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Synthesis and Characterization of Substituted Half-Sandwich Cobalt Complexes

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SYNTHESIS AND CHARACTERIZATION OF SUBSTITUTED HALF-SANDWICH COBALT COMPLEXES

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ABSTRACT

The substituted cyclopentadienyl dicarbonyl cobalt complexes (η^5-C_5H_4R)$Co(CO)_2$ **1-4** [**1**, R = $-CO_2CH_2C_6H_5$; **2**, R = $-CO_2C(CH_3)=CH_2$; **3**, R = $-CO_2CH_2CH=CH_2$; **4**, R = $-CH_2CO_2CH_2CH=CH_2$] were prepared from the corresponding substituted cyclopentadienyl sodium salts, octacarbonyl dicobalt and iodine. Compounds **1** and **3** reacted with iodine to afford the monocarbonyl diiodide derivatives (η^5-C_5H_4R)$Co(CO)I_2$ **5** (R = $-CO_2CH_2C_6H_5$) and **8** (R = $-CO_2CH_2CH=CH_2$). Compounds **5** and **8** reacted further with triphenylphosphine to give the monophosphine derivatives (η^5-C_5H_4R)$Co(PPh_3)I_2$ **6** (R = $-CO_2CH_2C_6H_5$) and **9** (R = $-CO_2CH_2CH=CH_2$) in high yields. The diphosphine compound **7** ((η^5-C_5H_4R)$Co(PPh_3)_2$, R = $-CO_2CH_2C_6H_5$) was synthesized by the reaction of $NaC_5H_4CO_2CH_2C_6H_5$ with $ClCo(PPh_3)_3$. Compounds **1-9** were isolated and fully characterized by analytical and spectroscopic methods.

INTRODUCTION

Cyclopentadienyl dicarbonyl cobalt has played an important role in the development of organocobalt chemistry since its discovery in 1955[1]. Recently, functionally substituted cyclopentadienyl compounds have attracted substantial attention[2,3]. Various kinds of structural modifications on the cyclopentadienyl ring have been made to improve its chemical and catalytic properties[4]. We are interested in the synthesis, structure and reactivity of functionally substituted cyclopentadienyl metal carbonyl compounds. The substituents should have the possibility of intramolecular coordination with the metal. These chelated compounds have potential use in chemical technology and in the development of new catalytic systems[5]. In order to incorporate the properties of forming coordinatively unsaturated compounds easily without chelation, the functional group on the substituents should have weak interaction with a metal center, such as a carbon carbon double bond.

In this paper we report the synthesis of several new cobalt half-sandwich compounds with functionalized substituents on the cyclopentadienyl ligands and their characterization by elemental analyses, IR and ^{1}H NMR spectra.

RESULTS AND DISCUSSION

Methods of Syntheses

Substituted cyclopentadienyl metal compounds may be synthesized by direct metalation of the corresponding cyclopentadienyl metal compounds followed by functionallization. However, for most cyclopentadienyl metal compounds, other competing reactions occur under the reaction condition of ring substitution, except for ferrocene and a few other η^5-cyclopentadienyl metal compounds [6,7]. This makes people turn to an another method for this synthetic purpose. In this synthetic method, the functionalized ligand is synthesized first and then is reacted with a metal compound to form the desired half-sandwich compound. With this approach, C_5H_5R can be obtained easily by reaction of NaC_5H_5 with a chlorocarbonate ester or chloroacetate ester [eq (1)]. The resulting C_5H_5R can be separated by distillation[8], but this may cause a yield loss by thermal dimerization[9].

To minimize the dimerization loss, we did not try to separate C_5H_5R but deprotonated it right after its formation. Two deprotonation reagents can be used. In a case of slower dimerization where R is a strong electron withdrawing group, sodium sand is a good choice owing to it being cheap and clean [eq (2)], though it takes several hours to finish the deportonation process. However, the deprotonation and the dimerization are two competitive reactions. In some cases, especially in the case where R is an electron donating group, the dimerization is dominant even at very low temperature. Significant loss due to dimerization occurs during the conversion process of C_5H_5R to its salt form via slow deprotonation[10]. In such cases, $NaOC_2H_5$ was selected to speed up the rate of the deprotonation process [eq (3)].

$$NaC_5H_5 + RCl \longrightarrow C_5H_5R + NaCl \qquad (1)$$

$$2C_5H_5R + 2\,Na \longrightarrow 2NaC_5H_4R + H_2 \qquad (2)$$

$$R= -CO_2CH_2C_6H_5,\ -CO_2C(CH_3)=CH_2,\ -CO_2CH_2CH=CH_2$$

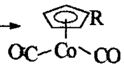
$$C_5H_5R + C_2H_5ONa \longrightarrow NaC_5H_4R + C_2H_5OH \qquad (3)$$

$$R= -CH_2CO_2CH_2CH=CH_2$$

KOC_2H_5 is not a good choice here because of its low solubility at low temperature. With the shorter time needed for the deprotonation by $NaOC_2H_5$, the side reaction of dimerization was minimized and the purity of the salt was improved. $TlOC_2H_5$ can also be used, but does not have much advantage over $NaOC_2H_5$, it is toxic, expensive and results in low yield of the desired cobalt half-sandwich compounds from the reaction of TlCpR (CpR = $C_5H_4R^-$) and $Co_2(CO)_8$.

The half-sandwich cobalt compounds were obtained via the reaction of NaC_5H_4R with iodine and $Co_2(CO)_8$ [eq (4)].

$$NaC_5H_4R + Co_2(CO)_8 + I_2 \longrightarrow \qquad (4)$$

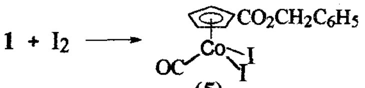


(1-4)

The products were purified by column chromatography. Although there was no problem to synthesize $NaCpCO_2C(CH_3)=CH_2$, attempts to synthesize $NaCpCO_2CH=CH_2$ and $NaCpCH_2CO_2CH=CH_2$ using the deprotonation reagents, either sodium sand or $NaOC_2H_5$, were unsuccessful. The synthesis of the cobalt half-sandwich compounds with these substituents by a different approach is being continued in our laboratory.

Upon the addition of triphenylphosphine to a benzene solution of compound **1**, carbon monoxide is released immediately. The IR spectrum indicated the formation of a monocarbonyl phosphine derivative, the disappearance of the absorption at 2032 and 1970 cm^{-1} and a growing peak at 1950 cm^{-1}. However, the isolation of the pure product from the reaction mixture was unsuccessful. For compounds **2-4**, the same situation resulted.

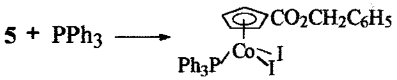
With iodine as an oxidizing reagent, compound **1** was easily converted to a black solid **5** [eq (5)].



(5)

(5)

CO in compound **5** was easily substituted by triphenylphosphine [eq (6)] and the product **6** was separated by crystallization.

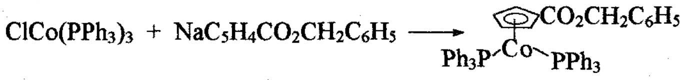


(6)

(6)

A diphosphine derivative of compound **1** was obtained by the following reaction[11] [eqs (7) and (8)]:

$$CoCl_2 + Zn + PPh_3 \longrightarrow ClCo(PPh_3)_3 + ZnCl_2 \qquad (7)$$



(8)

The compounds (η^5-$C_5H_4CO_2CH_2CH{=}CH_2$)Co(CO)I_2 (**8**) and (η^5-$C_5H_4CO_2CH_2$-$CH{=}CH_2$)Co(PPh_3)I_2 (**9**) were obtained by the same approach described by eqs (5) and (6).

Attempts to synthesize the chelated form of compounds **2-4** by photolysis were unsuccessful. During photolysis, slow decomposition of compounds **2-4** was observed. Research work of making interesting chelates from the diiodo compounds **8** and **9** are now in progress.

Analytical Results and Related Data

The analytical and other related data of the nine cobalt compounds are listed in TABLEs I and II. The dicarbonyl compounds **1- 4** can be easily dissolved in common organic solvents. The derivatives **5-9** are soluble in benzene, toluene and methylene chloride, slightly soluble in ethyl ether and insoluble in alkanes like hexane.

Infrared Spectra

The terminal CO and organic carbonyl stretching frequencies of compounds **1-9** are summarized in TABLE III and are comparable to values reported for the ν(CO) absorption in related cobalt compounds such as (η^5-$C_5H_4C(O)R$)Co$(CO)_2$ and (η^5-$C_5H_4C(O)R$)Co(CO)I_2[12]. For terminal COs, the ν(CO, sym) are all at 2032 cm^{-1}, ν(CO, asym) frequencies vary from 1967 to 1975 cm^{-1}. It is indicated that the terminal COs of the cobalt half-sandwich compounds are not sensitive to the change of ring substituents from electron withdrawing to electron donating. On the other hand, these CO stretching frequencies in cymentrene (CpMn$(CO)_3$) and its derivatives show the influence of the substituents on the Cp ring[5a]. The organic carbonyl stretching frequencies ν(C=O) of the cobalt compounds show the

TABLE I. The Physical Data of Cobalt Compounds

	Compound	Color	Yield (%)	M.p. (°C)
1	(η^5-$C_5H_4CO_2CH_2C_6H_5$)$Co(CO)_2$	red	45	liquid[a]
2	(η^5-$C_5H_4CO_2C(CH_3)=CH_2$)$Co(CO)_2$	red	30	liquid[a]
3	(η^5-$C_5H_4CO_2CH_2CH=CH_2$)$Co(CO)_2$	red	44	liquid[a]
4	(η^5-$C_5H_4CH_2CO_2CH_2CH=CH_2$)$Co(CO)_2$	red	35	liquid[a]
5	(η^5-$C_5H_4CO_2CH_2C_6H_5$)$Co(CO)I_2$	black	90	117[b]
6	(η^5-$C_5H_4CO_2CH_2C_6H_5$)$Co(PPh_3)I_2$	black-blue	88	141[b]
7	(η^5-$C_5H_4CO_2CH_2C_6H_5$)$Co(PPh_3)_2$	brown	80	166[b]
8	(η^5-$C_5H_4CO_2CH_2$ $CH=CH_2$)$Co(CO)I_2$	dark purple	80	82[b]
9	(η^5-$C_5H_4CO_2CH_2$ $CH=CH_2$)$Co(PPh_3)I_2$	black-blue	88	126[b]

[a] At room temperature. [b] Decomposed on melting.

TABLE II. Molecular Weights and Elemental Analyses of Cobalt Compounds

	Compound and Formula	Molecular Weight	Calcd. % (Found) C	Calcd. % (Found) H
1	$C_{15}H_{11}O_4Co$	314.00	57.33 (57.40)	3.53 (3.68)
2	$C_{11}H_9O_4Co$	263.89	50.00 (50.38)	3.44 (3.44)
3	$C_{11}H_9O_4Co$	263.89	50.00 (50.19)	3.44 (3.52)
4	$C_{12}H_{11}O_4Co$	278.00	51.80 (52.21)	3.99 (4.18)
5	$C_{14}H_{11}O_3I_2Co$	539.81	31.12 (31.24)	2.05 (2.17)
6	$C_{31}H_{26}O_2PI_2Co$	773.91	48.07 (48.18)	3.39 (3.51)
7	$C_{49}H_{41}O_2P_2Co$	782.19	75.17 (75.10)	5.28 (5.20)
8	$C_{10}H_9O_3I_2Co$	489.80	24.50 (24.60)	1.85 (2.01)
9	$C_{27}H_{24}O_2PI_2Co$	723.89	44.76 (44.83)	3.34 (3.40)

TABLE III. CO Stretching Frequencies in cm^{-1}.

Compound	ν(CO,sym)	ν(CO,asym)	ν(C=O)	Reference
1[a]	2032	1969	1716	this work
2[a]	2032	1975	1731	this work
3[a]	2032	1967	1722	this work
4[a]	2032	1967	1691	this work
5[b]	2073		1731	this work
6[b]			1725	this work
7[b]			1725	this work
8[a]	2073		1728	this work
9[b]			1725	this work
10[a, e]	2029	1969	1690	5a
11[a, f]	2015	1970	1720	12
12[a, g]	2024	1935	1961	5a
13[d, h]	2015	1970	1720	13
14[d, i]	2020	1965	1720	12
15[c, j]	2020	1935	1745	5a

[a] Neat sample. [b] KBr pellet. [c] Benzene solution. [d] CH_2Cl_2 solution.

[e] $(\eta^5\text{-}C_5H_4C(O)CH_2OCH_3)Co(CO)_2$. [f] $(\eta^5\text{-}C_5H_4CO_2CH_3)Co(CO)_2$.

[g] $(\eta^5\text{-}C_5H_4C(O)CH_2OCH_3)Mn(CO)_3$. [h] $(\eta^5\text{-}C_5H_4CO_2CH_3)Mn(CO)_3$.

[i] $(\eta^5\text{-}C_5H_4CO_2CH_2\,CH_3)Mn(CO)_3$. [j] $(\eta^5\text{-}C_5H_4\,CH_2CO_2CH_3)Mn(CO)_3$.

influence of a conjugation effect either from the Cp (Cp = $C_5H_5^-$) ring or from the ester oxygen. Two interesting features can be shown from their ν(C=O) data. In compounds **1-3**, the organic carbonyls are connected directly to the Cp ring. The conjugation effect from the ring system makes the carbonyl ν(C=O) a blue-shift. In compound **2**, there is a large delocalized π system consisting of the electrons from the Cp ring, carbonyl, a lone electron pair of the ester oxygen and the vinyl group. This largest delocalized π system makes ν(C=O) show a largest value among these compounds. If a methylene group is inserted between the Cp ring with organic carbonyl and between the vinyl group with the ester oxygen as in compound **4**, the organic carbonyl should have a lower π electron density and a smaller bond order, resulting in a red-shift of ν(C=O). Considering the ν(C=O) values in $C_5H_4CH_2CO_2CH_2CH{=}CH_2^-$ in compound **4** and $C_5H_4COCH_2OCH_3^-$ in $(\eta^5\text{-}C_5H_4C(O)CH_2OCH_3)Co(CO)_2$ [5a], they have the same value of 1691 cm^{-1}. It is surprising that the oxygen lone pair has the same influence on ν(C=O) as the π electrons of the Cp ring. An another interesting feature is that in the Co(III) diiodo compounds **5**, **6**, **8** and **9**, their organic carbonyl ν(C=O) stretching frequencies show some blue-shifts compared to their parent Co(I) compounds **1** and **3**. A blue-shift of 12 and 9 cm^{-1} for compounds **5** and **6** compared with compound **1** and a blue-shift of 6 and 3 cm^{-1} for compounds **8** and **9** compared to compound **3** were found, respectively. This implies that due to the π interaction from the two filled p orbitals of the coordinated iodine atoms, the Co(III) metal center takes less electron density from the Cp ring than Co(I). Therefore, the electron density on the Cp ring of the former compound becomes richer. The π interaction between the Cp ring and the organic carbonyl increases and this makes ν(C=O) shift towards higher frequencies. Comparing the influence on the ligands of terminal CO and PPh_3 in compounds **5-9**, the organic carbonyl stretching frequencies ν(C=O) of compounds **5** and **8** have a slightly higher blue-shift than that of compounds **6** and **9**.

^{1}H NMR Spectra

^{1}H NMR spectra of all complexes and the corresponding sodium salts are listed in TABLEs IV and V.

All protons of the cyclopentadienyl ring show a pair of pseudo triplets. The protons of the vinyl group of the substituent couple with its neighboring groups

TABLE IV. ^{1}H NMR Data of Some Substituted Cyclopentadienyl Salts[a]

Salt	δ (ppm)
$NaCpCO_2CH_2C_6H_5$	6.14 (t, 2H, Cp, J=3.0 Hz), 5.53 (t, 2H, Cp, J=3.0 Hz), 7.39~7.21 (br, 5H, $-C_6H_5$), 5.03 (s, 2H, $-CH_2-$)
$NaCpCO_2CH_2CH=CH_2$	6.10 (t, 2H, Cp, J=3.0 Hz), 5.50 (t, 2H, Cp, J=3.0 Hz), 5.94 (m, 1H, -CH=), 5.26 (d, 1H, $=CH_2$ *trans*, J=15.6 Hz), 5.08 (d, 1H, $=CH_2$ *cis*, J=9.0 Hz), 4.43 (s, 2H, $-CH_2-$)
$NaCpCO_2C(CH_3)=CH_2$	6.1 (t, 2H, Cp, J=2.7 Hz), 5.54 (t, 2H, Cp, J=2.9 Hz), 4.44 (s, 1H, $=CH_2$ *trans*), 4.41 (s, 1H, $=CH_2$ *cis*), 1.84 (s, 3H, $-CH_3$)
$NaCpCH_2CO_2CH_2CH=CH_2$	6.18 (t, 2H, Cp, J=2.7 Hz), 5.62 (s, 2H, Cp), 5.91 (m, 1H, -CH=), 5.16 (d, 1H, $=CH_2$ *trans*, J=17.2 Hz), 4.98 (d, 1H, $=CH_2$ *cis*, J=10.4 Hz), 4.27 (s, 2H, $-CH_2-$), 3.97 (d, 2H, $-OCH_2-$, J=7.6 Hz)

[a] In DMSO-d_6.

and have a typical spectral pattern. Fig. 1 shows the ^{1}H NMR spectrum of compound **3**, having a typical pattern of a vinyl group. The substituted Cp ring gives a AA'BB'CKLM spin system pattern in the ^{1}H NMR spectrum. The protons AA'BB' show two typical pseudo triplets. Careful examination at the vinyl group in the pendent side chain can detect the couplings between the protons of C, K, L and M. The methine proton K is split into 10 peaks of a pattern of a doublet of a quintet centered at δ 6.00 ppm with J_{KM} = 17.3, J_{KL} = 10.5 and J_{CK} = 5.4 Hz, respectively. The proton M gives a doublet of a quartet pattern centered at δ 5.39 ppm with J_{KM} = 17.3, J_{CM} = 1.63 and J_{LM} = 1.60 Hz, respectively. Proton L also shows a doublet of a quartet centered at δ 5.24 ppm with J_{KL} = 10.5, J_{CL} = 1.43 and J_{CM} = 1.63 Hz. Protons from a methylene group (C) give a doublet of a triplet

Table V. ^{1}H NMR Data for Compounds **1-9**

Compound	δ (ppm)
1[a]	5.49 (t, 2H, Cp, J=2.1 Hz), 5.27 (t, 2H, Cp, J=2.0 Hz), 7.39 (br, 5H, -C_6H_5), 5.27 (s, 2H, -OCH_2-)
2[a]	5.51 (t, 2H, Cp, J=2.1 Hz), 5.29 (t, 2H, Cp, J=2.1 Hz), 4.77 (s, 2H, =CH_2), 2.00 (s, 3H, -CH_3)
3[b]	5.64 (t, 2H, Cp, J=2.1 Hz), 5.50 (t, 2H, Cp, J=2.1 Hz), 6.00 (m, 1H, -CH=), 5.39 (d, 2H, =CH_2 *trans*, J=17.3 Hz), 5.24 (d, 1H, =CH_2 *cis*, J=10.5 Hz), 4.71 (d, 2H, -OCH_2-, J=5.4 Hz)
4[b]	5.71 (t, 2H, Cp, J=2.1 Hz), 5.55 (t, 2H, Cp, J=2.0 Hz), 6.00~5.90 (m, 1H, -CH=), 5.31 (d, 1H, =CH_2 *trans*, J=17.1 Hz), 5.18 (d, 1H, =CH_2 *cis*, J=10.2 Hz), 4.46 (d, 2H, -CH_2-, J=14.7 Hz), 4.10 (d, 2H, -OCH_2-, J=5.7 Hz)
5[a]	6.16 (t, 2H, Cp, J=2.1 Hz), 5.75 (t, 2H, Cp, J=2.1 Hz), 7.42 (br, 5H, -C_6H_5), 5.37 (s, 2H, -OCH_2-)
6[a]	5.91 (t, 2H, Cp, J=2.1 Hz), 5.45 (t, 2H, Cp, J=2.1 Hz), 4.25 (s, 2H, -OCH_2-), 7.58 (br, m, 20H, -C_6H_5)
7[c]	5.12 (s, 2H, Cp), 4.48 (t, 2H, Cp, J=2.1 Hz), 7.03 (br, m, 20H, -C_6H_5), 4.48 (s, 2H, -OCH_2-)
8[a]	6.17 (t, 2H, Cp, J=2.1 Hz), 5.78 (t, 2H, Cp, J=2.1 Hz), 6.03 (m, 1H, -CH=), 5.47 (d, 1H, =CH_2 *trans*, J=16.2 Hz), 5.36 (d, 1H, =CH_2 *cis*, J=9.9 Hz), 4.86 (d, 2H, -OCH_2-, J=6.0 Hz)
9[a]	5.93 (s, 2H, Cp), 4.23 (t, 2H, Cp, J=2.1 Hz), 6.10 (m, 1H, -CH=), 5.51 (d, 1H, =CH_2 *trans*, J=17.4 Hz), 5.31 (d, 1H, =CH_2 *cis*, J=10.5 Hz), 4.93 (d, 2H, -OCH_2-, J=5.7 Hz), 7.51~7.84 (br, 15H, PPh)

[a] In $CDCl_3$. [b] In $(CD_3)_2CO$. [c] In C_6D_6.

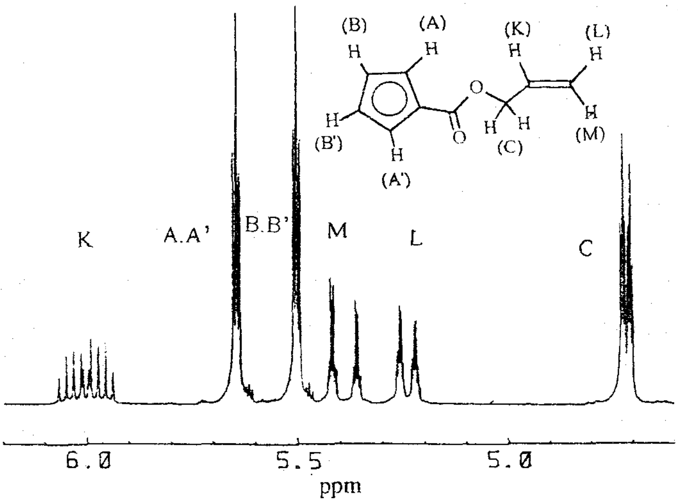


Fig. 1. ^1H NMR Spectrum of (η^5-$C_5H_4CO_2CH_2CH{=}CH_2$)$Co(CO)_2$

pattern centered at δ 4.70 ppm with $J_{CK} = 5.36$, $J_{CL} = 1.43$ and $J_{CM} = 1.63$ Hz. All of the J values are verified by simulation of the spectra. These J values show specific couplings of vinyl groups and are good guides of assigning ^1H NMR spectra for other compounds with carbon carbon double bond.

EXPERIMENTAL

Materials

All operations including column chromatography were carried out under a nitrogen atmosphere utilizing standard Schlenk techniques. Hexane, tetrahydrofuran (THF), ethyl ether and toluene were predried over sodium wire and finally distilled under a nitrogen atmosphere from sodium/benzophenone. Benzene and methylene chloride were dried and distilled from calcium hydride. Neutral alumina and silica gel used in column chromatography had been dried in an oven for several days, and then heated under reduced pressure on a rotary evaporator to remove residual water and oxygen. The alumina was subsequently deactivated with 5 % (by weight) of degassed water. Octacarbonyl dicobalt was obtained as a gift from Prof. Ziling Jing of the School of Chemical Engineering, Dalian University of Science and Technology. Benzyl chloroformate, isopropenyl chloroformate, chloroacetic acid allyl ester and allyl chloroformate were obtained from Acros Organics. These chemicals were used without further purification. $CoCl(PPh_3)_3$ was synthesized by a literature method[11,14]. PPh_3 was recrystallized from methanol prior to use.

Measurements

The elemental analyses were performed on a Rapid CHN-O 240C Analyzer (Heraeus, Germany) at the Shanghai Institution of Organic Chemistry, Science Academy of China. IR spectra were recorded on a Nicolet FT-IR-50-X spectrophotometer. ^1H NMR spectra were recorded on a Bruker MSL-300 NMR spectrometer and chemical shifts are reported in ppm relative to tetramethylsilane as internal reference.

Synthesis of NaC_5H_4R

Method I. NaCp was synthesized according to a literature method[15]. In a typical experimental procedure, NaCp (21.7 mmol) was dissolved in THF (80 mL) and was cooled to -60 °C. RCl (21.7 mmol) was added and the reaction mixture was stirred for 2 h while the temperature was kept at -60 °C. Then the mixture was transferred into a 3-neck round bottom flask where there was sodium sand (about 0.5 g, 21.7 mmol) preprepared. The reaction mixture was stirred and maintained at -20 °C until all sodium sand had disappeared. The volume of the reaction mixture was then reduced to about 10 mL *in vacuo*. Hexane was added to precipitate the substituted sodium cyclopentadienide. The precipitate was washed with hexane several times and dried *in vacuo* to afford a tan solid. The by-product sodium chloride was not separated because it is inert to the subsequent reaction. The products were characterized by ^1H NMR spectra.

Method II. The general procedure is the same as described in Method I except that the deprotonation reagent is $NaOC_2H_5$ instead of sodium sand. This method was carried out when the substituent of the cyclopentadienyl ring is an electron donating group, such as chloroacetate ester. $NaOC_2H_5$ was prepared by the reaction of sodium sand with ethanol in THF. After reaction of NaCp with RCl at -40 °C for 2 h, an equimolar amount of $NaOC_2H_5$ in THF solution was added dropwise into the reaction mixture. The temperature of the reaction mixture was maintained at -40 °C for additional 2 h, and then warmed up to room temperature. The solvent was removed *in vacuo* and the residues were washed with hexane as in Method I to give a cream colored solid. The products were characterized by ^1H NMR spectra.

Synthesis of (η^5-C_5H_4R)$Co(CO)_2$ (1-4)

Octacarbonyl dicobalt (1.00 g, 2.9 mmol) was dissolved in THF (60 mL). Iodine crystals (0.74 g, 2.9 mmol) were added and the reaction mixture was stirred for 2 h at room temperature. The evolution of released carbon monoxide was observed through a mercury check valve interfaced with an exhaust outlet. The green solution was stirred for 1 h to insure the completion of the reaction. NaC_5H_4R (5.8 mmol) was then added. The solution turned brown with evolution of carbon monoxide. The reaction mixture was stirred for additional 12 h. and then concentrated to about 20 mL. Ethyl ether was added and the resulting slurry was filtered through alumina. Alumina (~15 g) was added to the filtrate and the solvent was removed *in vacuo*. The residue was placed on an alumina-packed column and eluted with 1/8 ethyl ether/hexane. The second band was collected. Evaporation of the solvent afforded substituted cyclopentadienyl dicarbonyl cobalt as red liquid.

Synthesis of (η^5-$C_5H_4COOCH_2C_6H_5$)$Co(CO)I_2$ (5)

To a solution of compound **1** (1.3 g, 4.1 mmol) in ether (6 mL) was added dropwise a solution of iodine (1.05 g, 4.1 mmol) in ether (10 mL) at 0°C. The solution turned to purple immediately and gas evolved vigorously. After 2 h stirring at 0°C, the reaction mixture was allowed to warm up to room temperature. The dark purple solution was filtered and the volatiles were removed *in vacuo*. The residue was eluted on a silica gel column (5×1.5 cm) with ether and a black solid was obtained from the eluant of a dark violet band. Recrystallization from benzene/CH_2Cl_2 (2:1 in volume ratio) gave compound **5** as black crystals (2.01 g, 90 %).

Synthesis of $(\eta^5\text{-}C_5H_4COOCH_2C_6H_5)Co(PPh_3)I_2$ (6)

Compound **5** (0.17 g, 0.31 mmol) was dissolved in ether (10 mL) at room temperature. Triphenylphosphine (0.15 g, 0.57 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 ethyl ether and hexane. The solid was dried *in vacuo* to give a dark green solid of compound **6** (212 mg, 88 %).

Synthesis of $(\eta^5\text{-}C_5H_4COOCH_2C_6H_5)Co(PPh_3)_2$ (7)

$NaCpCO_2CH_2C_6H_5$ (1.69 mmol) was dissolved in THF (35 mL). $ClCo(PPh_3)_3$ (1.50 g, 1.70 mmol) in THF (15 mL) was added dropwise and stirring was continued for 2 h. All volatiles were removed *in vacuo*. The residue was taken up in benzene (20 mL) and filtered through celite. The solvent of the filtrate was removed under reduced pressure and the residue was recrystallized from hexane to give compound 7 as brown crystals (1.06 g, 80 %).

Synthesis of $(\eta^5\text{-}C_5H_4CO_2CH_2\,CH{=}CH_2)Co(CO)I_2$ (8)

To a solution of compound **3** (1.2 g, 4.5 mmol) in ether (8 mL) was added dropwise a solution of iodine (1.15 g, 4.5 mmol) in ether (10 mL) at 0°C and the reaction mixture was stirred for 2 h. The reaction mixture was then filtered through celite and eluted on a silica gel column (5×1.5 cm) with ether. A dark purple solid (1.76 g, 80 %) was obtained from the eluant after evaporating the volatiles *in vacuo*.

Synthesis of $(\eta^5\text{-}C_5H_4CO_2CH_2CH{=}CH_2)Co(PPh_3)I_2$ (9)

This compound was synthesized by a similar procedure as described for $(\eta^5\text{-}C_5H_4CO_2CH_2C_6H_5)Co(PPh_3)I_2$ (**6**). Compound **8** (0.25 g, 0.51 mmol) and triphenylphosphine (0.16 g, 0.61 mmol) were stirred in ether (15 mL) at room temperature for 6 h to give a black-blue precipitate. The precipitate was separated by a centrifuge and washed with ethyl ether and hexane. The solid was dried *in vacuo* to give compound **9** as black-blue solid (0.325 g, 88 %).

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