Letters to the Editor

Formation of dibenzenevanadium by the reaction of dysprosium diiodide with vanadocene in benzene

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Recently, we have found[1] that diiodides DyI_2 (**1**) and NdI_2 possessing strong reducing properties can successfully be used as an alternative to alkali metals in the synthesis of vanadocene (**2**) and cobaltocene. As part of our continuing investigations of the properties of these salts, in the present study we demonstrated that diiodide **1** can also be used for the preparation of dibenzenevanadium (**3**). Heating of a mixture of **1** and **2** in benzene at 85 °C was accompanied by a gradual change in the color of the solution from violet to red-brown. After separation of the precipitate and removal of benzene *in vacuo*, we obtained a solid dark-brown substance. The major portion of this substance is soluble in hexane. Study by ESR spectroscopy demonstrated that only traces of **2** were present in the hexane solution. However, heating of a brown crystalline substance, which was obtained after removal of hexane, *in vacuo* to 60 °C led to sublimation of compound **2** in an amount of >35% of that introduced into the reaction. Upon further heating of the residue to 110 °C, compound **3** was sublimed in a yield of 15% with respect to the amount of compound **2** used in the reaction. In benzene, diiodide **1** readily reacts with VCl_4, but this reaction results only in reduction of the latter to VCl_3. An attempt to synthesize compound **3** in the $Dy—DyI_3—VCl_4—C_6H_6$ system analogous to the Fischer system $(Al—AlCl_3—VCl_4—C_6H_6)$[2] failed. An attempt to use compound **2** instead of VCl_3 under these conditions was also unsuccessful.

The above-described reaction is unsuitable for preparative purposes because of a low yield of the product. However, the results of the present study are of basic importance, because they demonstrated that the reactions of "new" diiodides of divalent lanthanides (Nd, Dy, and Tm) with substrates can be carried out not only in solvating ethereal solutions[3] but also in benzene.

The synthesis and isolation of compound **3** were carried out under conditions precluding exposure to atmosphere. Diiodide **1** (97%) was purchased from SINOR (Nizhny Novgorod, Russia). A solution of compound **2** (0.265 g, 1.46 mmol) in benzene (10 mL) was added to a powder of **1** (1.224 g, 2.94 mmol) at ~20 °C. The reaction mixture was heated with stirring to 85 °C for 10 h. The solution was separated from the precipitate, the benzene was removed *in vacuo*, and the residue was extracted with hexane (2×10 mL). The extract was placed into a sublimation apparatus, the solvent was removed at room temperature, and the residue was heated *in vacuo* by gradually raising the temperature to 110 °C. A mixture of violet and brown crystals in a receiver was subjected to repeated sublimation. At 50—60 °C,

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violet crystals of **2** were sublimed. The yield of **2** was 0.101 g (38%). ESR: 77 K, $g_{\perp} = 4.0$, $a_{\perp}$ (^{51}V) = 2.8 mT, $g_{\|} = 2.0$. Dark-brown crystals of **3** remained in the apparatus; the yield was 0.045 g (15%); m.p. 275—277 °C (*cf.* lit. data[2]: 277—278 °C). ESR: a_{i} (^{51}V) = 6.35 mT, $g_{\mathrm{i}} = 1.986$.

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