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ELECTROCHEMICAL STUDIES ON ORGANOMETALLIC COMPOUNDS

V *. ELECTROCHEMICAL OXIDATION OF THE ANIONS $[Co(CO)_4]^-$ AND $[Co(CO)_3PPhMe_2]^-$

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Summary

In tetrahydrofuran with tetrabutylammonium hexafluorophosphate as supporting electrolyte, 1*e* electrochemical oxidation of $[Co(CO)_4]^-$ gives $Co_2(CO)_8$; in the presence of dimethylphenylphosphine (DMPP), the process consumes two electrons and $[Co(CO)_3(DMPP)_2]^+$ is obtained. The same cation is also obtained by 2 F oxidation of $[Co(CO)_3DMPP]^-$ in the presence of DMPP. In all cases a radical intermediate is formed.

Introduction

Electrochemistry provides a convenient method of obtaining information about the mechanism of ligand substitution reactions in organometallic compounds when the oxidation state of the metal changes [1]. However it has not previously been used to examine the important species octacarbonyldicobalt, $Co_2(CO)_8$, for which a radical chain mechanism for ligand exchange reactions was postulated recently [2]. In tetrahydrofuran (THF) containing tetrabutylammonium hexafluorophosphate as supporting salt, $Co_2(CO)_8$ is unstable, but the closely related $[Co(CO)_4]^-$ tetracarbonylcobalt anion, from which $Co_2(CO)_8$ can be generated, is quite stable. We report here the results of an electrochemical study of this anion and of the anion $Co(CO)_3L^-$, where L is dimethylphenylphosphine (DMPP).

Experimental

Reagents. $Co_2(CO)_6(DMPP)_2$ [3], $[Co(CO)_4]^-PPN^+$ * and $[Co(CO)_3(DMPP)_2]^+$ $[Co(CO)_4]^-$ [2] were prepared by literature procedures. The electro-

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* For part IV see ref. 1b.

* PPN = bis(triphenylphosphine)iminium, DMPP = dimethylphenylphosphine.

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chemical experiments were carried out under argon at room temperature. Tetrahydrofuran was purified by distillation from sodium benzophenone ketyl under argon. The supporting electrolyte was tetrabutylammonium hexafluorophosphate (0.2 *M*) in all cases; the salt (Fluka) was recrystallized twice from ethanol, dried, and deoxygenated before use.

Apparatus and procedure. The apparatus and technique have been described previously [1a]. The reference electrode was an aqueous saturated calomel electrode (Tacussel C_4 electrode), separated from the solution by a sintered glass disk. The auxiliary electrode was a platinum wire. The rotation rate of the rotating disc electrode (rde) was 400 rev. per minute. Infrared (IR) spectra were recorded on a Perkin-Elmer model 580B spectrometer.

Results

Voltammetry

On a platinum rotating disk electrode (rde), $[Co(CO)_4]^-$ shows a 1*e* wave A′, with a half-wave potential at +0.20 V (Fig. 1); a potential of +0.12 was found in ethanol [5]. In cyclic voltammetry, the corresponding peak A′ is obtained; during the reverse scan, a peak A is observed at −0.30 V (Fig. 2).

In the presence of DMPP, a twofold increase of the height of wave or peak A′ is observed (Fig. 1). During the cathodic sweep two peaks B and C appear at −0.90 and −1.25 V, respectively; the height of peak C becomes larger relatively to that of B when the sweep rate is decreased. A new anodic peak A″ is observed at −0.45 V when the sweep direction is reversed after B or C (Fig. 3).

The cyclic voltammograms of $[Co(CO)_3(DMPP)_2]^+$ obtained chemically (when it is always in stoechiometric amounts with $[Co(CO)_4]^-$) shows peaks B, C, A″ and A′.

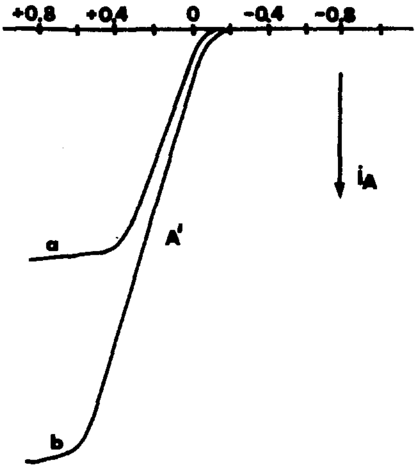


Fig. 1. Voltammogram of $[Co(CO)_4]^-$ in THF on the rde, (a) alone, (b) with DMPP in excess.

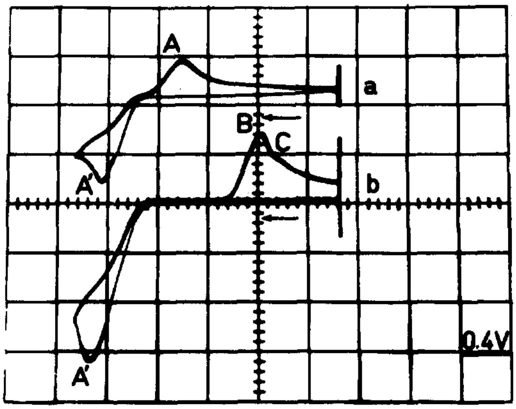


Fig. 2. Voltammogram of $[Co(CO)_4]^-$ in THF; (a) alone, (b) with DMPP in excess. Starting potential −1.66. Sweep rate 0.200 V s^{-1}.

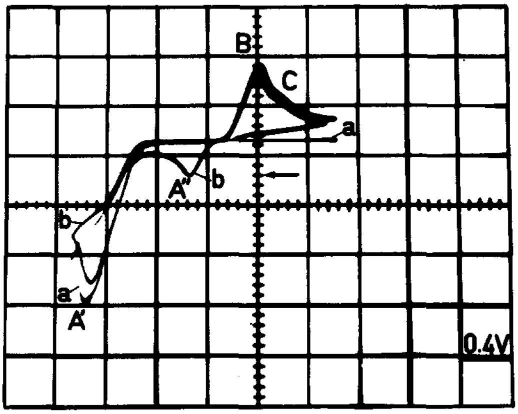


Fig. 3. Voltammogram of $[Co(CO)_4]^-$ in THF with DMPP in excess, (a) first sweep, (b) second sweep. Starting potential −1.66 V. Sweep rate 0.200 V s^{-1}.

When it is prepared electrochemically (vide infra), $[Co(CO)_4]^-$ is absent, and only peaks B, C and A″ are observed (Fig. 4).

$Co_2(CO)_6(DMPP)_2$ gives peaks C, followed by A″ when the scan is reversed (Fig. 5). $[Co(CO)_3L]^-$ gives the same voltammogram when the scan is swept first anodically and cathodically. On the rde, an anodic 1 F wave A″ is observed (Fig. 6). When DMPP is added to the solution, the height of this wave doubles (Fig. 6); in cyclic voltammetry, the height of peak A″ also doubles, and in addition to peak C, peak B appears during the cathodic sweep (Fig. 7).

Controlled potential electrolyses

Exhaustive electrolysis of $[Co(CO)_4]^-$ in the presence of DMPP at +0.40 V consumes 1.92 F; the solution, which was originally light green becomes yellow. The rde voltammogram of this solution shows wave B, and the voltammogram peaks B and C; in THF, three IR bands are observed at 1996 cm^{-1} (strong), 1945 and 1910 cm^{-1} (weak).

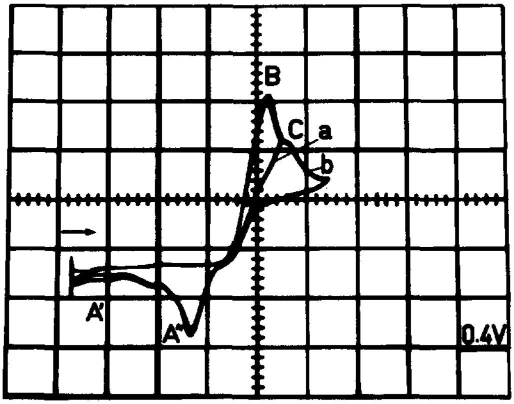


Fig. 4. Voltammogram of $[Co(CO)_3(DMPP)_2]^+$ (prepared electrochemically). Starting potential +0.5 V, sweep rate 0.100 V s^{-1}, (a) first sweep, (b) second sweep.

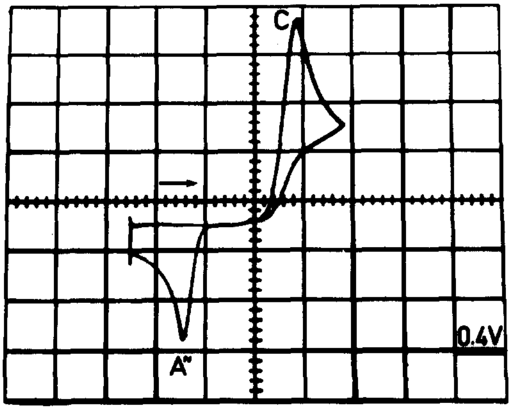


Fig. 5. Voltammogram of $Co_2(CO)_6(DMPP)_2$. Starting potential 0 V. Sweep rate 0.200 V s^{-1}.

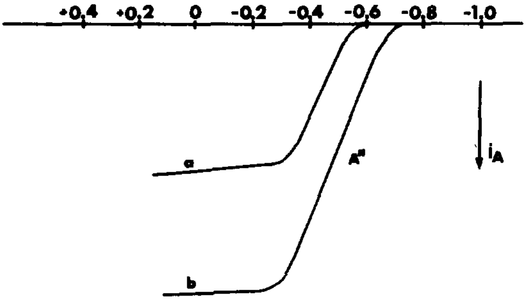


Fig. 6. Voltammogram of $[Co(CO)_3DMPP]^-$ (prepared electrochemically) on the rde, (a) alone, (b) with excess DMPP.

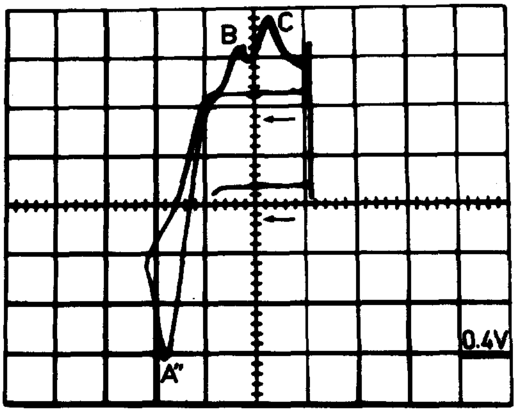


Fig. 7. Voltammogram of $[Co(CO)_3DMPP]^-$ (prepared electrochemically) with excess of DMPP. Starting potential − 1.48 V. Sweep rate 0.050 V s^{-1}.

At −15°C, exhaustive electrolysis of $Co_2(CO)_6(DMPP)_2$ at −1.40 V consumes 1.95 F to give a yellow solution (the starting solution was dark red). The rde voltammogram of the electrolysed solution shows wave A″; the IR spectrum consists of 3 bands at 1923, 1836 and 1820 cm^{-1}. When the electrolysis is carried out at room temperature, 1 to 1.5 F are consumed, and complexes reducible at more negative potentials are obtained. (These complexes are being studied.) To the electrolysis solution, which contained $[Co(CO)_3DMPP]^-$ was added a slight excess of DMPP; a controlled potential electrolysis was carried out at room temperature on the plateau of wave A″ (−0.2 V). Two F were consumed and the rde voltammogram showed wave B. The IR spectrum consisted of the three bands at 1996, 1945 and 1910 cm^{-1}.

A solution of $[Co(CO)_3(DMPP)_2]^+$, obtained by electrolysis of $[Co(CO)_4]^-$ in the presence of DMPP, was electrolysed at the potential of peak B (−1.10 V). After completion of the electrolysis, 1 F is consumed, and the wave of the dimer $Co_2(CO)_6(DMPP)_2$ appears at −1.20 V. The IR spectrum of the solution shows the characteristic band at 1951 cm^{-1}.

Discussion

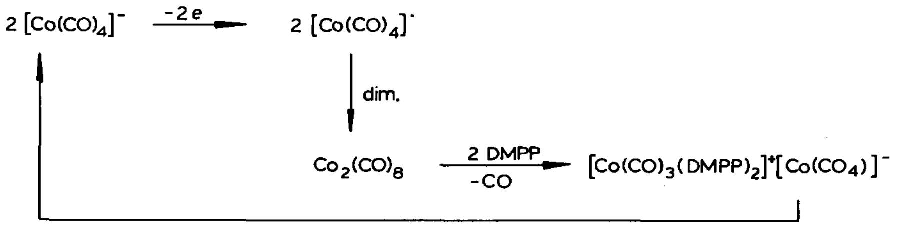
Wave or peak A′ corresponds to the 1e oxidation of $[Co(CO)_4]^-$, according to eq. 1 and 2 [6,7].

$$[Co(CO)_4]^- \xrightarrow{-1e} [Co(CO)_4]^{\cdot} \qquad (1)$$

$$[Co(CO)_4]^{\cdot} \rightarrow \tfrac{1}{2}Co_2(CO)_8 \qquad (2)$$

In the presence of DMPP the process becomes bielectronic, and, as the experimental data (see Results) indicate that $[Co(CO)_3DMPP_2]^+$ is obtained. This result can be explained in terms of one of the mechanisms (a)–(c).

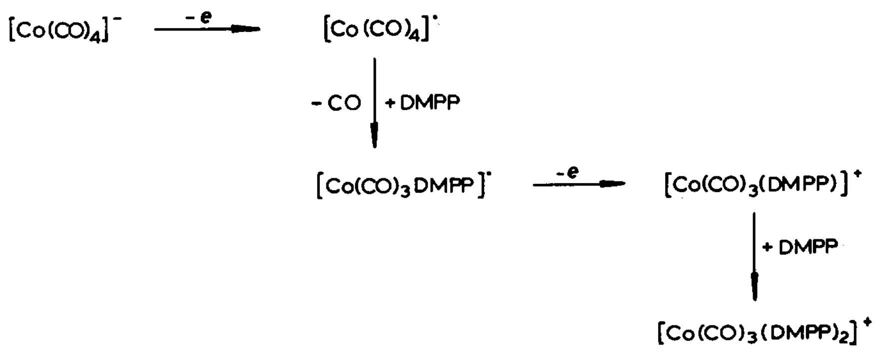
(a) E-dimerisation-disproportionation (global half-regeneration mechanism)



(3)

It has been shown that in the presence of phosphines, $Co_2(CO)_8$ disproportionates very rapidly [2].

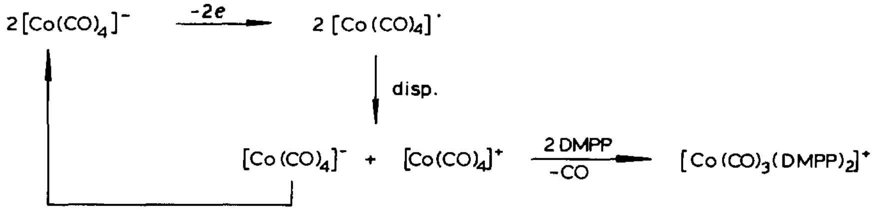
(b) ECEC



(4)

This implies that [Co(CO)$_3$DMPP]$^\cdot$ is more readily oxidized than [Co(CO)$_4$]$^-$.

(c) E-disproportionation-C (half-regeneration)

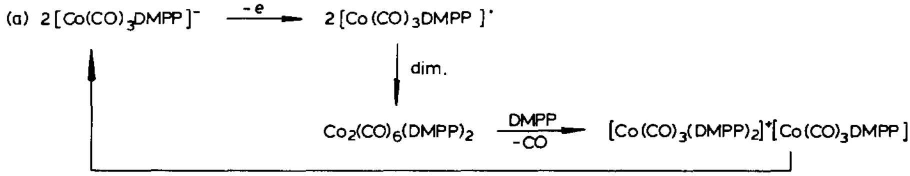


(5)

The disproportionation does not take place in the absence of DMPP. This mechanism could operate only if the reaction of [Co(CO)$_4$]$^+$ with DMPP was very fast. This reaction must, indeed, be fast, since the species [Co(CO)$_3$(DMPP)$_2$]$^+$ is very stable.

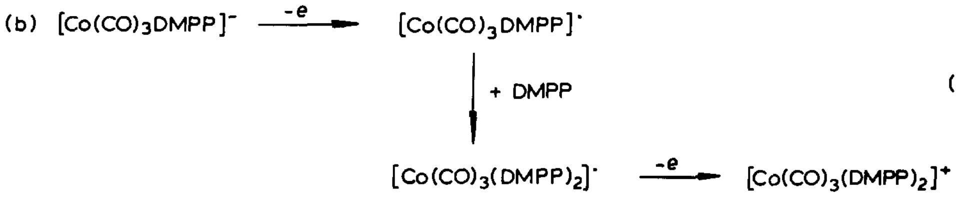
As shown by the results of controlled potential electrolyses, at low temperatures (−15°C) the reduction of Co$_2$(CO)$_6$(DMPP)$_2$ gives a quantitative yield of [Co(CO$_3$)DMPP]$^-$. This confirms the conclusion reached by analysis of the polarograms [8]. At room temperature, the reaction becomes more complex; we are currently investigating it.

The oxidation of [Co(CO)$_3$DMPP]$^-$ in the presence of DMPP yields, [Co(CO)$_3$(DMPP)$_2$]$^+$ in the case of the oxidation of [Co(CO)$_4$]$^-$. Here again, three mechanisms can be considered.



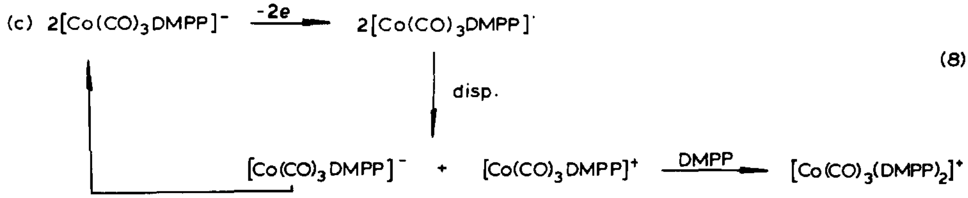
(6)

However, since we have shown that Co$_2$(CO)$_6$(DMPP)$_2$ reacts only slowly with DMPP (1 h at room temperature), and that products other than [Co(CO)$_3$(DMPP)$_2$]$^+$ are formed, we can reject this mechanism.



(7)

Direct removal of an electron from [Co(CO)$_3$DMPP]$^\cdot$ at the same potential as that of the first seems improbable. Furthermore participation of this intermediate 19*e* complex [Co(CO)$_3$(DMPP)$_2$]$^\cdot$ is unlikely. Thus this mechanism cannot satisfactorily account for the results.



(8)

This mechanism is the most probable.

As shown by the voltammograms (cf. Fig. 4), electrolysis along peak B or C yields the same species, which is reoxidized along peak A″, i.e. $[Co(CO)_3DMPP]^-$. Along peak B, we have reaction 9.

$$[Co(CO)_3(DMPP)_2]^+ \xrightarrow[-DMPP]{2e} [Co(CO)_3DMPP]^- \tag{9}$$

Peak C corresponds to the reduction of the dimer (cf. results). Its formation can be explained by reaction 10.

$$[Co(CO)_3(DMPP)_2]^+ + [Co(CO)_3DMPP]^- \xrightarrow[-DMPP]{} Co_2(CO)_6(DMPP)_2 \tag{10}$$

In other words, the anion which is formed in reaction 9 couples with the cation to give the dimer. This mechanism is favoured by the observation that peak C increases relatively to B when the scan rate is decreased, and by the results of the electrolysis at the potential of B, where 1 F is consumed and the dimer is formed.

Acknowledgement

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References

1 (a) Y. Mugnier, C. Moise and E. Laviron, J. Organomet. Chem., 204 (1981) 61; (b) Y. Mugnier, A. Fakhr, M. Fauconet, C. Moise and E. Laviron, Acta Chem. Scand., in press.
2 N.P. Forbus, R. Oteiza, S.G. Smith and T.L. Brown, J. Organomet. Chem., 193 (1980) C71; M. Absi Halabi, J.D. Atwood, N.P. Forbus and T.L. Brown, J. Am. Chem. Soc., 102 (1980) 6248.
3 A.R. Manning, J. Chem. Soc. A, (1968) 1135; W. Hieber and W. Freyer, Chem. Ber., 91 (1960) 492.
4 Inorganic Synthesis, XV, McGraw-Hill, New York, 1972, p. 87.
5 A.A. Vleck, Coll. Czech. Chem. Commun., 24 (1959) 1748; Chem. Listy, 52 (1958) 1460.
6 A. Giraudeau, P. Lemoine, M. Gross and P. Braunstein, J. Organomet. Chem., 202 (1980) 455.
7 R.E. Dessy, R.B. King and M.J. Waldrop, J. Am. Chem. Soc., 88 (1966) 5117.
8 D. de Montauzon and R. Poilblanc, J. Organomet. Chem., 104 (1976) 99.