on reverse sweep, each oxidation wave had a responding wave. The cyclic voltammetric data for the complexes **4**—**9** are listed in Table 2.

Table 2 Cyclic voltammetric data for the complexes **1**—**3**[a]

Complexes	$E_{1/2}^{red}(\Delta E^{red})^{b,c}$	$E_{1/2}^{ox}(\Delta E^{ox})^{b,c}$	$E_p^{ox\,d}$	$\Delta E(Fc^+/Fc^0)^c$
1	^{I}0.065(312)		^{II}0.385	250
			^{III}0.581	
2	^{I}0.184(348)		^{II}0.662	266
			^{III}0.772	
3	^{I}0.250(258)		^{II}0.613	216
		^{III}0.782		
4		^{II}0.207(340)	^{III}1.22	193
5		^{II}0.201(262)	^{III}1.19	246
6		^{II}0.189(368)	^{III}1.24	246
7		^{II}0.362(278)		549
		^{III}0.551(192)		
8		^{II}0.408(36)		328
		^{III}0.642(60)		
9		^{II}0.431(224)		238
		^{III}0.600(122)		
10		−0.39(85)		232
11		−0.34(96)		212

[a] Values of potential in volts vs. SCE measured at a scan rate of 100 mV/s at Pt electrode, in 0.2 M TBAP/CH_2Cl_2 by using the ferricinium/ferrocene redox couple ($E_{1/2}^{ox}$ = 0.40 V vs. SCE) as internal standard. [b] $E_{1/2}$ indicates half-wave potential in V. [c] ΔE is the peak separation of redox couple in mV. [d] E_p indicates wave potential in V.

In oxidation process, the complexes **4**—**6** show one redox couple at $E_{1/2}^{ox}$ = 0.21—0.19 V and an irreversible oxidation wave at E_p^{ox} = 1.24—1.19 V; the cyclic voltammogram of complexes **7**—**9** show two redox couples at $^{I}E_{1/2}^{ox}$ = 0.43—0.36 V and $^{II}E_{1/2}^{ox}$ = 0.64—0.55 V versus SCE (A typical cyclic voltammogram of **9** is displayed in Fig.2). Compared with complexes **1**—**3**, it seems that the reversibility of complexes **4**—**9** for oxidation was enhanced by the coodination of phosphine ligand. This phenomenon was also found in the substituted cyclopentadienyl cobalt(I) complexes.[18] Increasing scan rate from 50 to 2000 mV/s, the redox couple vanished gradually.

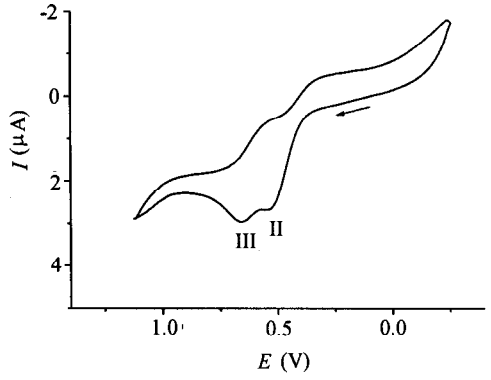


Fig. 2 Cyclic voltammogram of **9** in CH_2Cl_2, Pt electrode, 0.2 M TBAP supporting electrolyte. ν = 100 mV/s.

α,α′-Substituted cobaltocene

The cyclic voltammograms of α, α′-substituted cobaltocenes **10** and **11** both showed one redox couple in CH_2Cl_2. Data analysis of cyclic voltammograms of **10** and **11** for scan rates ν from 10 to 2000 mV/s showed that: (I) the i_p^{red}/i_p^{ox} ratio was 0.87—1.04, close to unity; (II) the peak seperations of the redox potential ΔE_p were 85 or 96 mV respectively, smaller than those of the ferrocene redox couple; (III) a linear relationship was present between the peak current i_p and the square root of the sweeping rate $\nu_{1/2}$. All of these are diagnostic conditions for a reversible process of one-electron transfer. The slight departure from the pure electrochemical reversibility may be attributed to the large resistance in

organic system.[19]

Considering the oxidation potentials reported for the cobaltocene ($E_{1/2} = -0.91$ V) and pentamethyl cobaltocene ($E_{1/2} = -1.47$ V),[20,21] the higher oxidation potentials found in **10** and **11** might be attributed to the electron-withdrawing substituents in their cyclopentadienyl ring.

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