Convenient method of synthesis of Cp_2TaH_3

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Modified method for preparation of Cp_2TaH_3 by reaction between $TaCl_5$, CpNa, and $LiAlH_4$ in dimethoxyethane is described. The yield of Cp_2TaH_3 is 25 %.

Key words: tantalocene, hydride, synthesis.

Tantalocene trihydride is the least available among molecular hydrides of transition metals with two cyclopentadienyl ligands. Previously we have thoroughly studied the different ways to synthesize this substance given in the literature.[1] The most convenient and reproducible way appeared to be the so-called one-stage method of synthesis using (2-methoxy)ethoxy-substituted sodium aluminum hydride:

$$TaCl_2 + CpNa \xrightarrow{NaAlH_2(OC_2H_4OCH_3)_2,\ DME}$$

$$Cp_2TaAlH_2(OC_2H_4OCH_3)_2 \xrightarrow{H_2O} Cp_2TaH_3 \qquad (1)$$

In this case the yield of target product can be up to 25 % (after a single sublimation). Under the same conditions, the use of readily available $LiAlH_4$ as the reducing agent results in a drop in the yield (to 5—10 %) and reproducibility of the method.

Changing the conditions of the reaction, we found that $LiAlH_4$ can be used in this process without lowering the yield of the target product. These changes concern the order of adding a reductant, rather than the essence of the process.

As is known,[1] at the first stages of the reaction tantalum pentachloride is reduced to tantalum tetrachloride, then bis-metalocene is formed and dissolved in the reaction mixture in the form of complex Cp_2TaCl_2:

$$TaCl_5 + 2CpNa + H_{hydr} \rightarrow Cp_2TaCl_2 \qquad (2)$$

It appeared that when using $LiAlH_4$ as the reductant in dimethoxyethane (DME) it was necessary to avoid introducing excess $LiAlH_4$ (compared to the stoichiometry of reaction (2)) at the first stage, to achieve as complete a reaction as possible. Apparently, this is caused by the Cp_2TaCl_2 formed in reaction (2) rapidly reacting with excess $LiAlH_4$, producing the poorly soluble complex Cp_2TaAlH_4, which prevents completion of reaction (2). Thus, it is imperative to introduce the required amount of $LiAlH_4$ in two portions, adding the second portion just after completion of reaction (2), which is easy to check by the appearance of the intensive green color of Cp_2TaCl_2. Lithium aluminum hydride can be added to the reaction mixture also in a crystalline form; however, in doing so one should take into account that the yield of tantalocene trihydride decreases, with no significant increase in reaction time, because of the poor solubility of lithium aluminum hydride at the proposed synthesis temperature (−60 °C).

When using $NaAlH_2(OC_2H_4OCH_3)_2$ as the reductant, such problems do not arise because all alumohydride complexes produced are high soluble in the reaction mixture.[1]

Experimental

One quarter (38 mL) of the volume of a solution containing 4.2 g (0.11 mol) of $LiAlH_4$ in 150 mL of DME was added to a solution of CpNa (0.3 mol) in 400 mL of DME at a temperature of −60 °C with vigorous stirring; then 35.0 g (0.1 mol) of finely ground $TaCl_5$ was carefully added. The mixture was vigorously stirred for 1 h at a temperature between −50 and −60 °C. When the reaction mixture got dark green, nearly black, the rest of the solution of $LiAlH_4$ in DME (112 mL) was added. The mixture was stirred for 30 min at −50 °C; then it was slowly heated to room temperature and stirred for 5 h. The brown reaction mixture was evaporated *in vacuo*, 300 mL of toluene was added to the residue, it was cooled down to −10 °C, and 30 mL of degassed ice-cold water was carefully added with vigorous stirring. The precipitate formed was filtered off and washed with 150 mL of toluene. The filtrate and toluene solution were combined and evaporated *in vacuo*; the residue was washed three times with dry pentane and then dried *in vacuo* at 50—60 °C. Cp_2TaH_3 (7.8 g, 25 %) was obtained from the residue by sublimation *in vacuo* (10^{-3} Torr) at 100 °C. Found (%): C, 38.9; H, 4.22. $C_{10}H_{13}Ta$. Calculated (%): C, 38.2; H, 4.14.

References

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