Electrochemical synthesis and properties of σ-fluoroacyl and σ-perfluoroalkyl transition metal complexes

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The electrochemical synthesis of σ-fluoroacyl complexes [M]—σ-COR_f (M = $C_5H_5(CO)_3W$ or $(CO)_5Mn$; R_f = CF_3 or C_4F_9) was performed according to two procedures: (1) the preliminary electrochemical synthesis of $[M]^-$ from $[M]_2$ followed by reaction with a fluorine-containing compound and (2) the electrochemical synthesis of $[M]^-$ in the presence of a fluorine-containing compound. Trifluoroacetic anhydride was demonstrated to be the best acylating agent in these reactions. The electrochemical properties of the resulting complexes were studied.

Key words: cyclic voltammetry, electrochemical synthesis, fluoroacyl transition metal complexes.

The electrochemical introduction of a fluorine-containing group into the molecule of an organic compound can be performed using both anodic and cathodic processes. Anodic processes are generally associated with generation of fluoroalkyl radicals, which can add at multiple bonds or replace H atoms in aromatic compounds. For this purpose, electrooxidation of fluorocarboxylates[1] or anions of perfluoroalkanesulfonic acids[2] is used. However, fluoroalkyl radicals are generated only at high positive potentials, which hinders functionalization of many rather readily oxidized organic substrates. A commonly used procedure for the cathodic synthesis of fluorine-containing aromatic compounds involves the replacement of the Hal atom by the trifluoromethyl group. For this purpose, electroreduction of trifluoromethyl bromide was carried out in the presence of halogen-containing organic compounds in a system with a dissolving copper anode to form CF_3Cu as an active intermediate.[3] A limitation of this procedure is the necessity of using expensive fluoroalkyl halides and halogen-containing organic substrates.

The drawbacks of the above-mentioned electrochemical procedures for the introduction of fluorine-containing substituents into organic compounds gave impetus to a search for new approaches to the solution of this problem. It is known[4] that electrochemical reduction and oxidation of transition metal complexes with σ-bonded ligands proceed generally with the cleavage of the σ bond to form reactive radical or ionic organic intermediates.[4] Based on these data, in the present work we proposed to use σ-fluoroalkyl and fluoroacyl transition metal complexes for electrochemical functionalization of organic substrates (Sub). Their participation in electrochemical fluoroalkylation can be presented by Scheme 1.

The reactions with the participation of a fluorine-containing alkylating reagent through intermediate formation of a σ-alkyl complex [M]—σ-R_f can be described by an analogous scheme.

According to Scheme 1, the σ-complex is formed *in situ* upon electrolysis of a mixture of a fluoroacylating or fluoroalkylating reagent and the initial $[M]_n$ complexes. Metal carbonyl dimeric complexes $[M]_2$ or chelate cobalt complexes with organic ligands (Salen, dimethylglyoxime, *etc.*) can be used as the starting complexes.

Scheme 1

$$[M]_n + ne \longrightarrow n[M]^- \xrightarrow{\text{Fluorine-containing acylating reagent}}$$

$$\longrightarrow [M]\text{—}\sigma\text{-}COR_f \xrightarrow{\pm ne}$$

$$\longrightarrow [M]^- + [R_fCO]^{n-} \text{ (or } R_fCO^{\cdot}) \xrightarrow{SubH,\ -CO} SubR_f$$

Chemical procedures for the synthesis of fluoroacyl and fluoroalkyl transition metal complexes with different ligand environments have been reported previously.[5] However, data on their electrochemical preparation are lacking and the data on the electrochemical properties of fluoroacyl and fluoroalkyl transition metal complexes are scarce. In addition, to perform electrochemical synthesis of fluorine-containing compounds with the use of σ-complexes, it is necessary to know the electrochemical properties of all components of the process represented in Scheme 1, *viz.*, of the initial $[M]_n$ complexes, alkylating and acylating reagents, σ-complexes, and the products of their reduction. In the present work, we studied metal carbonyl σ-perfluoroacyl com-

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plexes by cyclic voltammetry. The electrochemical synthesis of these complexes was carried out in two modes, *viz.*, with the preliminary synthesis of $[M]^-$ and with the simultaneous introduction of the $[M]^-$ anions and an acylating reagent into the reaction.

Results and Discussion

The potentials of the peaks of the compounds under study are given in Table 1. The measurements were carried out in 0.1 *M* Bu_4NBF_4 solutions in THF or MeCN with the use of a glassy-carbon cathode. Under these conditions, reduction of the $[M]_2$ dimers (M = $C_5H_5(CO)_3W$ or $(CO)_5Mn$) proceeded in one irreversible two-electron stage at close potentials. The $[M]^-$ anions that formed were oxidized at −0.03 V ($[W]^-$) and −0.1 V ($[Mn]^-$). The reduction potentials of fluoroorganic compounds **5**—**11** are in the range from −1.90 to −2.50 V, whereas perfluoroacyl chlorides **3** and **4** are reduced at potentials close to the reduction potentials of dimers **1** and **2**. This should impair the process shown in Scheme 1. In addition, it was found that under the experimental conditions, compounds **3** and **4** were rapidly hydrolyzed. As a result, the peaks in the cyclic voltammograms at −1.42 and −1.30 V disappeared and only a reduction peak of the corresponding acid was observed. It is known that the latter can react with $[M]^-$ anions to form [M]—H hydrides. The reduction potentials of other fluorine-containing compounds (**6**—**11**), which can act as alkylating and acylating reagents, meet the requirements of Scheme 1. However, according to the data of cyclic voltammetry, only trifluoroacetic anhydride reacts with $[M]^-$ at a noticeable rate to form σ-derivatives. The cyclic voltammograms for a solution of $[M]_2$ before and after addition of $(CF_3CO)_2O$ are shown in Fig. 1. It can be seen that a new cathodic peak appears at more negative potentials in the region corresponding to reduction potentials of σ-derivatives and the oxidation peak of $[M]^-$ disappears. After addition of compound **6** or **8**—**11** to solutions of $[M]_2$, no new peaks in the cyclic voltammograms were observed. Based on our results, it can be concluded that $(CF_3CO)_2O$, which we used in the electrochemical syntheses, is the best acylating agent of all the reagents under study.

Table 1. Potentials of the peaks for the transition metal complexes and fluoroorganic compounds

Compound	$-E_p^{ox}$/V		E_p^{red}/V
	THF	MeCN	MeCN
$[C_5H_5(CO)_3W]_2$ (**1**)		1.25	−0.03 (for $[W]^-$)
$[(CO)_5Mn]_2$ (**2**)		1.25	−0.1 (for $[Mn]^-$)
C_3F_7COCl (**3**)		1.42	
C_4F_9COCl (**4**)	1.30		
C_4F_9COOH (**5**)	2.25		
$CF_3COOC_2H_5$ (**6**)	2.50		
$(CF_3CO)_2O$ (**7**)		1.90	
$(CF_3)_2CFCF_2CF{=}CF_2$ (**8**)		1.42	
$(CF_3)_2CFCF{=}CFCF_3$ (**9**)		2.2	
$CF_3CF{=}CF_2$ (**10**)		2.3	
Perfluoromethyl-cyclopentene-1 (**11**)		1.98	
$C_5H_5(CO)_3W{-}COCF_3$ (**12**)		1.61	1.51
$(CO)_5Mn{-}COCF_3$ (**13**)		1.75	>1.80

Note. Experimental conditions: 0.1 *M* Bu_4NBF_4, a glassy-carbon electrode, S = 1 mm^2, relative to a saturated calomel electrode, 200 mV s^{-1}.

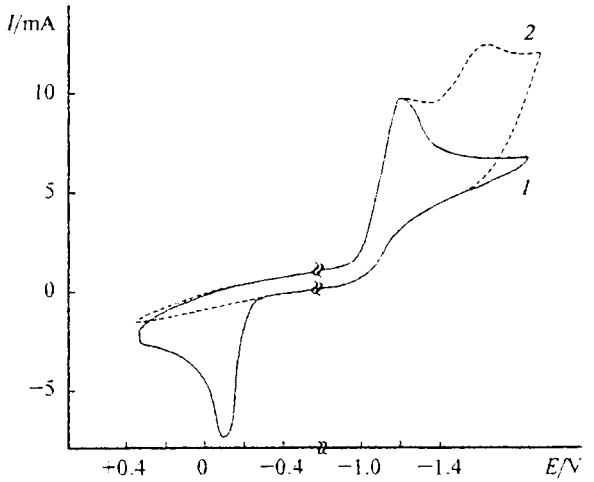

Fig. 1. Cyclic voltammograms for $[C_5H_5(CO)_3W]_2$ ($C = 2 \cdot 10^{-3}$ mol L^{-1}; acetonitrile; 0.1 *M* Bu_4NBF_4; glassy-carbon cathode; 200 mV s^{-1}) (*1*) and in the presence of $(CF_3CO)_2O$ (*2*).

The acyl complexes were prepared according to two procedures, *viz.*, either by the electrochemical synthesis of the $[M]^-$ anions from $[M]_2$ followed by the introduction of $(CF_3CO)_2O$ into the reaction or by the electrochemical synthesis of the $[M]^-$ anions in the presence of $(CF_3CO)_2O$ (see Scheme 1). The course of these processes was controlled by cyclic voltammetry. It was found that after electrolysis at the reduction potential of $[M]_2$, its reduction peak (−1.25 V) disappeared, and the formation of $[M]^-$ was confirmed by the appearance of the anodic peak of its oxidation. The addition of $(CF_3CO)_2O$ to the resulting solution led to the disappearance of the oxidation peak of $[M]^-$. At the same time, a large excess of $(CF_3CO)_2O$ hindered the detection of a new peak (in the potential region, which is expected based on the data of cyclic voltammetry) corresponding to reduction of the acyl complex that formed. In both cases, electrolysis was carried out in an undivided cell with the use of a Zn dissolving anode. The $(CO)_5Mn{-}COC_4F_9$ complex was prepared also with the use of a Li dissolving anode (in THF). The yields of the acyl complexes obtained with the use of R_fCOCl were always substantially lower (26%) than those obtained with the use of $(CF_3CO)_2O$ (60—70%).

The resulting acyl complexes can undergo both electrochemical reduction and oxidation. Reduction proceeds in one irreversible one-electron stage. The

fluoroacyl radical and the $[M]^-$ anion are possible primary reduction products. Oxidation of the complexes proceeded in one two-electron irreversible stage also, apparently, with the cleavage of the metal—carbon bond. It was also noted that the σ-acyl manganese complex $[Mn(CO)_5]$—σ-$COCF_3$ underwent decarbonylation upon heating in a solution to form the corresponding fluoroalkyl complex, which was reduced at more negative potentials (−2.20 V) than the fluoroacyl complex (−1.87 V).

Experimental

The cyclic voltammograms were measured with the use of a PI-50-1 potentiostat. Electrolysis was carried out at a controlled potential using a P-5827 potentiostat. The IR spectra were recorded on a UR-20 instrument.

Electrochemical synthesis of σ-fluoroacyl complexes $C_5H_5(CO)_3W$—σ-$COCF_3$ (12). *A.* The $[C_5H_5(CO)_3W]_2$ complex (**1**) (0.1 g) in a 0.1 *M* Bu_4NBr solution in anhydrous acetonitrile (50 mL) was placed into an undivided cell containing a Pt cathode, a Zn anode, and a saturated calomel electrode. Electrolysis was carried out at −1.40 V for 60 min, during which the initial current of 50 mA smoothly decreased to 1 mA. The quantity of electricity passed (Q_{exp}) was 29.7 C, which corresponds to the addition of two electrons (Q_{theor} = 28.9 C). An excess of $(CF_3CO)_2O$ (1.41 g, 1 mL) was added to the solution obtained after electrolysis. The mixture was stirred for 10 min, poured into water, and extracted with benzene. The extract was washed with water and dried with $MgSO_4$. After evaporation of benzene *in vacuo* and separation of the reaction mixture on a column with SiO_2 (benzene as the eluent), compounds **1** and **12** were isolated in yields of 0.02 and 0.09 g (69%), respectively. IR, $\nu(CO)/cm^{-1}$ (in CH_2CL_2) : (CH_2Cl_2) 2040, 1942, 1634.

Electrolysis, which was performed under analogous conditions but with the use of C_3F_7COCl instead of $(CF_3CO)_2O$, afforded compound **13** in 26% yield.

B. Electrolysis was performed analogously to method *A* but with the use of $(CF_3CO)_2O$ (4.23 g). The reaction solution containing dimer **1** and $(CF_3CO)_2O$ was placed into a cell before electrolysis. The initial current of 120 mA remained unchanged in the course of electrolysis for 60 min. Then the current was smoothly decreased to 80 mA. Electrolysis was carried out until compound **2** disappeared. The course of the reaction was monitored by TLC on SiO_2. After treatment of the resulting solution (see method *A*), compound **12** was isolated in a yield of 0.087 g (67%). IR, $\nu(CO)/cm^{-1}$ (in CH_2Cl_2): 2041, 1942, 1634.

C. Electrolysis of $[(CO)_5Mn]_2$ (0.2 g) in the absence and in the presence of $(CF_3CO)_2O$ was carried out as described in methods *A* and *B* at a potential of −1.40 V; **13** was obtained in a yield of 0.21 g (70%). IR (cyclohexane), $\nu(CO)/cm^{-1}$: 2150, 2040, 1625.

D. Electrolysis of $[(CO)_5Mn]_2$ (0.2 g) was carried out in a 0.2 *M* Bu_4NBF_4 solution with the use of a Li anode and a Pt cathode in the direct current mode (10 mA) using an undivided cell. The $[(CO)_5Mn]_2$ complex was completely reduced to the $[(CO)_5Mn]^-$ anion during 32 min (control by cyclic voltammetry). An excess of C_4F_9COCl was added to the resulting solution and the mixture was stirred for 30 min. After distillation of the solvent, the residue was washed three times with benzene. After evaporation of benzene in a vacuum of a water-jet pump, $(CO)_5Mn$—COC_4F_9 was obtained from an oily residue by vacuum distillation at 58—60 °C in a yield of 0.1 g (23%).

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