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Synthesis of Bis(tricarbonylcyclopentadienylmolybdenum)-bismuth(III) Chloride and Its Reaction with Metals

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Abstract—Polynuclear organometallic compounds $[CpMo(CO)_3]_2BiCl$ and $[CpMo(CO)_3]BiCl_2$ were prepared by reaction of bismuth with tricarbonylcyclopentadienylmolybdenum chloride in dimethyl sulfoxide (DMSO). $[CpMo(CO)_3]_2BiCl$ is reduced with magnesium or indium in tetrahydrofuran to give bismuth, $[CpMo(CO)_3]_3Bi$, and magnesium or indium chloride. In the presence of DMSO, the reaction of $[CpMo(CO)_3]_2BiCl$ with magnesium or indium yields bismuth and the organomolybdenum derivative of magnesium or lithium, respectively.

Synthesis of organometallic compounds by direct oxidation of metals with halohydrocarbons readily occurs with Group II elements [1, 2]. With tricarbonylcyclopentadienylmolybdenum (**I**) or -tungsten chloride as oxidant, it is feasible to prepare in donor solvents under mild conditions polynuclear organometallic derivatives of not only magnesium [3], zinc, and cadmium [4], but also tin [5] and indium [6].

Antimony does not react with **I** in dimethylformamide, dimethyl sulfoxide (DMSO), and pyridine, whereas bismuth reacts with $CpMo(CO)_3Cl$ in these solvents. The highest reaction rate was observed in DMSO. At 323 K, at a fourfold molar excess of the metal powder relative to the oxidant ($C_\mathbf{I}$ 0.2 M), the reaction is complete in ~50 h. The color of the reaction mixture changes from red to dark green. Three moles of the oxidant is consumed per 2 mol of the metal. After removal of the unchanged bismuth, the solvent was removed, and the oily residue was extracted with diethyl ether. From the extract, a green compound sensitive to atmospheric oxygen and moisture was isolated. It was identified as $[CpMo(CO)_3]_2 \cdot BiCl$ (**II**): decomposition point 89°C; ν_{CO} 2050, 2010, 1980, 1910 cm^{-1} (published data [7]: ν_{CO} 2051, 2010, 1978, 1912 cm^{-1}). Found, %: Bi 28.0; Cl 4.6; Mo 25.7. $C_{16}H_{10}BiClMo_2O_6$. Calculated, %: Bi 28.5; Cl 4.8; Mo 26.1. The residue insoluble in ether was treated with tetrahydrofuran (THF). Treatment of the resulting solution with heptane resulted in precipitation of an orange substance identified as $[CpMo(CO)_3] \cdot BiCl_2$ (**III**): decomposition point 111°C; ν_{CO} 2005, 1925 cm^{-1} (published data [7]: ν_{CO} 2007, 1927 cm^{-1}). Found, %: Bi 39.8; Cl 13.5; Mo 18.3. $C_8H_5BiCl_2 \cdot MoO_3$. Calculated, %: Bi 39.5; Cl 13.1; Mo 18.0. Thus, the reaction of bismuth with **I** is described by Eq. (1):

$$3CpMo(CO)_3Cl + 2Bi \longrightarrow [CpMo(CO)_3]_2BiCl + [CpMo(CO)_3]BiCl_2. \quad (1)$$

The yield of **II** and **III** is 0.3 mol each per mole of **I**.

When a solution of **II** in diethyl ether is cooled below 157 K, its color changes from dark green to red. This may be due to the fact that equilibrium (2), shifted at room temperature toward formation of $[CpMo(CO)_3]_2BiCl$ [7], shifts to the right.

$$3[CpMo(CO)_3]_2BiCl \rightleftarrows 2[CpMo(CO)_3]_3Bi + BiCl_3. \quad (2)$$

Compound **II** is of particular interest for preparing polynuclear organometallic compounds by direct oxidation of metals with RX compounds, where R is an organometallic fragment and X is a halogen. In this connection, we studied some reactions of $[CpMo \cdot (CO)_3]_2BiCl$ with metals.

Compound **II** vigorously reacts with magnesium and indium in THF. At a fourfold excess of metal turnings relative to the oxidant ($C_\mathbf{II}$ 0.03 M) and 293 K, the reaction is complete in 30 min. The color of the reaction mixture changes from dark green to red, and a black precipitate forms. The precipitate was identified as metallic bismuth by the melting point (271.3°C; published data [8]: 271.3°C) and qualitative reactions [9]. From the solution, we isolated the compound $[CpMo(CO)_3]_3Bi$ (**IV**), which was characterized by IR spectroscopy (ν_{CO} 2005, 1965, 1930, 1895 cm^{-1}; published data [7]: ν_{CO} 2004, 1966, 1929, 1896 cm^{-1}) and elemental analysis (found, %: Bi 22.6; Mo 30.1. $C_{24}H_{15}BiMo_3O_9$. Calculated, %: Bi 22.1; Mo 30.5). Compound **II** and magnesium react in a 2 : 1 ratio; with indium, this ratio is 3 : 1. Thus, the reaction equation is as follows:

$$n[CpMo(CO)_3]_2BiCl + M \longrightarrow 2/3\,n[CpMo(CO)_3]_3Bi + (n - 2/3\,n)Bi + MCl_n, \quad (3)$$

$$M = Mg,\ n = 2;\ M = In,\ n = 3.$$

Let us consider the scheme of reaction (3) in detail. According to [3, 10], organometallic halides react with magnesium to give analogs of Grignard reagents:

$$R^mCl + Mg \longrightarrow R^mMgCl, \quad (4)$$

where R^m is an organometallic fragment.

According to [10], R^mMgCl can react with a second R^mCl molecule to give a symmetrical derivative:

$$R^mCl + R^mMgCl \longrightarrow R^m_2 + MgCl_2. \quad (5)$$

Reduction of **II** with sodium naphthalenide also yields compound **IV** and bismuth. Apparently, unstable polynuclear dibismuthine arising in the first step disproportionates by scheme (6) suggested previously for tetraphenyldibismuthine [11]:

$$3\{[CpMo(CO)_3]_2Bi\}_2 \longrightarrow 4[CpMo(CO)_3]_3Bi + 2Bi. \quad (6)$$

When the reactions of **II** with magnesium and indium are performed in a mixed solvent (THF–DMSO), a new pathway arises. At a low DMSO content (THF : DMSO = 5 : 1), the color of the reaction mixture changes from green to red and then gradually disappears. At a higher DMSO content (THF : DMSO = 1 : 1), the red coloration does not appear at all, and the initial green solution decolorizes.

The ratio of the reacted metal and oxidant is in this case 3 : 2 for magnesium and 1 : 1 for indium. The reaction products contain bismuth in the amount of 1 mol per mole of **II**. Treatment of the liquid phase with $HgCl_2$ yields $CpMo(CO)_3HgCl$. The organomolybdenummercury derivative was isolated in the amount of 2 mol per mole of reacted **II** and identified by comparing its melting point and IR spectrum with the published data (mp 190°C dec.; ν_{CO} 2024, 1954, 1936 cm^{-1} [12]). Formation of $CpMo(CO)_3HgCl$ proves, by analogy with [3, 6], the presence in the reaction mixture of compounds containing $CpMo(CO)_3$ bound to magnesium or indium. Thus, reaction of **II** with bismuth in a mixed solvent follows scheme (7):

$$n[CpMo(CO)_3]_2BiCl + 3M \longrightarrow 2[CpMo(CO)_3]_nM + nBi + MCl_n, \quad (7)$$

$$M = Mg,\ n = 2;\ M = In,\ n = 3.$$

Such a reaction pattern can be explained as follows. At a low DMSO content, the reaction follows two parallel pathways: that described by Eq. (3) and metal interchange of polynuclear bismuth derivatives with magnesium or indium. At a high DMSO content, the rate of the metal interchange exceeds that of formation of **IV**.

EXPERIMENTAL

The IR spectra were taken on an IKS-29 spectrophotometer.

All manipulations with organometallic compounds were performed in an inert atmosphere.

In the study, we used Bi of pure grade, TU (Technical Specifications) 3153-54; Mg of MCh-1 grade, GOST (State Standard) 804–56; and In of IN-8 grade, GOST 10297–75. Compound **I** was prepared as described in [13]; it contained no less than 99% main substance, according to analysis for chlorine [9] and molybdenum [14]. Organic solvents (chemically pure grade) were dried by common procedures [15].

Polynuclear organometallic compounds were mineralized according to [16]. Analysis for chlorine, magnesium, indium, bismuth [9], and molybdenum [14] was performed by common procedures.

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