

Synthesis, characterization and properties of new organocobalt complexes containing η^5 -functionally substituted cyclopentadienyl and [60]fullerene ligands

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Abstract

The organocobalt complexes containing functionally substituted cyclopentadienyl ligands (η^5 -RC₅H₄)Co(PPh₃)₂ (**1a**, R = EtO₂C; **1b**, R = MeCO) were synthesized by reactions of the corresponding functionalized cyclopentadienides RC₅H₄Na with (PPh₃)₃CoCl in 65 and 85% yields, respectively. The ligand exchange reaction of **1a** with PhC≡CPh afforded (η^5 -EtO₂CC₅H₄)Co(PPh₃)(η^2 -PhC≡CPh) (**2a**) in 72% yield, whereas (η^5 -RC₅H₄)Co(PPh₃)₂ (**1a**, R = EtO₂C; **1b**, R = MeCO; **1c**, R = H) reacted with C₆₀ through ligand exchange to give (η^5 -RC₅H₄)Co(PPh₃)(η^2 -C₆₀) (**3a**, R = EtO₂C; **3b**, R = MeCO; **3c**, R = H) in 34–68% yields. **3a** could be also obtained similarly by ligand exchange reaction of **2a** with C₆₀ in 83% yield. In addition, reaction of **2a** or **3a** with excess iodine I₂ produced (η^5 -EtO₂CC₅H₄)Co(PPh₃)(I)₂ (**4a**) in 90–91% yields. The new compounds **1a**, **1b**, **2a**, **3a**–**3c** and **4a** were characterized by ¹H-NMR, ³¹P-NMR, IR, UV–Vis spectra and elemental analysis, whereas the reverse saturable absorption properties of the organocobalt fullerene complexes **3a** and **3c** along with C₆₀ were studied by Z-scan method.

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Keywords: Organocobalt complexes; [60]Fullerene complexes; Synthesis; Reverse saturable absorption

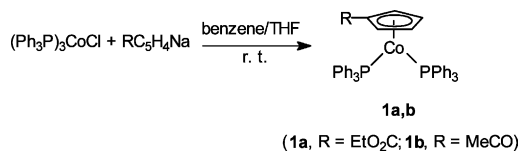
1. Introduction

In recent years, the organocobalt complexes containing functionally substituted cyclopentadienyl ligands have played an important role in the development of organocobalt chemistry. However, the studies in this area were mainly focused on the transformation reactions of the functional groups on the cyclopentadienyl ring [1–4], while no report is so far concerned about the ligand exchange reactions with fullerenes that take place at the cobalt metal center, although a few of such reactions are known to occur with other common

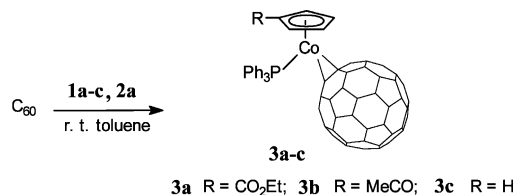
ligands [5]. In this article, we wish to report the formation and characterization of the new complexes containing η^5 -functionally substituted cyclopentadienyl ligands (η^5 -RC₅H₄)Co(PPh₃)₂ (**1a**, R = EtO₂C; **1b**, MeCO), and a series of ligand exchange reactions occurring at the cobalt metal center with PhC≡CPh, C₆₀ and I₂, leading to the corresponding new cobalt complexes (η^5 -EtO₂CC₅H₄)Co(PPh₃)(η^2 -PhC≡CPh) (**2a**), (η^5 -RC₅H₄)Co(PPh₃)(η^2 -C₆₀) (**3a**, R = EtO₂C; **3b**, MeCO; **3c**, R = H) and (η^5 -EtO₂CC₅H₄)Co(PPh₃)(I)₂ (**4a**), respectively. Furthermore, the reverse saturable absorption properties of organocobalt fullerene complexes were first studied by Z-scan method, which indicated that the organocobalt [60]fullerene complexes **3a** and **3c** possess much better reverse saturable absorption properties than C₆₀ itself.

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Scheme 1.



Scheme 3.

2. Results and discussion

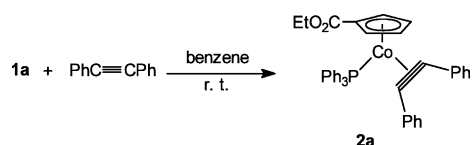
2.1. Synthesis and characterization of (η^5 -RC₅H₄)-Co(PPh₃)₂ (1a**, R = EtO₂C; **1b**, R = MeCO), (η^5 -EtO₂CC₅H₄)Co(PPh₃)(η^2 -PhC≡CPh) (**2a**), (η^5 -RC₅H₄)Co(PPh₃)(η^2 -C₆₀) (**3a**, R = EtO₂C; **3b**, MeCO; **3c**, R = H) and (η^5 -EtO₂CC₅H₄)Co(PPh₃)(I)₂ (**4a**)**

We found that **1a** and **1b** could be prepared by reaction of the corresponding functionalized cyclopentadienyls RC₅H₄Na with (PPh₃)₃CoCl in benzene/THF at room temperature in 65 and 85% yields, respectively (Scheme 1), whereas further reaction of **1a** with diphenylacetylene in benzene at room temperature, through ligand exchange reaction produced **2a** in 72% yield (Scheme 2).

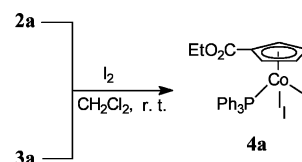
Interestingly, we further found that the [60]fullerene organocobalt complexes (η^5 -RC₅H₄)Co(PPh₃)(η^2 -C₆₀) (**3a**, R = EtO₂C; **3b**, MeCO; **3c**, R = H) could be prepared by ligand exchange reaction of **1a–1c** (**1c**, R = H [6]) with C₆₀ in toluene at room temperature in 34–68% yields, whereas **3a** could be also obtained by a ligand exchange reaction of **2a** with C₆₀ in 83% yield (Scheme 3).

Finally, we found that both **2a** and **3a** reacted with excess iodine I₂ in CH₂Cl₂ at room temperature, through ligand exchange reactions, to give **4a** in 90–91% yields (Scheme 4).

All the complexes **1a**, **1b**, **2a**, **3a–3c** and **4a** prepared above are air-sensitive, which were characterized by elemental analysis and spectroscopy. The IR spectra of **1a**, **1b**, **2a**, **3a**, **3b** and **4a** each displayed one absorption band in the range 1666–1724 cm⁻¹ for the carbonyl functionalities in EtO₂C and MeCO groups. For the complexes with a general formula of (η^5 -EtO₂CC₅H₄)Co(PPh₃)L (**1a**, L = PPh₃; **2a**, L = PhC≡CPh; **3a**, L = C₆₀; **4a**, L = 2I), the $\nu_{C=O}$ values increase in the order of **1a** (1686 cm⁻¹) < **2a** (1696 cm⁻¹) < **3a** (1713 cm⁻¹) < **4a** (1724 cm⁻¹). This implies that the electron-withdrawing effects of the ligands L increase in



Scheme 2.



Scheme 4.

the order of PPh₃ < PhC≡CPh < C₆₀ < 2I. This is because that the stronger electron-withdrawing ability of the ligands L would make the weaker π -back donation from cobalt metal center to functionally substituted cyclopentadienyl ligand [7].

In the ¹H-NMR spectra, while the protons of the parent cyclopentadienyl ring in **3c** showed one singlet at 4.32 ppm, those of the substituted cyclopentadienyl rings in **1a**, **1b**, **2a**, **3a**, **3b** and **4a** exhibited two singlets in the range 3.33–5.90 ppm, the downfield one being assigned to H² and H⁵ protons and the upfield one to H³ and H⁴ protons since the substituents EtO₂C and MeCO are both electron-withdrawing [8].

Although numerous transition-metal η^2 -[60]fullerene complexes have been reported so far [9], little is known for the complexes in which C₆₀ is directly bound to cobalt atom in an η^2 -fashion [10]. In this article, as part of our fullerene project [11], we report the above two routes for synthesizing such complexes. **3a–3c** are very air-sensitive, dark-green solids, which do not dissolve in hexane and acetone but are fairly soluble in benzene, toluene, CS₂, CHCl₃ and THF. The solutions of **3a–3c** in such solvents are extremely air-sensitive and thermally unstable, which decompose to give C₆₀ completely within 24 h even at room temperature under an argon atmosphere. The elemental data coincide with their formulas, while the FAB-MS spectra displayed their molecular ion [M⁺] peaks and the fragment ion [C₆₀]⁺ peak, respectively. Except the IR bands mentioned above, **3a–3c** each showed four absorption bands in the region 523–1434 cm⁻¹, which are characteristic of the C₆₀ cage [12]. The UV-Vis spectra of **3a** and **3c** displayed two intense bands between 200 and 400 nm, which are very close to those of free C₆₀; the small changes in their UV-Vis spectra, as compared with free C₆₀, may be regarded as an evidence for the η^2 -coordinating fashion of the C₆₀ ligand through its [6:6] bond to the cobalt metal center [10]. In addition, each of the ³¹P-NMR spectra of **3a–3c** exhibited one singlet at

ca. 50 ppm, which is also consistent with the structures described in Scheme 3.

2.2. Reverse saturable absorption properties of $(\eta^5\text{-RC}_5\text{H}_4)\text{Co}(\text{PPh}_3)(\eta^2\text{-C}_{60})$ (**3a** and **3c**) and C_{60}

The nonlinear optical properties of [60]fullerene and its derivatives have attracted much attention, largely due to their potential applications as optical limiting materials [13–16]. Recently, we studied the nonlinear optical reverse saturable absorption properties of the triplet excited state of C_{60} and its derivatives **3a** and **3c** by means of Z-scan techniques. Fig. 1 presents the reverse saturable absorption curves of C_{60} , **3a** and **3c**, and the reverse saturable absorption coefficients calculated from the minimum relative transmission values are listed in Table 1.

As can be seen from Fig. 1 and Table 1, the minimum transmission values (T_{\min}) of **3a** and **3c** are remarkably lower than that of free C_{60} and the reverse saturable absorption coefficients ($\Delta\alpha$) of **3a** and **3c** are as large as ca. 2.5 and 3.3 times of [60]fullerene, respectively. These suggest that **3a** and **3c** possess stronger reverse saturable absorption behavior than C_{60} itself, since T_{\min} and, particularly, $\Delta\alpha$ obtained under the same power density and the same concentration of the samples can reflect the magnitude of reverse saturable absorption. It follows that the reverse saturable absorption property of free C_{60} has been well improved through its coordination with cobalt atom in organometallic compounds.

3. Experimental

All reactions were carried out under a highly purified nitrogen atmosphere using standard Schlenk or vacuum-line techniques. Toluene, benzene and tetrahydrofuran were dried and deoxygenated by distillation from Na/benzophenone ketyl. All organic solvents and water were bubbled with nitrogen before use for at least 15 and 30 min, respectively. [60]Fullerene (99.9%) was available

Table 1

The minimum relative transmission values (T_{\min}) and the reverse saturable absorption coefficients ($\Delta\alpha$) of C_{60} , **3a** and **3c**

	T_{\min}	$\Delta\alpha$ ($\text{cm}^2 \text{W}^{-1}$)
C_{60}	0.60	3.9×10^{-10}
3a	0.43	9.9×10^{-10}
3c	0.34	1.3×10^{-9}

commercially. $\text{MeCOC}_5\text{H}_4\text{Na}$ [1], $\text{EtO}_2\text{CC}_5\text{H}_4\text{Na}$ [3], $\text{CpCo}(\text{PPh}_3)_2$ [6] and $(\text{PPh}_3)_3\text{CoCl}$ [17] were prepared according to literature methods. Products **2a**, **3a–3c** and **4a** were separated by column chromatography ($1.5 \times 30 \text{ cm}^2$, silica gel) and purified by recrystallization from toluene/petroleum ether at low temperature (-20 – 0°C) under anaerobic conditions. ^1H - and ^{31}P -NMR spectra were recorded on a Bruker AC P200 and a Varian Mercury VX300 spectrometer, respectively. UV–Vis and IR spectra were determined using a Shimadzu UV 240 and a Bio-Rad FTS 135 spectrometer, respectively. Elemental analysis was performed on an Elementar Vario EL analyzer, while FAB-MS spectra were determined by a Zabspec spectrometer. Melting points were determined in a sealed capillary by a Yanaco MP-500 apparatus and are uncorrected.

3.1. Preparation of $(\eta^5\text{-EtO}_2\text{CC}_5\text{H}_4)\text{Co}(\text{PPh}_3)_2$ (**1a**)

A 50 ml three-necked flask equipped with a magnetic stir-bar, a serum cap and a nitrogen inlet tube was charged with 1.90 g (2.16 mmol) of $(\text{PPh}_3)_3\text{CoCl}$, 20 ml of benzene and 0.50 g (3.10 mmol) of $\text{EtO}_2\text{CC}_5\text{H}_4\text{Na}$ in 4 ml of THF. The mixture was stirred at room temperature for 2 h and then 10 ml of water was added. The organic layer was separated from the mixture, dried over sodium sulfate and filtered. The filtrate was concentrated to ca. 8 ml under reduced pressure, and then 8 ml of petroleum ether was added to give a precipitate. The precipitate was washed with petroleum ether and dried in vacuo to give 1.00 g (65%) of **1a** as dark-red powders. m.p.: 154°C (dec.). Anal. Found: C,

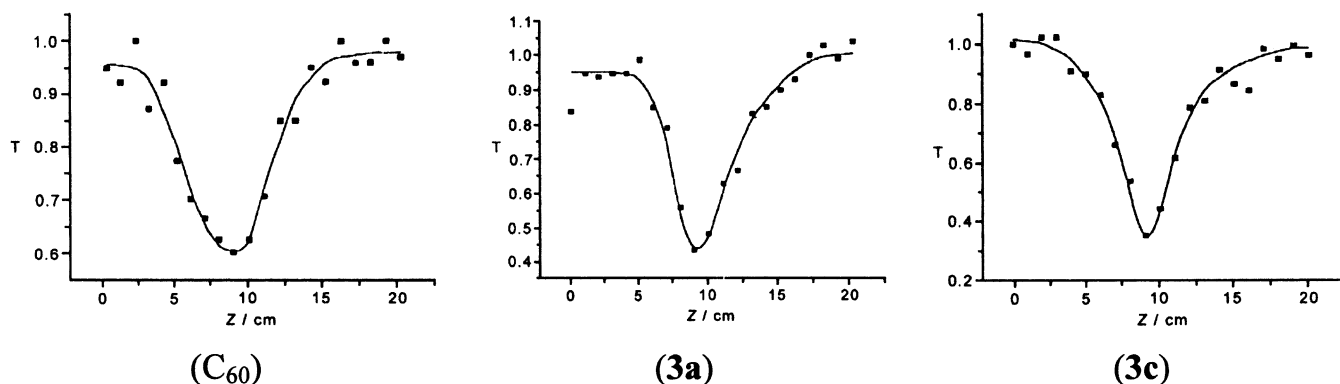


Fig. 1. Reverse saturable absorption curves of the toluene solutions ($1.0 \times 10^{-3} \text{ mol/l}$) of C_{60} , **3a** and **3c**.

73.03; H, 5.51. Calc. for $C_{44}H_{39}CoO_2P_2$: C, 73.33; H, 5.45%. IR (KBr disk, cm^{-1}): $\nu_{C=O}$ 1686s. 1H -NMR (C_6D_6): δ = 1.31(t, J = 7.0 Hz, 3H, CH_3), 4.20 (s, 2H, H^3 , H^4), 4.49 (q, J = 7.0 Hz, 2H, CH_2), 4.85 (s, 2H, H^2 , H^5), 7.07–7.78 (m, 30H, $6C_6H_5$) ppm.

3.2. Preparation of $(\eta^5\text{-MeCOC}_5\text{H}_4)\text{Co}(\text{PPh}_3)_2$ (**1b**)

The flask described above was charged with 1.90 g (2.16 mmol) of $(\text{PPh}_3)_3\text{CoCl}$, 20 ml of benzene and 0.406 g (3.12 mmol) of $\text{MeCOC}_5\text{H}_4\text{Na}$ in 4 ml of THF. After the same procedure as in the preparation of **1a**, 1.30 g (85%) of **1b** was obtained as dark-red powders. m.p.: 121 °C (dec.). Anal. Found: C, 74.71; H, 5.15. Calc. for $C_{43}H_{37}CoOP_2$: C, 74.78; H, 5.40%. IR (KBr disk, cm^{-1}): $\nu_{C=O}$ 1666s. 1H -NMR (CD_3COCD_3): δ = 3.03 (s, 3H, CH_3), 3.33 (s, 2H, H^3 , H^4), 4.66 (s, 2H, H^2 , H^5), 7.17–7.33 (m, 30H, $6C_6H_5$) ppm.

3.3. Preparation of $(\eta^5\text{-EtO}_2\text{CC}_5\text{H}_4)\text{Co}(\text{PPh}_3)(\eta^2\text{-PhC}\equiv\text{CPh})$ (**2a**)

The flask described above was charged with 0.60 g (0.83 mmol) of **1a**, 8 ml of benzene and 0.135 g (0.76 mmol) of diphenylacetylene. The mixture was stirred at room temperature for 2 h. Solvent was removed and the residue was subjected to column chromatography. The major green band was eluted using benzene to give 0.35 g (72%) of **2a** as green powders. m.p.: 99 °C (dec.). Anal. Found: C, 75.33; H, 5.38. Calc. for $C_{40}H_{34}CoO_2P_2$: C, 75.47; H, 5.35%. IR (KBr disk, cm^{-1}): $\nu_{C=O}$ 1696s, $\nu_{C=C}$ 1827m. 1H -NMR (C_6D_6): δ = 1.08 (t, J = 7.0 Hz, 3H, CH_3), 4.19 (q, J = 7.0 Hz, 2H, CH_2), 5.06 (s, 2H, H^3 , H^4), 5.32 (s, 2H, H^2 , H^5), 7.04–8.15 (m, 25H, $5C_6H_5$) ppm. UV–Vis (toluene, nm): λ (log ϵ) 282.0 (1.960), 288.0 (1.695), 298.0 (1.660) ppm.

3.4. Preparation of $(\eta^5\text{-EtO}_2\text{CC}_5\text{H}_4)\text{Co}(\text{PPh}_3)(\eta^2\text{-C}_{60})$ (**3a**)

The flask described above was charged with 0.036 g (0.05 mmol) of C_{60} and 20 ml of toluene. The C_{60} solution was stirred at room temperature and 0.04 g (0.06 mmol) of **1a** in 6 ml of toluene was added gradually. The mixture was stirred for 2 h at this temperature and then was subjected to column chromatography. The main green band was eluted using toluene to give 0.025 g (43%) of **3a** as dark-green powders. m.p.: 135 °C (dec.). Anal. Found: C, 87.40; H, 1.95. Calc. for $C_{86}H_{24}CoO_2P_2$: C, 87.61, H 2.05%. IR (KBr disk, cm^{-1}): $\nu_{C=O}$ 523vs, 580m, 1179m, 1434s; $\nu_{C=O}$ 1713s. 1H -NMR (CS_2 , CD_3COCD_3 lock signal): δ = 0.60 (t, J = 6.7 Hz, 3H, CH_3), 3.60 (q, J = 6.7 Hz, 2H, CH_2), 3.93 (s, 2H, H^3 , H^4), 4.68 (s, 2H, H^2 , H^5), 6.70–7.30 (m, 15H, $3C_6H_5$) ppm. ^{31}P -NMR (C_6D_6): δ = 50.76 ppm. UV–Vis (tolu-

ene, nm): λ (log ϵ) 282.0 (1.535), 336.0 (1.370). FAB-MS m/z : 1178[M^+].

Similarly, when 0.038 g (0.06 mmol) of **2a** was used instead of **1a**, 0.049 g (83%) of **3a** was also obtained.

3.5. Preparation of $(\eta^5\text{-MeCOC}_5\text{H}_4)\text{Co}(\text{PPh}_3)(\eta^2\text{-C}_{60})$ (**3b**)

Similar to the preparation of **3a**, when 0.035 g (0.051 mmol) of **1b** was used instead of **1a**, 0.039 g (68%) of **3b** was obtained as dark-green powders. m.p.: 80 °C (dec.). Anal. Found: C, 88.95; H, 2.14. Calc. for $C_{85}H_{22}CoOP_2$: C, 88.85; H, 1.93%. IR (KBr disk, cm^{-1}): $\nu_{C=O}$ 526vs, 577s, 1183m, 1430s; $\nu_{C=O}$ 1669s. 1H -NMR (CS_2 , CD_3COCD_3 lock signal): δ = 2.54 (s, 3H, CH_3), 3.56 (s, 2H, H^3 , H^4), 5.46 (s, 2H, H^2 , H^5), 7.38–7.94 (m, 15H, $3C_6H_5$) ppm. ^{31}P -NMR (C_6D_6): δ = 51.71 ppm. FAB-MS m/z : 1148[M^+].

3.6. Preparation of $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{PPh}_3)(\eta^2\text{-C}_{60})$ (**3c**)

Similar to the preparation of **3a**, when 0.033 g (0.05 mmol) of $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{PPh}_3)_2$ was used instead of **1a**, 0.190 g (34%) of **3c** was obtained as dark-green powders. m.p.: 110 °C (dec.). Anal. Found: C, 90.21; H, 1.58. Calc. for $C_{83}H_{20}CoP_2$: C, 90.06; H, 1.82%. IR (KBr disk, cm^{-1}): $\nu_{C=O}$ 523vs, 580m, 1179m, 1417s. 1H -NMR (CS_2 , CD_3COCD_3 lock signal): δ = 4.32 (s, 5H, C_5H_5), 6.69–7.36 (m, 15H, $3C_6H_5$) ppm. ^{31}P -NMR (C_6D_6): δ = 53.11 ppm. UV–Vis (toluene, nm): λ (log ϵ) 283.1 (0.773), 337.7 (0.693). FAB-MS m/z : 1106[M^+].

3.7. Preparation of $(\eta^5\text{-EtO}_2\text{CC}_5\text{H}_4)\text{Co}(\text{PPh}_3)\text{I}_2$ (**4a**)

The flask described above was charged with 0.087 g (0.140 mmol) of **2a**, 10 ml of dichloromethane and 0.072 g (0.28 mmol) of I_2 . The mixture was stirred at room temperature for 0.5 h and then was subjected to column chromatography. The dark-blue band was eluted with dichloromethane, from which 0.09 g (90%) of **4a** was obtained as dark-blue powders. m.p.: 138 °C (dec.). Anal. Found: C, 43.69; H, 3.60. Calc. for $C_{26}H_{24}CoI_2O_2P_2$: C, 43.85; H, 3.40%. IR (KBr disk, cm^{-1}): $\nu_{C=O}$ 1724s. 1H -NMR ($CDCl_3$): δ = 1.44 (t, J = 7.2 Hz, 3H, CH_3), 4.19 (s, 2H, H^3 , H^4), 4.45 (q, J = 7.2 Hz, 2H, CH_2), 5.90 (s, 2H, H^2 , H^5), 7.47–7.80 (m, 15H, $3C_6H_5$) ppm.

Similarly, when using 0.012 g (0.01 mmol) of **3a** instead of **2a**, 0.0065 g (91%) of **4a** was obtained.

3.8. Determination of the reverse saturable absorption properties of **3a** and **3c** and C_{60}

The reverse saturable absorption properties of **3a** and **3c** and C_{60} were determined by the Z-scan method [18]. The wave length, pulse width and pulse frequency of the

laser beam (generated by a T49-ZE quadruple Nd:YAG laser manufactured by Beijing Radio Equipment Plant) are 532 nm, 18 ns and 10 Hz, respectively. The laser beam passed through a lens (15-cm focal length), and irradiated on a sample cell (5-mm in thickness), which was filled with a 1.0×10^{-3} mol/l toluene solution of **3a**, **3c** or C_{60} . The transmitted light was detected by an LPE-1B laser power/energy detector manufactured by Beijing Wu-Ke Photoelectric Technology Company. The intensity values of the transmitted light were recorded at every 1-cm of the Z-value in the range 0–20 cm, with which the absorption curves were drawn and the coefficients of reverse saturable absorption were calculated.

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