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# Synthesis of Bis($\eta^5$-cyclopentadienyldicarbonyliron)stannane Dichloride by Direct Oxidation of Tin and Reaction of This Compound and Its Analogs with Magnesium

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**Abstract**—A procedure was developed for preparing $[\mathrm{Cp(CO)_2Fe}]_2\mathrm{SnCl_2}$ by direct oxidation of tin with $\eta^5$-cyclopentadienyldicarbonyliron chloride in polar solvents. The reaction kinetics was studied, and its scheme was suggested. Products of the reaction of magnesium with compounds $\mathrm{R_2SnCl_2}$ [R = $\mathrm{Cp(CO)_3Mo}$, $\mathrm{Cp(CO)_3W}$, $\mathrm{Cp(CO)_2Fe}$] were identified. The reaction mechanism was discussed.

In [1], we reported on preparation of compounds $[\mathrm{Cp(CO)_3M}]_2\mathrm{SnCl_2}$ (M = Mo, W) in high yield by oxidation of tin with $\mathrm{Cp(CO)_3MCl}$ in polar solvents. In this work, using $\mathrm{Cp(CO)_2FeCl}$ (**I**) as oxidant, we prepared by a similar procedure $[\mathrm{Cp(CO)_2Fe}]_2\mathrm{SnCl_2}$ (**II**). As solvents we used DMF, DMSO, and THF.

Gentle heating (313 K) of a solution of **I** ($C^0$ 0.15 M) for 20 h under stirring (120 rpm) with a tenfold (relative to the oxidant) excess of tin chips gives $[\mathrm{Cp(CO)_2Fe}]_2\mathrm{SnCl_2}$. Its yield per 2 mol of the oxidant was 0.89, 0.70, and 0.49 mol of the crude product in DMF, DMSO, and THF, respectively. After twofold recrystallization of the products from benzene–heptane (1 : 2 by volume), we obtained yellow-orange needle-shaped crystals with mp 167.95°C; according to [2], the melting point of **II** is 168°C. Found, %: Cl 16.72; Fe 26.48; Sn 28.14. $\mathrm{C_{14}H_{10}Cl_2Fe_2O_4Sn}$. Calculated, %: Cl 16.79; Fe 26.44; Sn 28.10. The IR spectrum of **II** (absorption bands at 2027, 2002, 1978, 1958 $\mathrm{cm^{-1}}$) virtually coincides with the IR spectrum (2026, 2000, 1975, 1956 $\mathrm{cm^{-1}}$) of the sample of $[\mathrm{Cp(CO)_2Fe}]_2\mathrm{SnCl_2}$ prepared from $[\mathrm{Cp(CO)_2Fe}]_2$ and $\mathrm{SnCl_2}$ [3].

The kinetics of tin oxidation with **I** was studied in DMF and its mixtures with *p*-xylene. The kinetic curves (Figs. 1, 2) show that, at the initial oxidant concentration $C^0 \le 0.25$ M, the reaction can be described by the Langmuir–Hinshelwood scheme for the case of adsorption of reactants on similar active centers of the metal surface [4]:

$$\mathrm{Ox} + \mathrm{S} \overset{K^{\mathrm{Ox}}_{\mathrm{ads}}}{\rightleftarrows} \mathrm{Ox\cdot S}, \qquad (1)$$

$$\mathrm{L} + \mathrm{S} \overset{K^{\mathrm{L}}_{\mathrm{ads}}}{\rightleftarrows} \mathrm{L\cdot S}, \qquad (2)$$

$$\mathrm{Ox\cdot S} + \mathrm{L\cdot S} \xrightarrow{k} \text{Products}. \qquad (3)$$

Here $K^{\mathrm{ox}}_{\mathrm{ads}}$ and $K^{\mathrm{L}}_{\mathrm{ads}}$ are the equilibrium constants of adsorption of the oxidant and ligand, respectively, on the solid phase surface. For a process following scheme (1)–(3), the kinetic equation has the form

$$V = k'\frac{K^{\mathrm{Ox}}_{\mathrm{ads}}[\mathrm{Ox}]K^{\mathrm{L}}_{\mathrm{ads}}[\mathrm{L}]}{(1 + K^{\mathrm{Ox}}_{\mathrm{ads}}[\mathrm{Ox}] + K^{\mathrm{L}}_{\mathrm{ads}}[\mathrm{L}])^2}. \qquad (4)$$

Here $k' = kS_0^2$; $S_0$ is the number of active centers per unit surface area.

Treatment of the experimental data in the coordinates $(C_{\mathrm{ox}}/V)^{1/2} = f(C_{\mathrm{ox}})$ at $C_{\mathrm{L}}$ = const and $(C_{\mathrm{Ox}}/V)^{1/2} = f(C_{\mathrm{L}})$ at $C_{\mathrm{Ox}}$ = const, followed by combined solution of the equations obtained, allowed calculation of the apparent rate constants of the process and equilibrium constant of adsorption of the reactants on the metal surface; from the temperature dependences of these quantities, we calculated the apparent activation energy of the reaction and the enthalpy and entropy of adsorption of the oxidant and ligand (Table 1).

Figure 1 shows that the curve of the reaction rate vs. oxidant concentration consists of two ascending portions separated by an inflection. This may be due to formation of the reaction product by different possible pathways. At the initial concentrations of **I** lower than 0.25 M, the intermediate $\mathrm{Cp(CO)_2FeSnCl}$ passes into solution, where it reacts with the second oxidant molecule:

$$\mathrm{Cp(CO)_2FeSnCl} + \mathrm{Cp(CO)_2FeCl} \longrightarrow [\mathrm{Cp(CO)_2Fe}]_2\mathrm{SnCl_2}. \qquad (5)$$

An increase in the rate of the heterogeneous reaction with an increase in the initial oxidant concentra-

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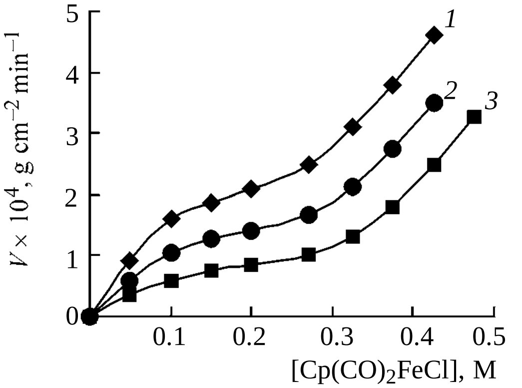

**Fig. 1.** Rate of tin oxidation with $Cp(CO)_2FeCl$ in DMF as a function of the oxidant concentration. $C^0_{DMF}$ 12.9 M. Temperature, K: (*1*) 333, (*2*) 323, and (*3*) 313.

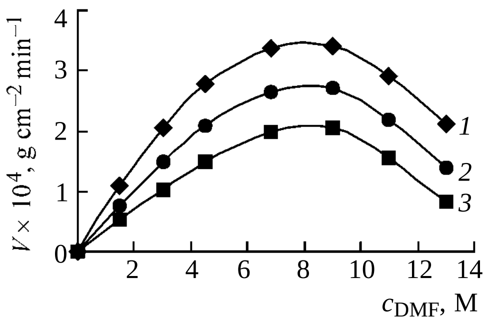

**Fig. 2.** Rate of tin oxidation in the system $Cp(CO)_2FeCl$–DMF–*p*-xylene. Initial $Cp(CO)_2FeCl$ concentration 0.2 M. Temperature, K: (*1*) 333, (*2*) 323, and (*3*) 313.

tion, after all the active centers of the surface are filled, is due to the bimolecular process involving attack of an active center with an adsorbed molecule of **I** by a similar molecule from the bulk of solution:

$$Cp(CO)_2FeCl + \frac{Cp(CO)_2Fe\cdots Cl}{/////\ Sn\ /////} \longrightarrow [Cp(CO)_2Fe]_2SnCl_2. \quad (6)$$

A similar pattern was observed in oxidation of magnesium with halogenated hydrocarbons in mixtures of benzene with diethyl ether [5] and in reaction of magnesium with triphenylchlorostannane in THF [6]. The following fact, however, should be taken into account. In the reactions studied in [5, 6], the oxidant and ligand are adsorbed on active centers differing in nature. In these systems, the ligand molecules cannot significantly compete with the oxidant molecules for the active centers of the metal surface even if the adsorption occurred on similar centers, since the adsorption constants of ethers are very low. In the system Sn–$Cp(CO)_2FeCl$–DMF the pattern is quite different: The reactant molecules are adsorbed on the similar centers, and the ligand molecules significantly compete with the oxidant molecules. This fact does not allow description of the kinetic curves in Fig. 1 by a single kinetic equation throughout the oxidant concentration range studied.

In accordance with [7], the $Cp(CO)_2Fe$ fragment is appreciably less electronegative than the $Cp(CO)_3Mo$ fragment. This fact, apparently, explains why the rate constant of tin oxidation with **I** in DMF at 323 K is by a factor of ~150 higher compared to the tin oxidation with $Cp(CO)_3MoCl$ under the same conditions. The curve of the rate of the tin oxidation vs. initial concentration of $\eta^5$-cyclopentadienyltricarbonylmolybdenum does not contain the second ascending portion which should be observed at the oxidant concentration exceeding 0.5 M [1].

Reduction of dichlorides of dialkyl and diaryl tin derivatives is a route to cyclic and linear oligomeric stannylenes [8]. Further oxidation of these compounds yields effective catalysts for polyurethane synthesis [9].

To assess the suitability of compounds $R_2SnCl_2$ [R = $Cp(CO)_3Mo$ (**III**), $Cp(CO)_3W$ (**IV**), $Cp(CO)_2Fe$] as starting compounds for such processes, we studied their reduction with magnesium in THF.

A solution of $R_2SnCl_2$ ($C^0$ 0.15 M) in THF was kept over magnesium turnings, taken in a tenfold ex-

**Table 1.** Apparent rate constants and activation energy of the reaction of $Cp(CO)_2FeCl$ with DMF and the equilibrium constants, enthalpies, and entropies of adsorption of the reactants

| $T$, K | $K^{Ox}_{ads}$ | $K^{L}_{ads}$ | $-\Delta H^{Ox}_{ads}$, kJ mol$^{-1}$ | $-\Delta S^{Ox}_{ads}$, J mol$^{-1}$ K$^{-1}$ | $-\Delta H^{L}_{ads}$, kJ mol$^{-1}$ | $-\Delta S^{L}_{ads}$, J mol$^{-1}$ K$^{-1}$ | $k \times 10^3$, g cm$^{-2}$ min$^{-1}$ | $E$, kJ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| 313 | 15.5 | 0.92 | 11±4 | 13±6 | 21±6 | 73±17 | 0.92 | 28±4 |
| 323 | 12.6 | 0.37 | | | | | 1.29 | |
| 333 | 12.0 | 0.26 | | | | | 1.43 | |

**Table 2.** Products of magnesium oxidation with $R_2SnCl_2$ ($C^0$ 0.15 M) in THF at 293 K

| Oxidant $R_2SnCl_2$ | Yield, mole per mole of oxidant | | | |
|---|---|---|---|---|
| | Sn | $Cp(CO)_nMMgCl$[a] | $[Cp(CO)_nM]_2Mg$[a] | $MgCl_2$ |
| $[Cp(CO)_2Fe]_2SnCl_2$ | 0.98 | 1.67 | 0.15 | 0.14 |
| $[Cp(CO)_3Mo]_2SnCl_2$ | 0.97 | 1.88 | 0.04 | 0.05 |
| $[Cp(CO)_3W]_2SnCl_2$ | 0.98 | 1.93 | 0.03 | 0.03 |

[a] $n = 2$, M = Fe; $n = 3$, M = Mo, W.

cess relative to the oxidant and preactivated with dibromoethane at 323 K, for 48 h under stirring with a magnetic stirrer at 120 rpm. In the process, the mixture changed color from yellow to dark brown, and a black precipitate of tin and a white precipitate very poorly soluble in THF formed.

The weight loss of magnesium after the reaction completion was 1.98 mol per mole of the starting oxidant. The amount of tin precipitated by the end of the reaction virtually corresponded to its content in the starting mixture (0.98 mol per mole of $R_2SnCl_2$).

The yield of the white precipitate per mole of the starting oxidant depends on the structure of the organometallic fragment bound to tin and decreases in the order $Cp(CO)_2Fe > Cp(CO)_3Mo > Cp(CO)_3W$.

The ratio of manesium and transition metal (Fe, Mo, W) in the white precipitate is 1 : 2, suggesting its formula $R_2Mg$. This assumption is confirmed by the following facts. The precipitates gradually dissolve on contact with a concentrated solution of $MgCl_2$ in THF; they are readily soluble in pyridine. The products containing Fe, Mo, and W melt with decomposition at 423, 433, and 458 K, respectively, which is consistent with the data given for $R_2Mg$ in [10, 11]. The yields of products of magnesium oxidation with **II**–**IV** are listed in Table 2.

Sisisdo and Kozima [12] suggest intermediate formation of compounds containing an Sn–M group (M = Mg) in oxidation of Mg with dibenzyltin dichloride. A similar process, apparently, takes place in the reaction of Mg with $R_2SnCl_2$:

$$\mathrm{R_2SnCl_2 + Mg \longrightarrow R_2Sn(Cl){-}MgCl}, \tag{7}$$

$$\mathrm{R_2Sn(Cl){-}MgCl \longrightarrow RSnCl + RMgCl}, \tag{8}$$

$$\mathrm{RSnCl}\begin{cases} \longrightarrow \mathrm{RSnMgCl} \longrightarrow \mathrm{Sn + RMgCl}, & (9) \\ \longrightarrow \mathrm{Sn + RCl}. & (10) \end{cases}$$

RCl, in accordance with [10, 11], fairly readily reacts with Mg:

$$\mathrm{RCl + Mg \longrightarrow RMgCl}, \tag{11}$$

$$\mathrm{2RMgCl \rightleftarrows R_2Mg + MgCl_2}. \tag{12}$$

## EXPERIMENTAL

Magnesium wire (0.5 mm in diameter) and magnesium turnings [MCh-1, GOST (State Standard) 804–86] containing 99.92% main substance were used without additional treatment. $[Cp(CO)_3Mo]_2SnCl_2$ and $[Cp(CO)_3W]_2SnCl_2$ were prepared as described in [1]. $Cp(CO)_2FeCl$ was prepared according to [13]. The main substance content in these compound, as determined by analysis for Mo, W, Fe, Sn, and Cl, was no less than 99.5% [14]. The physicochemical constants of the compounds were consistent with published data.

The solvents were purified and dried by standard procedures [15]. Syntheses of the organometallic compounds and manipulations with them were performed in an atmosphere of dry oxygen-free Ar or in a vacuum. Liquid mixtures were degassed by repeated freeze–pump–thaw cycles.

The reaction kinetics was studied by a resistometric procedure [16] modified for experiments with readily oxidizable and hydrolyzable compounds.

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