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ELECTROCHEMICAL SUBSTITUTION OF A CARBONYL GROUP BY A PHOSPHORUS LIGAND IN ARENECHROMIUM TRICARBONYL COMPLEXES

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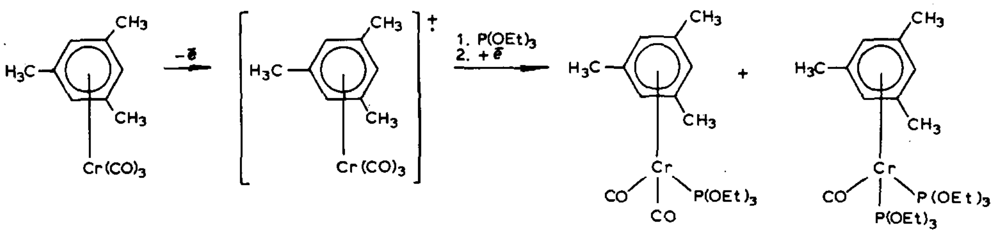
Summary

Electrochemical oxidation of (η-1,3,5-$Me_3C_6H_3$)$Cr(CO)_3$ in the presence of $P(OEt)_3$ with subsequent electrochemical reduction results in the formation of a (η-1,3,5-$Me_3C_6H_3$)$Cr(CO)_2[P(OEt)_3]$ and (η-1,3,5-$Me_3C_6H_3$)$Cr(CO)[P(OEt)_3]_2$ mixture. Under similar conditions (η^6-arene)$Cr(CO)_3$, where arene = 3,5-$Me_2C_6H_3(CH_2)_2OPR_2$ (R = OEt,OPh,F), yields the corresponding arenephosphite chelate complexes.

The substitution of a carbonyl ligand in arenechromium tricarbonyl complexes takes place only under UV irradiation [1]. We have shown that an analogous reaction proceeded also during preparative electrochemical oxidation of these compounds. It was found that the oxidation of I at a Pt electrode in CH_3CN medium in the presence of $P(OEt)_3$ and subsequent reduction resulted in the formation of compounds II and III in a total yield of 26%. The first stage of the electrochemical oxidation of arenechromium tricarbonyl complexes is known to include the abstraction of one electron yielding a cation-radical of type IV [2]. Therefore, the formation of II and III demonstrates the possibility of CO substitution occurring in complex IV, where the positive charge must weaken a Cr–CO bond.



(I) (IV) (II) (III)

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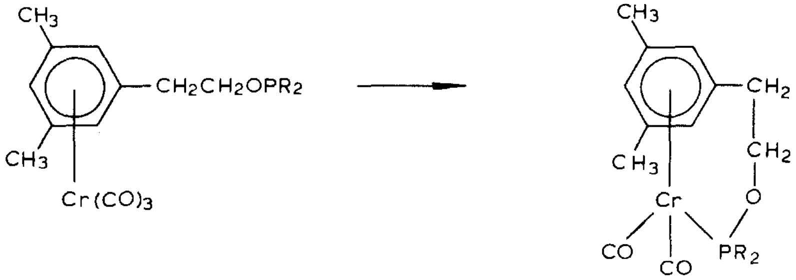
The substitution of CO in $CpMn(CO)_3$ by $P(OEt)_3$ proceeds similarly but with predominant formation of the disubstituted product. Arenechromium tricarbonyl complex Va with a diethylphosphite group in the ω-position of the side chain yields chelate complex VIa under the same conditions.

The examination of other chelate precursors (Vb,c) in this process reveals that the course of the reaction is dependent to a considerable extent on the nature of the phosphite group. Thus the successful substitution of CO in the case of Vb and Vc needs considerably higher potentials while carrying out the electrolysis (see Table 1). Moreover, it is necessary to conduct the electrolysis in the presence of $P(OEt)_3$ in order to obtain VIc. Yields of VIa–VIc are 30–40%.



(Va - Vc)

R = OEt(a), OPh(b), F(c)

(VIa - VIc)

The reasons for the abnormal behaviour of Vb and Vc are not clear. One reason may be the difference in adsorption of these complexes at the Pt electrode. But we cannot exclude also that it is caused by increased electron-withdrawing ability of the phosphite group in Vb and Vc compared to Va, and therefore more ready formation of intramolecular charge-transfer complexes; the latter would result in the increase in oxidation potential. In case of the OPF_2 group this tendency is apparently so high that one has to introduce in addition the more electron-releasing $P(OEt)_3$. At the same time we cannot rule out that triethylphosphite and phosphites with similar electron-releasing properties in general act as reducing agents in these processes, since we have found that quantity of electricity required for the reduction of the cationic products was significantly less than the theoretical value.

The products of electrolysis were isolated from the reaction mixture by preparative TLC on silica gel. The structure of the compounds obtained was confirmed by their IR and mass spectra and by comparison of spectral data and the melting points with those for the previously synthesized complexes VIb and VIc [3]. The yields of

TABLE 1

OXIDATION POTENTIALS OF ARENECHROMIUM TRICARBONYL COMPLEXES (Pt rotating disc electrode, CH_3CN, 0.2 *M* $NaBF_4$)

Compound	$E1/2$ (V)	E_{el} (V)
I	0.82	1.6
Va	0.80	1.6
Vb	> 1.80	2.4
Vc	> 1.80	2.4

electrochemically synthesized II, III and VIa–VIc are similar to those for photochemically obtained compounds.

A few cases of electrochemical substitution of CO ligands by phosphines are described in the literature. This process was observed for metal carbonyls [4,5] and carbonyl clusters [6,7] as well as for a mixture of σ-$CH_3Fe(CO)_2C_5H_5$-π with PPh_3, resulting in the substitution of CO by the phosphine and at the same time in conversion of the σ-methyl complex into a σ-acetyl one.

The data and results reported here present evidence that electrochemical oxidation offers a new general method of substitution of CO ligands by other ligands in transition metal complexes.

References

1 G.L. Geoffroy and M.S. Wrighton, Organometallic Photochemistry. Academic Press New York 1979, p.78.
2 M.K. Lloyd, J.A. McCleverty, J.A. Connor and E.M. Jones, J. Chem. Soc. Dalton Trans., (1973) 1768.
3 a) A.N. Nesmeyanov, V.V. Krivykh, P.V. Petrovskii and M.I. Rybinskaya, Dokl. Akad. Nauk SSSR, 231 (1976) 110; b) A.N. Nesmeyanov, V.V. Krivykh, G.A. Panosyan, P.V. Petrovskii and M.I. Rybinskaya, J. Organomet. Chem., 164 (1979) 167; c) N.I. Vasyukova, Yu.S. Nekrasov, V.V. Krivykh and M.I. Rybinskaya, J. Organomet. Chem., 201 (1980) 283.
4 J. Grobe and H. Zimmermann, Z. Naturforsch., B36 (1981) 482.
5 J. Grobe and H. Zimmermann, Z. Naturforsch., B36 (1981) 301.
6 A. Darchen, C. Mahe and H. Patin, J. Chem. Soc. Chem. Commun., (1982) 243.
7 A. Darchen, C. Mahe and H. Patin, Nouv. J. Chem., 6 (1982) 539.
8 D. Micholova and A.A. Vlcek, J. Organomet. Chem., 240 (1982) 413.