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# ELECTROCHEMICAL STUDIES ON ORGANOMETALLIC COMPOUNDS

## VIII *. LIGAND EXCHANGE REACTION IN CARBONYL COBALT COMPLEXES

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## Summary

The reaction of $Co(CO)_3DMPP^-$ with $Co_2(CO)_6(DMPP)_2$ (DMPP = dimethylphenylphosphine) yields $CoCO_4^-$ and $Co_2(CO)_5(DMPP)_3$. The DMPP ligand of $Co(CO)_3DMPP^-$ can be replaced by CO or triphenylphosphite.

## Introduction

It has been noted recently that paramagnetic metal carbonyls are especially reactive towards ligand substitutions [1]. These organometallic radicals can be readily generated electrochemically either by oxidation or reduction of mono- or poly-metallic complexes; facile and highly regioselective ligand substitution takes place with such species, and in certain cases the reaction proceeds catalytically [2].

In accordance with these views, we showed recently that in the presence of phosphorus ligands, the radicals generated by electrochemical oxidation of cobalt carbonyl derivatives undergo ligand substitution [3]. We report here new observations on the substitution of anionic species of cobalt carbonyls, which yield selectively polysubstituted binuclear couples.

## Results and discussion

The anions $Co(CO)_3DMPP^-$ (I) and $Co(CO)_3TPP^-$ (II), in which DMPP denotes dimethylphenylphosphine and TPP denotes triphenylphosphite, are obtained by controlled potential electrolysis of $Co_2(CO)_6(DMPP)_2$ (III) and $Co_2(CO)_6(TPP)_2$ (IV).

When the electrolysis of III is carried out below −15 °C on the plateau of wave C

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* For part VII, see ref. 10.

($E_{1/2}$ −1.25 V) (Fig. 1), I is formed quantitatively with consumption of 2 F. After completion of the electrolysis an oxidation wave A″ is observed at −0.47 V (Fig. 1).

At 20 °C, however, only 1 to 1.5 F are consumed, depending on the initial concentration of III. For example, when the concentration of III is about $7.4 \times 10^{-3}$ *M*, electrolysis at −1.4 V involves 1.06 F. The IR spectrum, obtained in situ, shows eight CO bands at 1996, 1945, 1923, 1887, 1836, 1820, 1765 and 1745 $cm^{-1}$ (Fig. 2).

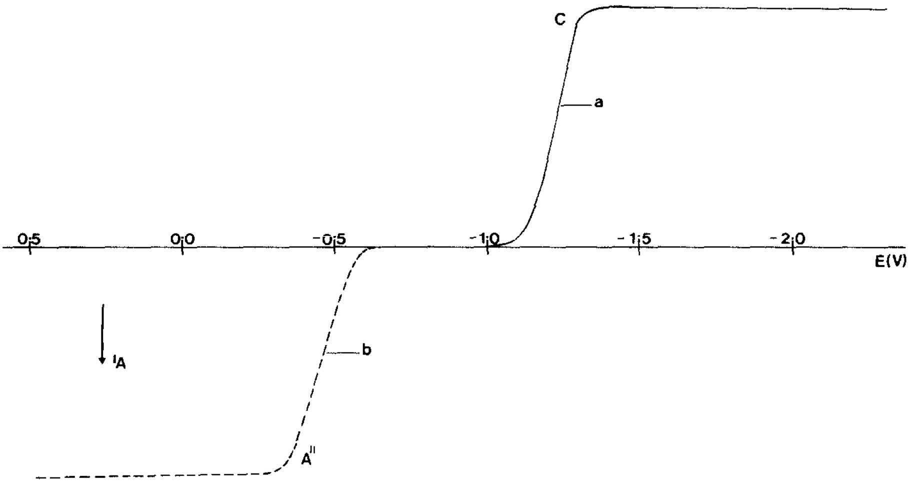

Fig. 1. rde voltammograms at −15 °C: (a) $Co_2(CO)_6(DMPP)_2$, before electrolysis; (b) after electrolysis at −1.40 V.

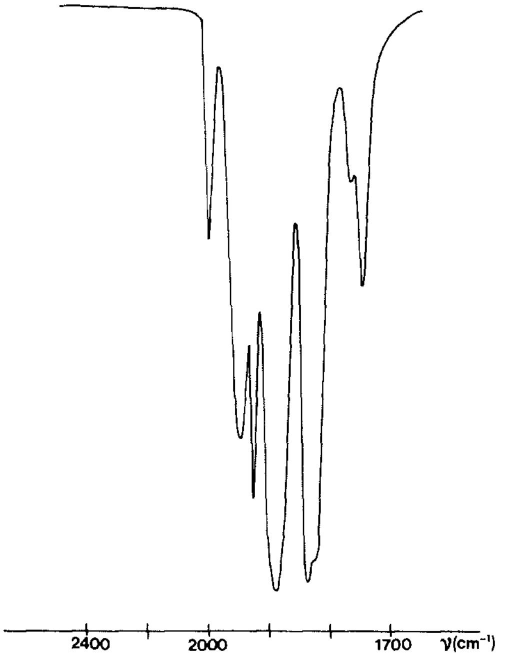

Fig. 2. IR spectrum of the electrolysis product of $Co_2(CO)_6(DMPP)_2$ (*E* −1.4 V) at 20 °C.

The rotating platinum disk electrode (rde) voltammogram shows three waves, two oxidation waves at +0.2 V (A′) and −0.47 V (A″) and one reduction wave at −1.7 V (D) (Fig. 3).

If the concentration of III is $3.5 \times 10^{-3}$ *M*, 1.57 F are consumed, and the same bands with different relative intensities are observed.

These results show that three products are formed during the electrolysis at room temperature. Two of them are known, $Co(CO)_3(DMPP)^-$ (I) (waves A″ [3] and bands at 1923, 1836 and 1820 $cm^{-1}$) and $Co(CO)_4^-$ (wave A′ [3,4] and band at 1887 $cm^{-1}$). We isolated the third (wave D and bands at 1996, 1945, 1765 and 1745 $cm^{-1}$; cf. Fig. 4), and showed it to be $Co_2(CO)_5(DMPP)_3$ cf. ref. 5. Note that this compound gives an oxidation wave D′ at the same potential as that of wave A′ (Fig. 4a).

$Co_2(CO)_5(DMPP)_3$ can also be obtained quantitatively by adding a solution of $Co_2(CO)_6(DMPP)_2$ at 20 °C to a stoichiometric amount of $Co(CO)_3(DMPP)^-$ prepared by electrolysis of $Co_2(CO)_6(DMPP)_2$ below −15 °C. The reaction takes several hours. The voltammograms of the mixture presents initially waves C and A″, which are replaced gradually by waves D and A′ (Fig. 5).

The above results point to the reaction:

$$\underset{(I)}{Co(CO)_3DMPP^-} + \underset{(III)}{Co_2(CO)_6(DMPP)_2} \rightarrow Co(CO)_4^- + Co_2(CO)_5(DMPP)_3 \quad (1)$$

DMPP is replaced by CO in the anionic species, whereas the reverse substitution takes place with the dimer.

We have also examined the same type of reaction in the case of $Co_2(CO)_6(TPP)_2$ (IV). Whatever the temperature and the concentration, electrolysis of IV on the plateau of wave $C_1$ yields quantitatively, the anion $Co(CO)_3(TPP)^-$ (II), which gives an oxidation wave $A'_1$ at −0.05 V (Fig. 6).

This shows that II does not react with IV in the same way as shown in eq. 1.

When two mol of I, prepared at low temperature are treated with one mol of IV, the following reaction takes place:

$$\underset{(I)}{2Co(CO)_3DMPP^-} + \underset{(IV)}{Co_2(CO)_6(TPP)_2} \rightarrow \underset{(II)}{2Co(CO)_3TPP^-} + \underset{(III)}{Co_2(CO)_6(DMPP)_2} \quad (2)$$

During this reaction, wave $A'_1$ (II) and the reduction wave C of III appear. The waves A′ and D are also observed because of the reaction of I with III; these waves remain small because reaction 2 is faster than reaction 1.

(Continued on p. 253)

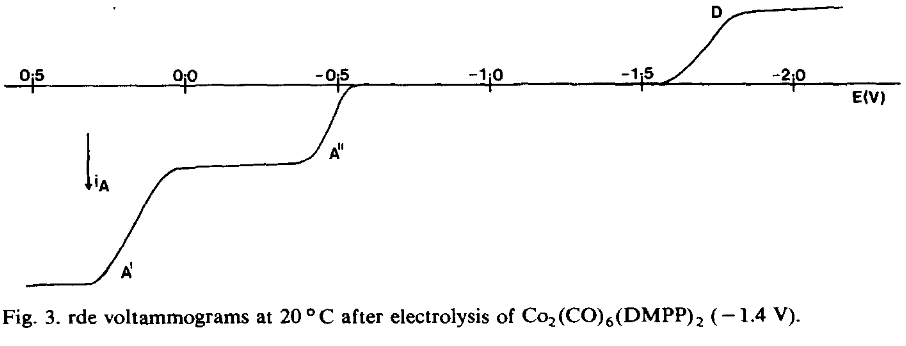

Fig. 3. rde voltammograms at 20 °C after electrolysis of $Co_2(CO)_6(DMPP)_2$ (−1.4 V).

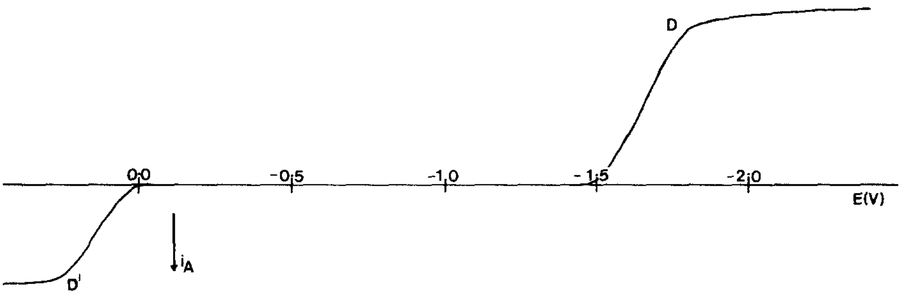

Fig. 4a. rde voltammogram of $Co_2(CO)_5(DMPP)_3$.

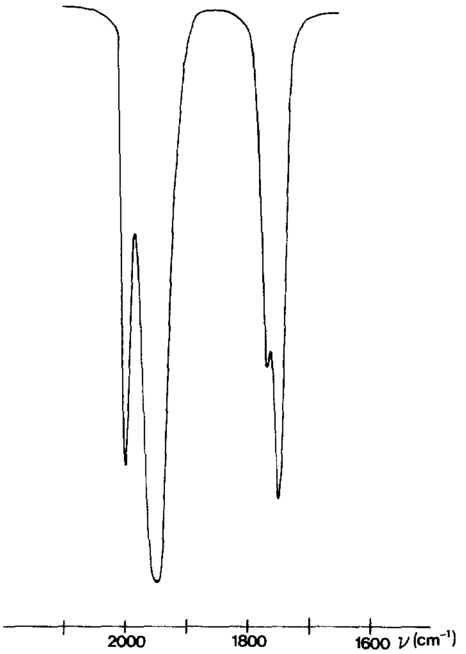

Fig. 4b. IR spectrum of $Co_2(CO)_5(DMPP)_3$ in THF.

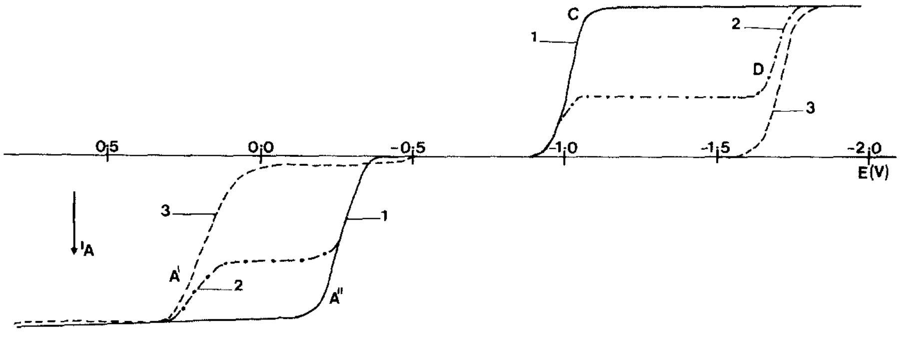

Fig. 5. rde voltammograms. Reaction between $Co_2(CO)_6(DMPP)_2$ and $(Co(CO)_3DMPP)^-$ (1) initial voltammograms (2) after 4 h (3) after 15 h.

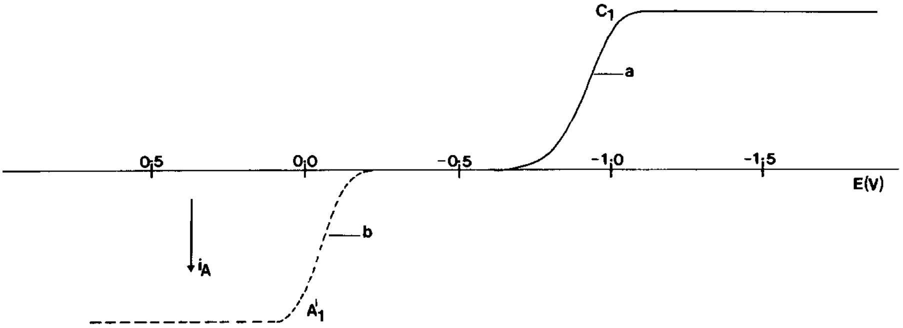

Fig. 6. rde voltammograms: (a) $Co_2(CO)_6(TPP)_2$ at ambiant temperature; (b) after electrolysis at $-1.20$ V.

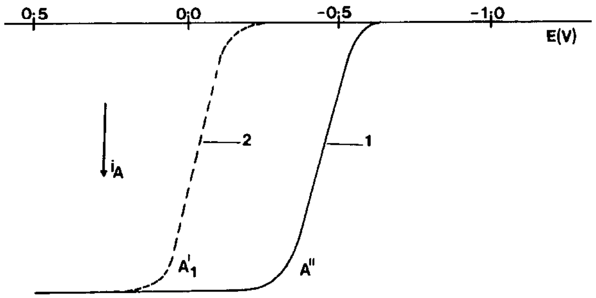

Fig. 7a. rde voltammograms: (1) $(Co(CO)_3DMPP)^-$ alone; (2) $(Co(CO)_3DMPP)^-$ + TPP.

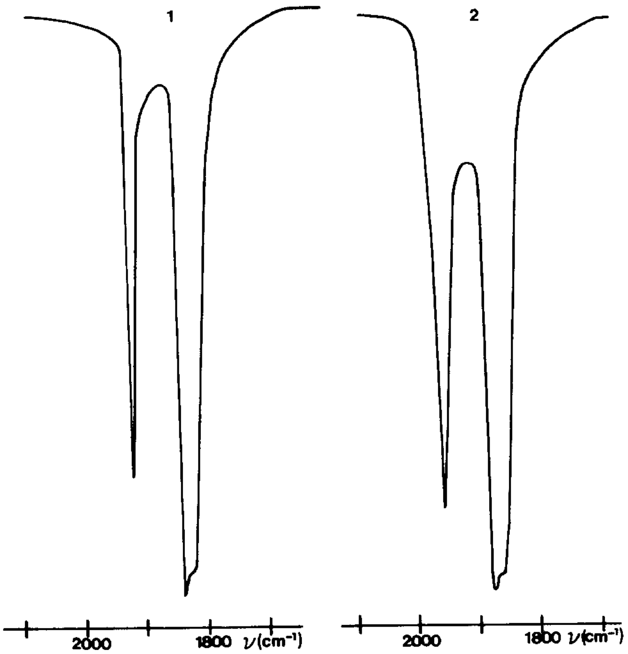

Fig. 7b. IR spectra: (1) $(Co(CO)_3DMPP)^-$ alone; (2) $(Co(CO)_3DMPP)^-$ + TPP.

TABLE 1

ELECTROCHEMICAL AND IR DATA FOR CARBONYL COBALT COMPLEXES

| | $Co(CO)_4^-$ | $Co(CO)_3DMPP^-$ (I) | $Co(CO)_3TPP^-$ (II) | $Co_2(CO)_6(DMPP)_2$ (III) | $Co_2(CO)_6(TPP)_2$ (IV) | $Co_2(CO)_5(DMPP)_3$ |
|---|---|---|---|---|---|---|
| rde oxidation wave | A′: +0.2 | A″: −0.47 V | $A'_1$: −0.05V | +0.6 V | – | +0.15 |
| rde reduction wave | – | – | – | C: −1.25 V | $C_1$: −0.9 | D: −1.7 V |
| IR $\nu(CO)(cm^{-1})$ | 1887(s) | 1923(s)<br>1836(s)<br>1820(sh) | 1960(s)<br>1876(s)<br>1863(sh) | 1951(s) | 1980(s) | 1996(s)<br>1945(s)<br>1765(sh)<br>1745(s) |

[a] s, strong; w, weak, sh, shoulder.

$Co(CO)_3(TPP)^-$ (II) and $Co_2(CO)_6(DMPP)_2$ (III) react very slowly (the reaction is not complete after 15 h) to give $Co(CO)_4^-$ and a product, reducible at −1.5 V, which we were not able to isolate; this product is presumably $Co_2(CO)_5(DMPP)_2TPP$.

As shown by the change in the IR spectrum and in the voltammogram (Fig. 7), reaction of I with TPP yields II and DMPP.

$$\underset{(I)}{Co(CO)_3DMPP^-} + TPP \rightarrow \underset{(II)}{Co(CO)_3TPP^-} + DMPP \qquad (3)$$

Finally I and CO give:

$$\underset{(I)}{Co(CO)_3DMPP^-} + CO \rightarrow Co(CO)_4^- + DMPP \qquad (4)$$

The electrochemical and IR data for the various compounds are summarized in Table 1.

## Conclusion

Reactions 3 and 4 show that TPP and CO have a greater affinity than DMPP for the anionic species. This is in good accord with the electron donor and electron acceptor properties of the three ligands. The electronic density on the metal decreases on going from DMPP to TPP and CO. In the light of reactions 1 and 2, the affinity of CO for the anionic species seems to be larger than that of TPP.

The sequence for the oxidation potentials of the anions is the same: $E_{1/2}(Co(CO)_4^-) > E_{1/2}(Co(CO)_3TPP^-) > E_{1/2}(Co(CO)_3DMPP^-)$. This is normal, since the oxidation will be the more difficult the smaller the electronic density on the metal.

The reduction potentials for the dimers are in the order $E_{1/2}(Co_2(CO)_8) > E_{1/2}(Co_2(CO)_6(DPP)_2) > E_{1/2}(Co_2(CO)_6(DMPP)_2) > E_{1/2}(Co_2(CO)_5(DMPP)_3)$, which is also in good agreement with an increase in the electronic density in the metal [6].

## Experimental

### *Apparatus and procedure*

The apparatus and techniques have been described previously [9].

The electrochemical experiments were carried out on a platinum rotating disk electrode (rde) under argon in tetrahydrofuran (THF) with 0.2 *M* tetrabutylammonium hexafluorophosphate $Bu_4NPF_6$ as supporting salt. The reference electrode was an aqueous saturated calomel electrode. Tetrahydrofuran was purified by distillation from sodium benzophenone ketyl under argon. $Bu_4NPF_6$ (Fluka) was recrystallized twice from ethanol, dried, and deoxygenated before use.

### *Reagents*

$Co_2(CO)_6(DMPP)_2$ [7] and $Co_2(CO)_6(TPP)_2$ [8] were prepared by literature procedures.

### *Electrochemical reduction of $Co_2(CO)_6(DMPP)_2$*

At −15 °C, exhaustive electrolysis of III at −1.40 V consumes 1.95 F to give a yellow solution (the initial solution was dark red). The rde voltammogram of the electrolysed solution shows wave A″ ($E_{1/2}$ −0.47 V); the IR spectrum consists of 3 bands at 1923, 1836 and 1820 $cm^{-1}$.

At room temperature, depending on the initial concentration of III, the electrolysis at −1.4 V consumes 1.06 or 1.57 F (vide supra); the complex $Co_2(CO)_5(DMMP)_3$ was isolated by evaporating the THF, followed by extraction by toluene. After evaporation of the toluene, the product is recrystallized in heptane. $\nu$(CO) (THF): 1996, 1945, 1765, 1745 $cm^{-1}$. Analysis. Found: C, 51.92; H, 5.05; P, 13.71. $Co_2H_{33}P_3C_{29}O_5$ calcd.: C, 51.80; H, 4.91; P, 13.83%. $^1$H NMR ($C_6D_6$) $\delta$ 1.48 (d, 6 H, $CH_3$, *J* 8 Hz); 1.24 (d, 12 H, $CH_3$ *J* 8 Hz). $\delta$: 7.53 at 7.02 (m, 15 H, $C_6H_5$) ppm.

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6 The disproportionation of binuclear complexes under the influence of a base confirms this conclusion. For example, the following reaction is observed: $Co_2(CO)_6(TPP)_2 + 2DMPP \rightarrow Co(CO)_3TPP^- + Co(CO)_3(DMPP)_2^+ + TPP$
This reaction is currently under investigation.

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