evacuation, and thawing to a residual pressure of 10^{-3} Torr; the tube was filled with argon, sealed, and kept at 120 °C for 6 h. The polymer that formed was precipitated with ethanol and dried to constant weight.

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Reactivity of ytterbium in liquid ammonia

1. Synthesis of the complex with the ytterbium—iron bond

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A solution of metallic ytterbium in liquid ammonia reacts readily with various carbonyl complexes of metals to form the corresponding lanthanide carbonylmetallates. The reaction of an excess of Yb in liquid NH_3 with $[CpFe(CO)_2]_2$ gave $(THF)_4Yb[Fe(CO)_2Cp]_2$ in 42% yield. It was suggested that the resulting complex contains two equivalent Yb—Fe bonds.

Key words: ytterbium, metal carbonyls.

It is known that ytterbium, samarium, and europium dissolve readily in liquid ammonia to form solutions of typical blue color (the color of solvated electrons).[1] The resulting product should be an active reducing agent of different organic and organometallic substrates, and its application is, apparently, a convenient method for the synthesis of a number of scarcely available organic derivatives of lanthanides. Recently, it has been demonstrated that $Fe(CO)_5$ is readily reduced by a solution of ytterbium in liquid ammonia to afford a polymeric heterometal complex having Yb—Fe bonds and an additional interaction with the participation of two isocarbonyl ligands per Yb atom.[2]

In this work, we report on the successful use of ytterbium in liquid ammonia as the reagent for selective reduction of $[CpFe(CO)_2]_2$ and for the preparation of the complex of divalent ytterbium having Yb—Fe bonds and in which no additional coordination with the bridging carbonyl ligands occurs.

Procedures for the synthesis of completely substituted metal carbonyl derivatives of lanthanides have been studied recently in detail.[3—5] Apparently, the reaction of the corresponding metallic rare-earth elements with dimeric carbonyl complexes of metals of composition $[M(CO)_nL_m]_2$ (M = Co, Cr, Mo, W, Mn, or Re; and L = Cp or PR_3) in THF is the most promising one. This procedure gave good results when readily reducible carbonyl derivatives of metals were used. On the contrary, hardly reducible complexes, such as $[CpM(CO)_2]_2$ (M = Fe or Ru),[6] do not enter into this reaction.

As part of the studies on the reactivity of a solution of ytterbium in liquid ammonia, it was demonstrated

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that this reagent readily reduces $Co_2(CO)_8$, $Mn_2(CO)_{10}$, $Re(CO)_{10}$, and $[CpMo(CO)_3]_2$ to the corresponding metal carbonyl complexes of di- or trivalent ytterbium depending on the ratio of the reagents. These reactions are completed in a few minutes, whereas the above-mentioned procedures with the use of metallic ytterbium in THF are completed in several hours (in some cases, even in several days) at room temperature.

The most important characteristic feature of a solution of ytterbium in liquid ammonia is its ability to readily reduce $[CpFe(CO)_2]_2$. The reaction with an excess of ytterbium was completed in a few minutes to yield the $(NH_3)_nYb[Fe(CO)_2Cp]_2$ complex. An excess of ytterbium prevents the formation of the corresponding Yb^{III} complex. In the course of the reaction, a slow elimination of ytterbium amide was also observed. The heterometal complex was extracted with THF. Recrystallization gave a beige crystal solvate of composition $(THF)_4Yb[Fe(CO)_2Cp]_2$ in 42% yield.

$$Yb^0 + [CpFe(CO)_2]_2 \xrightarrow[\text{2. THF}]{\text{1. NH}_3\text{(liq)}} (THF)_4Yb[CpFe(CO)_2]_2$$

The IR spectrum of a solution of the complex in THF has two absorption bands at 1934 and 1860 cm^{-1} in the region of stretching vibrations of CO groups. Such parameters of the IR spectrum should correspond to the compound that contains two equivalent Yb—Fe bonds without an additional coordination with the bridging carbonyl ligands.

Experimental

The synthesis was carried out in standard Schlenk vessels with the use of a high-vacuum line and purified argon. Ammonia used in the synthesis was twice distilled over metallic sodium. THF was distilled over $LiAlH_4$ and kept over sodium benzophenone ketyl. The IR spectra were recorded on a Perkin—Elmer 457 instrument.

The electron-probe microanalysis was carried out on a SEM-505 (Phillips) scanning electron microscope equipped with an Edax dispersion-analysis block.

Tetrakis(tetrahydrofurano)bis(dicarbonylcyclopentadienyliron)ytterbium(II), $(THF)_4Yb[Fe(CO)_2Cp]_2$. A mixture of liquid ammonia (~50 mL) freshly distilled over metallic sodium and powdered metallic ytterbium (1.97 g, 11.4 mmol) was placed in a flask equipped with a reflux condenser (into which a heat carrier cooled to −35 °C was fed). The reaction mixture was stirred using a magnetic stirrer for ~5 min. The $[CpFe(CO)_2]_2$ complex (2.0 g, 5.65 mmol) was added to a bright-blue solution, and the reaction mixture was stirred for 15 min. Ammonia was evaporated, and the residue was extracted with anhydrous THF (20 mL). The solution was separated from the precipitate of finely disperse ytterbium and ytterbium amide. Recrystallization of the resulting complex from a minimum amount of THF at −30 °C gave a beige crystalline powder of solvate $(THF)_4Yb[Fe(CO)_2Cp]_2$ in a yield of 1.80 g (42%). Found (%): C, 44.40; H, 5.64. $C_{30}H_{42}Fe_2O_8Yb$. Calculated (%): C, 44.17; H, 5.15. According to the data of the electron-probe microanalysis, Yb : Fe = 1 : 2. IR (THF), ν/cm^{-1}: 1934, 1860.

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