Neodymium and dysprosium diiodides in the synthesis of vanadocene and cobaltocene

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The reaction of NdI_2 or DyI_2 with VCl_3 and cyclopentadiene in THF at 65—70 °C without isolation of the intermediates afforded vanadocene in 55 and 68% yields, respectively. An analogous reaction of DyI_2 with $CoCl_2$ at 50 °C produced Cp_2Co in 38% yield.

Key words: neodymium diiodide, dysprosium diiodide, vanadocene, cobaltocene, synthesis.

Due to high reduction potentials of divalent neodymium and dysprosium diiodides, these compounds (a simple procedure for their synthesis has been debeloped recently[1]) can be used as a convenient and safe alternative to alkali metals. In particular, we have demonstrated that the LnI_2 salts (Ln = Nd (**1**) or Dy (**2**)) can be used for the preparation of Cp_2V without isolation of intermediates (Scheme 1).

Scheme 1

$$\underset{\mathbf{1},\ \mathbf{2}}{LnI_2} + VCl_3 + CpH \xrightarrow[-LnI_2Cl,\ -H_2]{THF} Cp_2V$$

The monocyclopentadienyl complex $CpLnI_2(THF)_x$ is generated in the first step proceeding at room temperature. The formation of such compounds in the reactions of LnI_2 (Ln = Nd or Dy) with cyclopentadiene has been observed in our earlier study.[2] Subsequent heating of the reaction mixture at 60—65 °C afforded vanadocene through metathesis between $CpLnI_2(THF)_x$ and vanadium trichloride. The reactions with salts **1** and **2** produced Cp_2V in 55 and 68% yields, respectively. This vanadocene was easily isolated by vacuum sublimation of a mixture of solid products obtained after the removal of the solvent, an excess of CpH, and volatile products. Interestingly, the reaction of $CpDyI_2(THF)_3$ with VCl_3 performed separately afforded vanadocene in a yield of no higher than 17% (Scheme 2).

Scheme 2

$$CpDyI_2(THF)_3 + VCl_3 \xrightarrow[-LnI_2Cl]{THF,\ 65\ ^\circ C} Cp_2V$$

It should be noted that an increase in the temperature to 80—90 °C in the second step of the synthesis caused further changes, resulting in a decrease in the yield of Cp_2V. Under these conditions, cyclopentadienyl iodide Cp_2VI was isolated from the reaction mixture in low yield along with vanadocene. The possibility of the formation of this complex from Cp_2V and neodymium trihalide, NdI_2Cl, which is one of the products generated in the second step, was confirmed by the reaction of vanadocene with NdI_3, which also gave green iodide Cp_2VI at 80—90 °C.

Taking into account the reduction potentials of vanadium ($E°(V^{3+}/V^{2+}) = -0.255$ V), neodymium ($E°(Nd^{3+}/Nd^{2+}) = -2.6$ V), and dysprosium ($E°(Dy^{3+}/Dy^{2+}) = -2.5$ V),[3] it can be hypothesized that the formation of vanadocene in the above-mentioned system involves also the step of reduction of vanadium trichloride to VCl_2 with iodides **1** and **2**. This leads to a sharp increase in the yield of Cp_2V in the synthesis involving DyI_2 compared to the reaction of VCl_3 with $CpDyI_2(THF)_3$. Earlier, it has been demonstrated[4,5] that preliminary reduction of VCl_3 to VCl_2 with zinc dust or $LiAlH_4$ in the conventional synthesis of vanadocene through CpNa made it possible to increase the yield of the target product from 40 to 60—78%. Actually, we found that diiodide **2** reacts with VCl_3 in THF even at −30 °C. However, this reaction afforded a dark-brown solution of several organodysprosium products instead of the expected $VCl_2(THF)_2$.[6] We failed to isolate individual compounds (except for dysprosium trihalides) from this mixture. Earlier,[7] analogous changes have been observed upon the addition of aromatic compounds to solutions of compounds **1** and **2** in THF or DME. To explain the observed effect, we hypothesize that LnI_2 undergoes disproportionation in a solvating medium to give triiodide and ex-

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tremely active monovalent iodide (LnI). The reaction of the latter with the solvent affords[7] a mixture of brown σ-complexes of composition RR´LnI (R and R´ are fragments of the solvent molecules). Apparently, vanadium chloride, like benzene, promotes disproportionation of LnI_2. It was demonstrated that LiI, ScI_3, and YI_3 exert the same effect on solutions of neodymium and dysprosium diiodides. The formation of the intermediates RR´LnI in the synthesis of Cp_2V cannot have a substantial effect on the yield of the target product, because the subsequent replacement of R and R´ with more acidic Cp groups, which is inevitable under the synthesis conditions, would give rise to cyclopentadienyl derivatives Cp_2LnI. It should be noted that the Cp_2LnI complexes can also be generated in the direct reaction of LnI with cyclopentadiene. The reaction of these products with VCl_3, analogously to the reaction with $CpLnI_2$, afforded vanadocene. We believe that the synthesis of Cp_2V involves both pathways, *viz.*, through $CpLnI_2$ and Cp_2LnI.

The reaction of diiodide **1** with $CoCl_2$ and CpH in THF at 20 °C produced a green solution, from which only trace amounts of Cp_2Co were isolated by sublimation. An increase in the reaction temperature to 50—60 °C did not lead to an increase in the yield of the product. By contrast, the use of dysprosium iodide **2** under the same conditions made it possible to synthesize cobaltocene in 38% yield. The characteristic brownish-green color of the solution as well as precipitation of dysprosium triiodide (which occurs upon disproportionation of LnI_2),[7] which were observed in the first step, indicate that this reaction follows primarily the pathway

$$LnI_2 \rightarrow LnI \rightarrow RR'LnI \rightarrow Cp_2LnI \rightarrow Cp_2Co.$$

Taking into account the simplicity of the procedure, availability of iodides **1** and **2**, and relatively high yields of metallocenes comparable to the yields achieved in conventional synthesis methods,[4,5,8] the proposed method can be recommended as a preparative approach. An important advantage of this approach is that it does not require inflammable alkali metals and $LiAlH_4$, which warrants the slightly higher prices of neodymium or dysprosium compared to sodium. The ease of the reactions and the preliminary data provide evidence that this procedure can be extended to cyclopentadienyl and related complexes of other d-transition metals. Studies in this field are currently underway.

To summarize, we demonstrated for the first time that divalent lanthanide diiodides, in particular, neodymium and dysprosium diiodides, can successfully be used for the synthesis of metallocenes of d-transition metals. The new procedure offers a number of advantages over conventional methods.

Experimental

All operations were carried out *in vacuo* or under argon using the Schlenk technique. Tetrahydrofuran was distilled over NaOH, degassed, dried with neodymium diiodide (THF (500 mL), NdI_2 (2 g), 20 °C, 30 min), and condensed into a reaction tube immediately before use. Anhydrous VCl_3 and $CoCl_2$ were purchased from Aldrich. Iodides NdI_2 (**1**) and DyI_2 (**2**) were purchased from Synor (Nizhny Novgorod, Russia). The $CpDyI_2(THF)_3$ complex was prepared according to a procedure described earlier.[2] The IR spectra were recorded on a Perkin Elmer 577 spectrometer. The samples were prepared as Nujol mulls. The ESR spectra were measured on a Bruker-ER 200D-1SRC instrument.

Vanadocene, Cp_2V. ***A.*** A solution of CpH (1.32 g, 20 mmol) in THF (30 mL) was placed in an evacuated tube containing DyI_2 (3.58 g, 8.6 mmol) and VCl_3 (0.31 g, 1.97 mmol) at ~20 °C. Gas evolution started immediately. The gas was periodically vented to atmosphere. The reaction mixture was stirred for 1.5 h until evolution of hydrogen completely ceased. The tube was evacuated, sealed, and heated with vigorous stirring at 65—70 °C for 2 h, resulting in dissolution of the violet precipitate of VCl_3 to give a colorless $DyI_2Cl(THF)_x$ precipitate. The solution turned violet-brown. The reaction mixture was transferred to a sublimation apparatus, and the solvent and volatile products were removed by vacuum condensation. Further heating of the solid residue to 80—100 °C (0.1 Torr) led to sublimation of dark-violet crystals of Cp_2V. The yield was 0.24 g (68%). IR, ν/cm^{-1}: 1100 m, 1005 m, 820 w. ESR (77 K): $g_{\perp} = 4.0$, $a_{\perp}(^{51}V) = 2.8$ mT, $g_{\parallel} = 2.0$.

B. Under analogous conditions, Cp_2V was prepared from NdI_2 (2.8 g, 7.0 mmol), VCl_3 (0.25 g, 1.5 mmol), and cyclopentadiene (1.0 g, 15.1 mmol) in THF (10 mL) in a yield of 0.16 g (55%).

C. A mixture of $CpDyI_2(THF)_3$ (0.74 g, 1.06 mmol) and VCl_3 (0.05 g, 0.32 mmol) in THF (20 mL) was heated with stirring to 65 °C for 2 h, after which the solution turned green. Vanadocene was isolated from solid products by vacuum sublimation at 90—100 °C in a yield of 0.01 g (17%).

Cobaltocene, Cp_2Co. The first step of the reaction of DyI_2 (1.89 g, 4.54 mmol), $CoCl_2$ (0.2 g, 1.54 mmol), and cyclopentadiene (1 g, 15.1 mmol) in THF (30 mL) was carried out as described above for the reaction of DyI_2 with VCl_3. The resulting greenish-brown mixture was heated with stirring at 55 °C for 1 h. The solvent and volatile products were removed *in vacuo*, and red crystals of cobaltocene were sublimed from a gray-brown solid residue at 40—50 °C (0.1 Torr). The yield was 0.11 g (38%), m.p. 173—174 °C (*cf.* lit. data[9]: m.p. 171—173 °C).

Dicyclopentadienylvanadium iodide, Cp_2VI. ***A.*** A violet reaction mixture, which was prepared from DyI_2 (1.54 g, 3.70 mmol), VCl_3 (0.13 g, 0.83 mmol), and cyclopentadiene (0.53 g, 8.03 mmol) in THF (30 mL) under the conditions of the above-described experiment, was heated with stirring at 90 °C for 4 h. The solution gradually turned blue-green. After removal of the solvent, the gray solid residue was heated *in vacuo*. At 80—100 °C (0.1 Torr), trace amounts of Cp_2V sublimed. Dark-green crystals of Cp_2VI sublimed when the temperature was raised to 170—180 °C. The yield was 52 mg (20%), m.p. 215—217 °C (*cf.* lit. data[10]: m.p. 214—215 °C). IR, ν/cm^{-1}: 1100 m, 1005 m, 820.

B. A mixture of Cp_2V (210 mg, 1.16 mmol) and $NdI_3(THF)_3$ (860 mg, 1.16 mmol) in THF (10 mL) was heated with stirring in a sealed tube at 80 °C for 3 h. The color of the solution gradually changed from violet to blue and then to blue-green. The solvent was removed *in vacuo* and the residue was extracted with toluene (3×10 mL). After removal of the toluene from the extract, the gray-green residue was heated *in vacuo*. At 170—180 °C (0.1 Torr), green crystals of Cp_2VI sublimed. The yield was 21 mg (6%), m.p. 215—217 °C. The IR spectrum of the product was identical to the spectrum of the compound prepared in the above experiment.

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References

1. M. N. Bochkarev and A. A. Fagin, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 1200 [*Russ. Chem. Bull.*, 1999, **48**, 1187 (Engl. Transl.)]; M. N. Bochkarev and A. A. Fagin, *Chem. Eur. J.*, 1999, **5**, 2990.
2. G. V. Khoroshen´kov, A. A. Fagin, M. N. Bochkarev, S. Dechert, and H. Schumann, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 1627 [*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 1715].
3. F. A. Cotton and G. Wilkinson, *Adv. Inorg. Chem.*, 5th ed., J. Wiley and Sons, New York (USA), 1988.
4. G. Wilkinson, F. A. Cotton, and J. M. Bormingham, *J. Inorg. Nucl. Chem.*, 1956, **2**, 95.
5. K. Handlir, J. Holecek, and J. Klikorka, *Z. Chem.*, 1979, **19**, 265.
6. F. H. Köhler and W. Prössdorf, *Z. Naturforsch.*, 1977, **32b**, 1026.
7. M. N. Bochkarev, A. A. Fagin, and G. V. Khoroshen´kov, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 1757 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 1909].
8. E. O. Fisher and R. Jira, *Z. Naturforsch.*, 1953, **8b**, 327; *Comprehensive Organometallic Chemistry*, Eds G. Wilkinson, F. Gordon, A. Stone, and E. W. Abel, Pergamon Press, Oxford, 1982, **5**.
9. G. Wilkinson, P. Pauson, and F. A. Cotton, *J. Am. Chem. Soc.*, 1954, **76**, 1970.
10. A. K. Fischer, F. A. Cotton, and G. Wilkinson, *J. Phys. Chem.*, 1959, **63**, 154.

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