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# Synthesis, Characterization and Electrochemical Properties of Substituted Half-Sandwich Cobalt(I) Complexes

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## SYNTHESIS, CHARACTERIZATION AND ELECTROCHEMICAL PROPERTIES OF SUBSTITUTED HALF-SANDWICH COBALT(I) COMPLEXES

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#### ABSTRACT

Organocobalt compounds  $C_5H_4RCoLL'$  (2a),(2b), (2b') and (2c) (L = CO, L' = PR<sub>3</sub>; **a**, R = -COOC(CH<sub>3</sub>)=CH<sub>2</sub>; **b**, R = -COOCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>; **c**, R = -COOCH<sub>2</sub>CH=CH<sub>2</sub>.) were prepared and characterized. The electronic spectra and the electrochemical properties of compounds (2a), (2b), (2b'), (2c) and their analogues (1a), (1b), (1c), (1d) (L = L' = CO; **d**, R = -CH<sub>2</sub>COOCH<sub>2</sub>CH=CH<sub>2</sub>) and (3) (L = L' = PR<sub>3</sub>, R = -COOCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>) were also studied. It was found that (2a), (2b), (2b'), (2c) exhibited two reversible peaks during electrochemical oxidation which were attributed to the formation of two reaction intermediates. Their dicarbonyl or bis(phosphine) analogues did not show such reversible peaks during electrochemical oxidation. The compounds (2a), (2b), (2b') and (2c) exhibited the best ability of anti-oxidation among the three types of the organocobalt compounds.

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#### INTRODUCTION

Cyclopentadienyl metal compounds are attracting increasing interest in the chemistry of metal complexes<sup>1-3</sup>. Many of these compounds found application in catalytic processes. Recently, some cyclopentadienyl metal systems with late transition metals revealed their special chemical properties<sup>6</sup>. Cycloaddition and cyclization catalyzed by organocobalt complexes have been reported<sup>7-10</sup>. Many new types of compounds were synthesized to verify their ability to stabilize highly reactive intermediates and the influence on the selectivity of catalytic processes. We are interested in the modification of the structure of the ring and ligands at the metal in cyclopentadienyl metal systems that influence the electronic and steric properties of the compounds. These influences may be studied spectroscopically. Here we report the synthesis, characterization and electrochemical investigation of some cyclopentadienyl cobalt derivatives. Three types of the cobalt complexes, carbonyl, phosphine and bis(phosphine) derivatives, were studied and their properties were compared.

#### EXPERIMENTAL

#### Solvents and Reagents

All of the operations of the synthesis were carried out using standard Schlenk techniques under a nitrogen atmosphere. The solvents 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. PPh<sub>3</sub> was recrystallized from methanol prior to use.  $PCy_3$  (Cy =

cyclohexyl) and  $P(tolyl-p)_3$  were obtained from Aldrich Chemicals and were used without further purification.

#### Instrumentation

The elemental analyses were performed on a Rapid CHN-O 240C Analyzer (Heraeus, Germany) at the Shanghai Institute of Organic Chemistry, Chinese Academy of Science. Mass spectra were measured on a HP 5989A instrument. Positive ion spectra for neutral compounds were obtained by the EI techniques (70 eV). IR spectra were recorded on a Nicolet FT-IR-50-X spectrophotometer. <sup>1</sup>H NMR spectra were recorded on a Bruker MSL-300 NMR spectrometer and chemical shifts are reported in ppm referenced to TMS. Electronic spectra were recorded on a Shimadzu UV 240 spectrometer in CH<sub>2</sub>Cl<sub>2</sub>.

Cyclic voltammetry (CV) was carried out in dry  $CH_2Cl_2$  containing 0.2 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte, using a m273A EG&G Princeton Applied Research Potentiostat. The electrochemical cell was a three-electrode system, with a Teflon cap assembled by a platinum disc electrode ( $\Phi = 2 \text{ mm}$ ) as working electrode, a platinum wire served as an auxiliary electrode and silver/saturated silver acetate (in  $CH_2Cl_2$  solution) separated by a salt bridge employed as a reference electrode. The potentials were reported *vs.* the ferrocenium/ferrocene (Fc) reference couple (+0.4 V *vs.* SCE) as recommended by IUPAC<sup>11</sup>. The experimental reference electrode was calibrated with an internal standard at the termination of each experiment.

#### **Preparation of Compounds**

The compounds of dicarbonyl and bis(phosphine) analogous ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>COOC(CH<sub>3</sub>)=CH<sub>2</sub>)Co(CO)<sub>2</sub> (**1a**), ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>COOCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)Co(CO)<sub>2</sub> (**1b**), ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>COOCH<sub>2</sub>CH=CH<sub>2</sub>)Co(CO)<sub>2</sub> (**1c**), ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>COOCH<sub>2</sub>CH=CH<sub>2</sub>)Co(CO)<sub>2</sub> (**1d**) and ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>COOCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)Co(PPh<sub>3</sub>)<sub>2</sub> (**3**) were synthesized by methods described in

the literature<sup>12,13</sup> and characterized by their <sup>1</sup>H NMR and IR spectra. The monophosphine substituted compounds, (n<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>COOC(CH<sub>3</sub>)=CH<sub>2</sub>)Co(CO)PPh<sub>3</sub> (2a),  $(\eta^{5}-C_{5}H_{4}CO_{2}(CH_{3})C=CH_{2})Co(CO)PCy_{3}$  (2a'),  $(\eta^{5}-C_{5}H_{4}COOCH_{2}C_{6}H_{5})Co-$ (η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>CO<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)Co(CO)PCy<sub>3</sub> (CO)PPh<sub>3</sub> (2b), (2b'), (n<sup>5</sup>- $C_5H_4CO_2CH_2C_6H_5)Co(CO)P(tolyl-p)$ ; (2b"), ( $\eta^5-C_5H_4COOCH_2C=CH_2)Co(CO)PPh_2$ (2c) were synthesized by stirring a mixture of the corresponding parent dicarbonyl compounds [(1a), (1b) or (1c)] (about 1.0 mmol, or about 0.3 g) and equimolar amount of phosphine (PPh<sub>3</sub>, P(tolyl-p)<sub>3</sub> or PCy<sub>3</sub>) in 15 mL of benzene at room temperature until no more gas evolved and then heated to reflux until the v(CO) band of the parent complex had disappeared. The solution was cooled to room temperature under nitrogen atmosphere and the solvent was removed under vacuum. The residue was dissolved in 15 mL of a diethyl ether and hexane mixture (1:5 ratio). The solution was filtered through Celite and then concentrated to about The products were crystallized under cooling to about -35 °C to -50 °C. saturation. Red-brown crystals were separated. These products were washed with cold hexane twice and dried in vacuo. The yields were about 70 %.

#### **RESULTS AND DISCUSSION**

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#### Synthesis

Substituted cyclopentadienyldicarbonylcobalt complexes are air-sensitive, redbrown oils. One of their carbonyl groups can be replaced with a strong  $\sigma$  donor like a phosphine<sup>14</sup>. The reaction of  $(\eta^5-C_5H_4R)Co(CO)_2$  with phosphines yields a monosubstituted product, as shown in eq 1.

$$\begin{array}{c} & & & \\ &$$

$$\begin{aligned} & \text{R} = -\text{COOC}(\text{CH}_3) = \text{CH}_2, \ \text{L} = \text{PPh}_3 \ \textbf{(2a)}, \ \text{L} = \text{PCy}_3 \ \textbf{(2a')}. \\ & \text{R} = -\text{COOCH}_2\text{C}_6\text{H}_5, \ \text{L} = \text{PPh}_3 \ \textbf{(2b)}, \ \text{L} = \text{PCy}_3 \ \textbf{(2b')}, \ \text{L} = \text{P}(\text{tolyl-}p)_3 \ \textbf{(2b'')} \\ & \text{R} = -\text{COOCH}_2\text{CH} = \text{CH}_2, \ \text{L} = \text{PPh}_3 \ \textbf{(2c)}. \end{aligned}$$

The data of elemental analyses of these products (calculated and found) are listed in Table I. The second carbonyl group cannot be substituted under normal reaction conditions. Compared to PPh<sub>3</sub> or P(tolyl-p)<sub>3</sub>, PCy<sub>3</sub> is a stronger  $\sigma$  donor, but PCy<sub>3</sub> substituted derivatives were more difficult to obtain owing to their steric bulk and low temperature is essential to prevent the decomposition of the product during the preparation. This decomposition may also be one of the reason that the bis(phosphine) analogue cannot be obtained by simple ligand substitution. Another approach was then taken to prepare the bis(phosphine) derivative of the cyclopentadienylcobalt compound<sup>12</sup>. The data of mass, infrared, <sup>1</sup>H NMR and electronic spectra are listed in Table II, III, IV and V, respectively.

#### **IR Spectra**

The isolation of the pure monophosphine derivatives (2a') and (2b") were not possible due to traces of PR<sub>3</sub> present. Their IR data are still listed in Table III, but are in a different matrix. The CO stretching frequencies at the metal compounds served as a measure of the electron density of the metal. The decreasing CO stretching frequencies v(CO) in the series of (1b) (v(CO) = 2032 and 1969 cm<sup>-1</sup>,  $v(C=O) = 1716 \text{ cm}^{-1})^{12}$ , (2b) and (2b') indicates that the electron density at the metal is increased when CO is replaced by a phosphine ligand and that PCy<sub>3</sub> is a stronger electron releasing ligand compared to PPh<sub>3</sub>. Although the ketone carbonyl stretching frequencies of these three compounds are declining in the same order, they are usually a less sensitive parameter for indication of the electron density. The same trend can be seen in the series of (1a), (2a) and (2a'); (1c) and (2c) from Table III.

|               | Compound and<br>Formula Weights                    |        | Yield | Calcd. (F             | ound)       | M.p. |
|---------------|--|--------|-------|-----------------------|-------------|------|
|               |  |        | (%)   | (%) C %               | Η%          | (°C) |
| (2a)          | C <sub>28</sub> H <sub>24</sub> O <sub>3</sub> PCo | 498.41 | 70    | 67.46 (67.24)         | 4.86 (4.80) | 110  |
| ( <b>2b</b> ) | C32H26O3PCo  | 548.47 | 65    | 70.06 (70.05)         | 4.78 (4.89) | 102  |
| (2b')         | $C_{32}H_{44}O_3PCo$                               | 566.61 | 70    | 67.82 (68.03)         | 7.83 (7.90) | 112  |
| (2c)          | C <sub>28</sub> H <sub>24</sub> O <sub>3</sub> PCo | 498.41 | 70    | 67.46 (67.31 <u>)</u> | 4.86 (4.79) | 120  |

Table I. Elemental Analyses and Melting Points of Organocobalt Derivatives.

Table II. Mass Spectra of the Compounds of Organocobalt Derivatives.

|          | MS, m/z (rel intens, %) |               |             |                              |  |  |
|----------|-------------------------|---------------|-------------|------------------------------|--|--|
| Fragment | (2a)                    | ( <b>2b</b> ) | (2b')       | (2c)<br>L = PPh <sub>3</sub> |  |  |
| ion      | $L = PPh_3$             | $L = PPh_3$   | $L = PCy_3$ |                              |  |  |
| M⁺       | 498                     | 548           | 566         | 498                          |  |  |
| M'-CO    | 470                     | 520           | 538         | 470                          |  |  |
| M⁺-CO-L  | 208                     | 258           | 258         | 207                          |  |  |
| L        | 262                     | 262           | 281         | 262                          |  |  |
| CpR      | 150                     | 199           | 198         | 207                          |  |  |
| CoL      | 321                     | 321           | 340         | 321                          |  |  |
| Со       | 59                      | 59            | 59          | 59                           |  |  |

#### <sup>1</sup>H NMR Spectra

The resonance of the protons of the substituted cyclopentadienyl ring of the phosphine complexes (2a), (2b), (2b') and (2c) in the 'H NMR spectra are split into two signals of multiplets instead of two pseudo-triplets as for their parent carbonyl complexes. This phenomenon was also observed in the ring-substituted cyclopentadienylmanganesetricarbonyl complexes and their phosphine substituted

| 140                         | ie in in optimie |        |        |                                   |
|-----------------------------|------------------|--------|--------|-----------------------------------|
| Compd                       | v(CO)            | v(C=O) | ν(C=C) | v(C <sub>6</sub> H <sub>5</sub> ) |
| (2a)*                       | 1934 s           | 1713 s | 1675 m | 1600 w                            |
| ( <b>2a'</b> ) <sup>b</sup> | 1922 s           | 1711 s | 1673 m |                                   |
| (2b) <sup>*</sup>           | 1931 s           | 1703 s |        | 1590 w, 1497 w                    |
| (2b') <sup>*</sup>          | 1922 s           | 1694 s |        | 1590 w, 1497 w                    |
| ( <b>2b"</b> ) <sup>b</sup> | 1940 s           | 1705 s |        | 1600 w, 1496 w                    |
| (2c) <sup>a</sup>           | 1934 s           | 1705 s | 1653 m |                                   |
| (1 <b>s</b> )°              | 2032 s, 1975 s   | 1731 s | 1678 m |                                   |
| (1b)°                       | 2032 s, 1969 s   | 1716 s |        | 1497 m                            |
| (1c) <sup>c</sup>           | 2032 s, 1967 s   | 1722 s | 1668 w |                                   |

Table III. IR Spectral Data of Organocobalt Derivatives in cm<sup>-1</sup>.

\* in KBr. <sup>b</sup> in benzene. <sup>c</sup> data of v(CO) and v(C=O) are cited from reference 12.

Table IV. <sup>1</sup>H NMR Data of Organocobalt Derivatives in C<sub>6</sub>D<sub>6</sub><sup>\*</sup>.

| Compd. | δ (ppm)   |  |  |  |
|--------|---|--|--|--|
| (2a)   | 4.91 (d, 2H, Cp, J=2.1Hz), 4.72 (m, 2H, Cp), 7.72~6.95 (m, 15H, Ph)   |  |  |  |
|        | 4.78 (s, 1H, =CH <sub>2</sub> , trans), 4.54 (s, 1H, =CH <sub>2</sub> , cis), 1.89 (s, 3H, -CH <sub>3</sub> ) |  |  |  |
| (2b)   | 5.56 (m, 2H, Cp), 5.35 (m, 2H, Cp), 8.09~7.40 (m, 20H, Ph), 5.15 (s,  |  |  |  |
|        | 2H, -CH <sub>2</sub> -)   |  |  |  |
| (2b')  | 5.24 (m, 2H, Cp), 4.92 (m, 2H, Cp), 7.34~7.06 (m, 5H, Ph), 5.12 (s,   |  |  |  |
|        | 2H, -CH <sub>2</sub> -), 1.87~1.10 (m, 33H, Cy)   |  |  |  |
| (2c)   | 5.70 (m, 2H, Cp), 5.55 (m, 2H, Cp), 7.75~7.12 (m, 15H, Ph), 6.25 (m,  |  |  |  |
|        | 1H, -CH=), 5.30 (d, 1H, =CH <sub>2</sub> trans, J=17.5Hz), 5.24 (d, 1H, =CH <sub>2</sub> cis                  |  |  |  |
|        | J=9.8Hz), 4.57 (d, 2H, -OCH <sub>2</sub> -, J=5.7Hz)  |  |  |  |

\* Chemical shifts were referenced to TMS.

|               | Assignment              |                   |                   |  |
|---------------|-------------------------|-------------------|-------------------|--|
| Compounds     | $\pi \rightarrow \pi^*$ | $M \rightarrow L$ | $d \rightarrow d$ |  |
| (1a)          | 258                     | 307               | 424               |  |
| (1b)          | 260                     | 306               | 426               |  |
| (1c)          | 258                     | 305               | 425               |  |
| (1d)          | 258                     | 296               | 324               |  |
| (2a)          | 280                     | 355               | 458               |  |
| ( <b>2b</b> ) | 278                     | 340               | 460               |  |
| (2b')         | 276                     | 345               | 450               |  |
| (2c)          | 276                     | 372               | 520               |  |
| (3)           | 266, 272                |                   | 560               |  |

Table V. Electronic Absorption Spectral Band Maxima (nm) in CH<sub>2</sub>Cl<sub>2</sub> of Organocobalt Derivatives<sup>n</sup>.

<sup>a</sup> Due to the air-sensitivity of all compounds, reliable extinction coefficients could not be obtained..

derivatives<sup>13</sup>. The larger the split of the NMR signals of the cyclopentadienyl ring protons the more disturbance to the ring protons by its ligand environment occurs. The split of the NMR signals,  $\Delta\delta$ , of the ring protons in **1b** and **2b**, are  $0.22^{11}$  and 0.21, respectively. In other compounds, these values are 0.22 or less. But in (**2b'**)  $\Delta\delta$  of the ring protons is 0.32. Considering that PCy<sub>3</sub> has a cone angle of 170 degrees<sup>16</sup>, one of the Cy groups must be very close to the cyclopentadienyl ring and exerts its steric effect on the chemical shift of the ring protons. If that is true, then (**3**) has the largest value of  $\Delta\delta$  of ring protons, which is 0.69, which will be understandable for it has two bulky PPh<sub>3</sub> ligands.



Figure 1. Electronic Absorption Spectra of (1b), (2b) and (3) in  $CH_2Cl_2$ . Due to the Air-sensitivity of all Compounds Reliable Extinction Coefficients could not be Obtained.

#### **UV-Vis Spectra**

The electronic spectra of the three types of the compounds has a distinct pattern of absorption in the UV-Visible region as depicted by Figure 1. All the dicarbonyl compounds show two strong absorption bands in the ultraviolet region and a very weak absorption band in the visible region. The highest-energy absorption band around 260 nm may be assigned to the  $\pi \to \pi^*$  transition which mainly occurs in Cp and the other strong band is a  $M \to L$  charge transfer<sup>17</sup>. This is consistent with the fact that when one of the strong  $\pi$  acceptor CO group is replaced by the  $\sigma$  donor phosphine ligand, the transfer of electron density from  $M \to L$  should be decreased and the intensity of the absorption band due to this transition should be reduced as we see in Figure 1.

When both of the two CO groups are replaced by phosphines, as in compound (3), this electronic transition disappeared as we see in Figure 1. The weak broad



Figure 2. Cyclic Voltammogram of 2 mM (1b) in CH<sub>2</sub>Cl<sub>2</sub>, Pt electrode, 0.2 M of TBAP Supporting Electrolyte.

band in the visible region is assigned to the  $d \rightarrow d$  transition. It shows a red-shift when the phosphine ligands replace both carbonyl groups and place more negative charge on the metal.

#### Electrochemical Behavior of the Dicarbonyl Complexe

Similar to the electronic spectra, the three types of the compounds show their own patterns of cyclic voltammetric responses in electrochemical studies. The cyclic voltammograms of the dicarbonyl compounds (1a), (1b), (1c) and (1d) are very similar to each other. Figure 2 illustrates a representative cyclic voltammetric response of compound (1b) in 2 mM  $CH_2Cl_2$  solution with 0.2 M TBAP (tetrabutylammonium perchlorate) as supporting electrolyte under nitrogen atmosphere.

The cyclic voltammogram exhibited an oxidation peak at 0.91 V. No reductive response was found on the back scan. It indicated that this oxidation process was irreversible and may be attributed to the cleavage of the metal carbonyl bond. In the range of 10-2000 mV/s a linear relationship was observed between the peak

| Compd.   | E <sup>ox, c</sup> | E <sub>11, 1/2</sub> <sup>ox</sup> | E <sub>1, 1/2</sub> °x | E <sup>red, c</sup> | ΔE <sup>b</sup>                     |
|--|--------------------|------------------------------------|------------------------|---------------------|-------------------------------------|
| _  |                    | (ΔE) <sup>ь</sup>                  | (∆E) <sup>ь</sup>      |                     | (Fc <sup>+</sup> /Fc <sup>0</sup> ) |
| $(C_3H_4CO_2C(CH_3)=CH_2)Co(CO)_2$   | 1.04               |                                    |                        |                     | 166                                 |
| $(C_5H_4CO_2CH_2C_6H_3)Co(CO)_2$   | 0.91               |                                    |                        | -0.59               | 276                                 |
| (C <sub>5</sub> H <sub>4</sub> CO <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> )Co(CO) <sub>2</sub>                 | 1.12               |                                    |                        |                     | 274                                 |
| (C <sub>5</sub> H <sub>4</sub> CH <sub>2</sub> CO <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> )Co(CO) <sub>2</sub> | 0.77               |                                    |                        |                     | 210                                 |
| $(C_5H_4CO_2C(CH_3)=CH_2)Co(CO)PPh_3$  |                    | 0.68(170)                          | 0.21(158)              |                     | 162                                 |
| (C <sub>5</sub> H <sub>4</sub> CO <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )Co(CO)PPh <sub>3</sub>   |                    | 0.78(226)                          | 0.23(164)              |                     | 160                                 |
| (C <sub>5</sub> H <sub>4</sub> CO <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )Co(CO)PCy <sub>3</sub>   | 1.29               | 0.77(110)                          | 0.11(138)              | -0.62               | 166                                 |
| (C <sub>5</sub> H <sub>4</sub> CO <sub>2</sub> CH <sub>2</sub> C=CH <sub>2</sub> )Co(CO)PPh <sub>3</sub>               |                    | 0.72(166)                          | 0.20(156)              |                     | 164                                 |

Table VI. Cyclic Voltammetric Data for the Compounds  $C_3H_4RCo(CO)_2$  and  $C_4H_4RCo(CO)PR_3$  in  $CH_2Cl_2^*$ .

 $E^{ox}$  and  $E^{red}$  are oxidation and reduction potentials, respectively.  $E_{I,I/2}^{ox}$  and  $E_{II,I/2}^{ox}$  are half wave potentials of peak I and II, respectively.

<sup>a</sup> Potentials in V are referred to the ferrocene (+/0) couple (+0.4 V vs. SCE) in 0.2 M TBAP as supporting electrolyte, see text. Scan rate 100 mV/s.

<sup>b</sup> ΔE in mV.

<sup>c</sup> Irreversible peak potentials.

current  $i_p$  and the square root of the sweep rate  $v^{1/2}$ , indicating that this was a diffusion-controlled process. In the reduction, a peak of strong intensity appeared at -0.59 V. The reductive process was assumed to be the cleavage of the metal-ring bond<sup>18</sup>. The corresponding cyclic voltammetric parameter of the dicarbonyl compounds are listed in Table VI. The similarity of the cyclic voltammograms is attributed to the similarity of the structures.

### **Electrochemical Behavior of Monophosphine Complexes**

When a phosphine ligand substituted one of the carbonyl groups, the compounds exhibited a different pattern in the cyclic voltammogram as we can see from the



Figure 3. Cyclic Voltammogram of (2b) (about 1 mM) in  $CH_2Cl_2$ , Pt Electrode, 0.2 M of TBAP Supporting Electrolyte.  $\nu = 100 \text{mV/s}$ .

typical cyclic voltammetric response of (2b) in Figure 3. Two consecutive oxidation peaks were observed with similar peak areas. Each of them had a peak of a re-reductive response on the back scan. They gave  $E_{1/2}$  at 0.23 and 0.78 V, respectively. The peak separation of the coupled potentials were large, but still are comparable to that of ferrocenium/ferrocene couples (see Table VI). The large peak separation for a reversible couple was also observed by Huttner<sup>19</sup> and his co-workers in studies of cyclopentadienylmanganese complexes and was attributed to the high resistance in the organic solvent. The same intensity of the peaks suggests two successive, single-electron transfer processes during oxidation. It thus was considered as two reversible redox processes of a one-electron transfer. Data of the peak current  $i_p$  and  $v^{1/2}$  in the scan rate range from 50 to 2000 mV/s also show a linear relationship, indicating that these oxidation processes were also diffusion controlled processes.

A larger scan range was used for (2b'). In addition to the two couples of reversible peaks at 0.11 V and 0.77 V, one peak appeared at 1.29 V with no reductive response in the oxidation scan and another peak at -0.615 V with no re-oxidation

Obviously, they could be assumed to be the cleavage of peak in the reductive scan. the metal-carbonyl bond and the cleavage of the metal-ring bond, respectively. As we observed in dicarbonyl compounds, these monophosphine substituted cyclopentadienylcobalt derivatives exhibited similar cyclic voltammograms and their cyclic voltammogram parameters are also listed in Table VI. These results revealed that replacing one carbonyl group with the phosphine ligand increases the stability of Being a strong  $\sigma$  donor, a phosphine ligand can help the metal the compounds. center bear two successive losses of one-electron losses. The mono-substituted phosphine carbonyl compound (2b') was not decomposed on oxidation until a potential of 1.29 V was reached, much higher than its dicarbonyl analogue. The potential leading to reductive decomposition is about the same as that of its dicarbonyl analogue. Obviously, the oxidation potential of the dicarbonyl parent compounds is increased due to the replacement of one carbonyl group with the phosphine ligand. We noticed that  $E_1$  of (2b') is lower than that of (2b). This is consistent with the fact that PCy<sub>3</sub> is a stronger  $\sigma$  donor compared to PPh<sub>3</sub>, so the cobalt in (2b') must have less positive charge than in (2b) and it easier loses its first But for the 17e species  $(\eta^5-C_4H_4R)Co^{11}(CO)PCy_3$  and  $(\eta^5-C_4H_4R)Co^{11}(CO)PCy_3$ electron.  $C_{3}H_{4}R$ )Co<sup>II</sup>(CO)PPh<sub>3</sub>, the ability of holding electrons is about the same. Thus, E<sub>II</sub> of (2b) and (2b') are about the same. Figure 4 illustrates the redox behavior in the electrochemical process of the monophosphine substituted cyclopentadienylcarbonylcobalt compounds.

#### Electrochemical Behavior of Bis(phosphine) Complexes

The cyclic voltammogram of the bis(phosphine) substituted compound (3) is shown in Figure 5. A couple of peaks,  $E_{1/2}$  at -0.39 V with a peak separation of 79 mV, appeared in the reductive scan. The current ratio of  $i_{pe}/i_{pa}$  is unity. It was reported by Koelle<sup>20</sup> that C<sub>5</sub>H<sub>5</sub>Co(PPh<sub>3</sub>)<sub>2</sub> had a reductive couple at -0.73 V vs. SCE in



Figure 4. Redox Behavior of Monophosphine Substituted Cyclopentadienyl Carbonyl Cobalt Compounds.



Figure 5. Cyclic Voltammogram of (3) (about 0.5 mM) in  $CH_2Cl_2$ , Pt Electrode, 0.2 M of TBAP Supporting Electrolyte. v = 100 mV/s.

CH<sub>2</sub>Cl<sub>2</sub> with a peak separation of 60 mV. The reductive potentials of C<sub>3</sub>H<sub>3</sub>Co(PR<sub>3</sub>)<sub>2</sub> were shifted towards the positive in the series of PEt<sub>3</sub>, PPh<sub>3</sub> and P(OMe)<sub>3</sub> (-1.01, -0.73 and -0.32 V, respectively) which is consistent with their electron donating ability decrease in the series. PEt<sub>3</sub> is considered to be a  $\sigma$  base as well as  $\pi$  base and P(OMe)<sub>3</sub> a  $\sigma$  base but  $\pi$  acid, although their difference in  $\pi$  component are very small<sup>16</sup>.

Compound (3) has an electron withdrawing substituent on the cyclopentadienyl ring, it should increase the ability of getting electrons for (3) compared to



Figure 6. Redox Behavior of Bis(phosphine) Substituted Cyclopentadienyl Cobalt Compounds.

 $C_5H_5Co(PPh_3)_2$ . We can expect that an electron withdrawing substituent on the cyclopentadienyl ring, like in compound (3), has a comparable influence on the redox potential as found for the ligand P(OMe)\_3 in Koelle's experiment. On oxidation, (3) exhibited an irreversible peak at about 0.6 V, meaning that it is easier to be oxidized compared to the other two types of cyclopentadienylcobalt compounds. This is consistent with the relatively electron-rich metal center of compound (3) due to the coordination of two strong electron releasing phosphine ligands. The possible redox processes of the diphosphine analogue are illustrated as in Figure 6.

#### Conclusions

For the three types of organocobalt compounds studied, phosphine ligands cause a red-shift in their electronic spectra in  $M \rightarrow L$  and  $d \rightarrow d$  transitions and affect the chemical shift of the resonances of the ring protons in the <sup>1</sup>H NMR spectra. The largest split of the NMR signals of the cyclopentadienyl ring protons for the bis(phosphine) derivative reflect the steric influence of its two bulky PPh<sub>3</sub> ligands. Monophosphine substituted derivatives exhibit two reversible peaks during oxidation which represent two reaction intermediates identified by cyclic voltammetric experiment. Dicarbonyl and bis(phosphine) derivatives are simply decomposed during oxidation, no intermediate was identified. Monophosphine substituted compounds are most difficult to be decomposed during the electrochemical oxidation. The bis(phosphine) derivative was decomposed at the lowest oxidative potential and this could be attributed to its two steric bulky phosphine substituents.

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#### REFERENCES

- 1, J. A. Migyel-garcil, H. Adams, N. A. Bailey and P. M. Maitlis, J. Organomet. Chem., <u>413</u>, 427 (1991).
- R. T. Kettenbach, C. Krüger and H. Butenschön, Angew. Chem., Int. Ed. Engl., <u>31</u>, 1066 (1992).
- (a) C. Charrier and F. Mathey, J. Organomet. Chem., <u>170</u>, C41 (1979).
  (b) A. M. Z. Slawin, D. J. Williams, J. Crosby, J. A. Ramsden and C. White, J. Chem. Soc., Dalton Trans. 2491 (1988).
- 4, (a) T.-F. Wang, T.-Y. Lee, Y.-S. Wen, L.-K. Liu, J. Organomet. Chem., 403, 353 (1991). (b) T.-F. Wang, T.-Y. Lee, J.-W. Chou and C.-W. Ong, J. Organomet. Chem., 423, 31 (1992). (c) T.-F. Wang and Y.-S. Wen, J. Organomet. Chem., 439, 155 (1992).
- (a) J. Okuda and K.-H. Zimmermann, Chem. Ber. <u>122</u>, 1645 (1989). (b) J. Okuda and K.-H. Zimmermann, Chem. Ber. <u>123</u>, 1641 (1990). (c) J. Okuda, K.-H. Zimmermann and E. Herdtweck, Angew. Chem. <u>103</u>, 446 (1991); Angew. Chem., Int. Ed. Engl. <u>30</u>, 430 (1991). (d) J. Okuda and K.-H. Zimmermann, Chem. Ber. <u>125</u>, 637 (1992). (e) K.-H. Zimmermann, R. S. Pilato, I. T. Horvàth and J. Okuda, Organometallics <u>11</u>, 3935 (1992).

- (a) R. P. Hughes, T. L. Husebo, A. L. Rheingold, L. M. Liable-Sands and G. P. A. Yap, Organometallics <u>16</u>, 5 (1997).
  (b) F. Pradella, D. Rehorek, M. Scoponi, S. Sostero and O. Traverso, J. Organomet. Chem., <u>453</u>, 283 (1993).
- 7, X. Wei, Y. Hu, T. Li and H. Hu, J. Chem. Soc., Perkin Trans, 2487 (1993).
- 8, N. Chatani and T. Hanafusa, J. Org. Chem., 56, 2166 (1991).
- (a) R. L. Halterman and K. P. C. Vollhardt, Organometallics, 7, 883 (1988), (b) H. Bönnemann, Angew. Chem. Int. Ed. Engl., 24, 248 (1985).
- 10, Y. Misuni, Y.Ishii and M. Hidai, Organometallics, 14, 1770 (1995).
- 11, G. Gritzner and J. Kuta, Pure Appl. Chem., 56, 461 (1984).
- X. Hou, Z. Pang, Z. Huang, R. Cai and X. Zhou, Synth. React. Inorg. Met.-Org. Chem., 28, 1505 (1998).
- (a) O. Alnaji, Y. Peres, F. Dahan, M. Dartiguenave and Y. Dartiguenave, Inorg. Chem., 25, 1383 (1986); (b) H.-F. Klein, H. König, S. Koppert, K. Ellrich and J. Riete, Organometallics, 6, 1341 (1987).
- C. Moreno, M. J. Macazaga and S. Delgado, Organometallics, <u>10</u>, 1124 (1991).
- (a) P-H. Yeh, Z. Pang and R. F. Johnston, J. Organomet. Chem., <u>509</u>, 123 (1996);
  (b) Z. Pang, R. F. Johnston and D. G. VanDerveer, J. Organomet. Chem., <u>526</u>, 25 (1996).
- M. N. Golovin, M. M. Rahman, J. E. Belmonte and W.P. Giering, Organometallics, 4, 1981 (1985).
- 17, P. J. Giordano and M. S. Wrighton, Inorg. Chem., 16, 160 (1977).
- 18, R. S. Nicholson and I. Shain, Anal. Chem., <u>36</u>, 706 (1964).
- P. Lau, H. Braunwarth, G. Huttner, D. Günauer, K. Evertz, W. Imhof, C. Emmerich and L. Zsolnai, Organometallics, 10, 3861 (1991).

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### 20, U. Koelle and S. Ohst, Inorg. Chem., 25, 2689 (1986).

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