THE OXIDATION OF GALLIUM BY BIS-(η^5 -CYCLOPENTADIENYLTRICARBONYLMOLYBDENUM) BISMUTH CHLORIDE

Stanislav V. Maslennikov*, Irina V. Spirina, Elena V. Malysheva and Irina V. Zhdanovich

Chemistry Research Institute at Nizhny Novgorod State University, 23/5 Gagarin av.,
603600 Nizhny Novgorod, Russia <masv@uic.nnov.ru>

ABSTRACT

Bis-(η^5 -cyclopentadienyltricarbonylmolybdenum) bismuth chloride reacts with gallium metal in THF, DMSO and their mixture forming in the first stage of interaction tris-(η^5 -cyclopentadienyltricarbonylmolybdenum)bismuth, metallic bismuth and gallium chloride. Further reaction leads to the formation of tris-(η^5 -cyclopentadienyltricarbonylmolybdenum)gallium. Magnesium and indium also react with tris-(η^5 -cyclopentadienyltricarbonylmolybdenum)bismuth forming tris-(η^5 -cyclopentadienyltricarbonylmolybdenum)magnesium and tris-(η^5 -cyclopentadienyltricarbonylmolybdenum)-indium correspondingly. Introducing DMSO in the reaction mixture significantly accelerates the rate of reaction.

INTRODUCTION

According to [1,2], cyclopentadienyltricarbonyl molybdenum chloride and cyclopentadienyl tricarbonyl tungsten chloride oxidize zinc, cadmium and lead in polar solvents forming polyorganometallic compounds. The goal of the present work is to synthesize polyorganometallic compounds by reacting gallium with bis-(η^5 -cyclopentadienyltricarbonylmolybdenum)bismuth chloride (I) in THF, DMSO and their mixture.

MATERIALS AND METHODS

All operations were carried out under vacuum or in the atmosphere of anhydrous and oxygen-free argon. Solvents used for the reactions (THF and DMSO) were purified and dried as described in [3]. Ga (99.999% purity), In (99.998% purity) and Mg (99.92% purity) were used for the experiments.

Bis-(η^5 -cyclopentadienyltricarbonylmolybdenum)bismuth chloride and tris-(η^5 -cyclopentadienyltricarbonylmolybdenum)bismuth were prepared by the method described in [4]. The purity of the obtained compounds according to the analysis on molybdenum [5], bismuth and chlorine [6] was not less than 98%. Gallium content in the products of the reaction was determined according to [7]. Mineralization of the polynuclear organometallic compounds was performed according to [8]. IR spectra were recorded on an IKS-29 spectrometer in CHCl_3 solution in 0.5-1.0 mm NaCl cells.

RESULTS AND DISCUSSION

The green solution of (I) in THF ($C_I=0.1$ mole/l) was added to a tenfold excess of gallium metal. After 12 hours of reaction at 313 K the solution became intense red and black powder precipitated from the reaction mixture. The powder was separated from the liquid phase and washed with water in order to extract gallium chloride. The content of bismuth in the precipitate was 0.32 mole per one mole of (I). In the liquid phase combined with water that was used for washing the precipitate, the ratio of Mo, Bi, Ga and Cl turned out to be 6.04: 2.02: 0.98: 2.96.

In the IR spectrum of the liquid phase there are bands corresponding to $\nu_{\text{CO}} = 2005 \text{ cm}^{-1}$, 1965 cm^{-1} , 1930 cm^{-1} and 1893 cm^{-1} . These numbers nearly coincide with the frequencies of the carbonyl group stretches in tris-(η^5 -cyclopentadienyltricarbonylmolybdenum)bismuth (II): $\nu_{\text{CO}} = 2004 \text{ cm}^{-1}$, 1965 cm^{-1} , 1929 cm^{-1} and 1896 cm^{-1} [4].

Thus, the first stage of the interaction of gallium metal with the solution of (I) in THF may be described by the equation (1):

The yield of (II) and GaCl_3 with respect to 1 mole of (I) is 0.61 and 0.34 correspondingly.

If the mixture of (I) with gallium in THF was allowed to react for a longer time than 12 hours the red color of the solution was gradually losing its intensity and in 40 hours after the beginning of the reaction became pale-yellow. Simultaneously additional formation of the black precipitate was observed. Thus, the compound (II) formed during the interaction of (I) with gallium undergoes further transformation. The analysis of the liquid phase combined with water that was used for washing the precipitate gave the ratio of Mo, Bi, Ga and Cl to be 6.09: 0.0: 2.98: 2.96. The results of the analysis show that (II) interacts with gallium

metal according to the equation (2), forming tris-(η^5 -cyclopentadienyltricarbonylmolybdenum)gallium (III):

The yields of (III) and GaCl_3 per one mole of (I) are 0.64 and 0.34 correspondingly. In the precipitate the amount of bismuth was found to be 0.99 mole per one mole of (I) introduced in the reaction.

It's worthwhile to note that at 313 K and $C_I=0.1$ mole/l the interaction between Ga and (I) in the DMSO or in the equimolar mixture of DMSO and THF proceeds with a much higher rate and is complete within 0.5 hour and 1.5 hour correspondingly.

The oxidation of gallium, indium and magnesium also occurs when these metals are introduced in the solution of (II) ($C_{II}=0.1$ mole/l in the equimolar mixture of THF and DMSO, tenfold excess of metal with respect to (II)). The interaction leads to the nearly quantitative formation of bismuth and η^5 -cyclopentadienyltricarbonylmolybdenum derivative of the corresponding metal (table).

Table: The composition and yields of the products of the oxidation of metals by (II) in the equimolar mixture of THF and DMSO.

Metal (M)	The yield, mole per mole of (II)	
	Bi	$[\text{Cp}(\text{CO})_3\text{Mo}]_n\text{M}$
Ga	0.95	0.97
In	0.98	0.92
Mg	0.97	1.46

$n=2$, $M=\text{Mg}$; $n=3$, $M=\text{Ga}$, In .

According to [9], a similar reaction is observed between the solution of triphenylbismuth and ytterbium in THF in the presence of catalytic amounts of YbJ_2 .

IR spectrum of the reaction mixture obtained upon completion of the interaction between gallium and the solution of (II) has bands corresponding to $\nu_{\text{CO}} = 2055 \text{ cm}^{-1}$, 1971 cm^{-1} , 1890 cm^{-1} , 1850 cm^{-1} and 1893 cm^{-1} . These frequencies differ from the ones obtained in the IR spectrum of the products of interaction between gallium and (I) in similar conditions ($\nu_{\text{CO}} = 2057 \text{ cm}^{-1}$, 2025 cm^{-1} , 1965 cm^{-1} , 1880 cm^{-1} and 1775 cm^{-1}). This difference may be caused by the fact that in the latter case the products of reaction contain not only (III), but also GaCl_3 . Due to the equilibrium (3) different organogallium compounds may be present in the reaction mixture.

A similar reaction of organogallium compounds is discussed in [10].

REFERENCES

- 1 A.V. Piskounov, S.V. Maslennikov, I. V. Spirina, V.P. Maslennikov, *Zhurn. Obsh. Khim.* 2001. **71**. 714 (in Russian).
- 2 A.V. Piskounov, S.V. Maslennikov, I.V. Spirina, V.P. Maslennikov, A.N. Artemov, *Zhurn. Obsh. Khim.* 2002. **72**. 72 (in Russian).
- 3 N. Gordon, R. Ford, *Chemist's Companion*. Mir: Moscow. 1976; 437 (Russian ed.).
- 4 W. Cleg, N.A. Compton, R.I. Errington, N.C. Norman, A.I. Tucker, M.I. Winter, *J. Chem. Soc. Dalton Trans.* 1988. **12**. 2941.
- 5 A.I. Busev, *Analytical Chemistry of Molybdenum*. Izd. Akad. Nauk SSSR: Moscow. 1962; 175 (in Russian).
- 6 G. Sharlo, *Methods of Analytical Chemistry. Part II*. Khimiya: Moscow. 1969; 1183 p. (in Russian).
- 7 A.I. Lazarev, *Organic Reagents in the Analysis of Metals*. Metallurgiya: Moscow. 1980; 365 p. (in Russian).
- 8 H.I. Evans, E.R. Purvis, F.E. Bear, *Anal. Chem.* 1950. **22**. 12. 1568.
- 9 L.N. Bochkarev, T.A. Zhezlova, A.V. Sofronova, M.S. Drozdov, S.F. Zhiztsov, L.N. Zakharov, G.K. Fukin, S.Y. Khorshev, *Izv. AN. Ser. Khim.* 1998. **1**. 163 (in Russian).
- 10 U. Barton, *General Organic Chemistry. V.7*. Khimiya: Moscow. 1984 (Russian ed.).

**Received: February 27, 2002 - Accepted: March 4, 2002 -
Accepted in publishable format: March 5, 2002**