Letters to the Editor

First molecular iodides of neodymium(II) and dysprosium(II)

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The first molecular compounds of bivalent neodymium and dysprosium, $NdI_2(THF)_5$ (**1**), $NdI_2(DME)_3$ (**2**), $DyI_2(THF)_5$ (**3**), and $DyI_2(DME)_3$ (**4**), were obtained by dissolution in tetrahydrofuran or 1,2-dimethoxyethane of diiodides NdI_2 and DyI_2, synthesized by burning a stoichiometric mixture of the corresponding metal and iodine, followed by the partial removal of the solvent *in vacuo*. It is noteworthy that the previous reports on the synthesis of $NdCl_2(THF)$[1] and $[(C_5Me_5)_2NdCl_2][K(THF)_n]_2$[2] were not confirmed.[3] Complexes **1**—**4** were isolated as finely crystalline substances. Neodymium compounds **1** and **2** are violet, and dysprosium analogs **3** and **4** are marshy-green. The magnetic moments of compounds **1** and **2** are equal to 2.7 and 2.8 μ_B, respectively, which correspond to the moment expected for Nd^{II} compounds (2.8 μ_B) and differ substantially from the value characteristic of the Nd^{III} cation (3.68 μ_B).[4] From the μ_{eff} value obtained for compounds **3** and **4** (10.6 μ_B) no definite conclusion about the oxidation state of dysprosium can be made, because the Dy^{II} and Dy^{III} derivatives have the same magnetic moment of 10.6 μ_B.[4] When evacuated at room temperature compounds **1** and **2** retain the initial crystallinity for at least 5 h. At a longer storage, the crystals become much lighter, and their magnetic moment increases to 3.2 μ_B. The dysprosium complexes are more stable: no changes in color of compounds **3** and **4** are observed for more than 1 day. The stability of iodides obtained in THF or DME solutions is somewhat lower; however, also in this case, the color of the solutions does not change at room temperature within several hours. The preliminary studies showed a very high reducing power of the compounds synthesized.

All procedures on synthesis and isolation of substances were carried out *in vacuo*. To obtain iodide **1**, a mixture of neodymium filings ((100—150 mesh, 0.41 g, 0.003 g-at.) and iodine powder (0.68 g, 0.0025 g-mol) was placed in a quartz ampule, which was evacuated, and the mixture was heated at one point to the onset of the reaction. The mixture ignited and melted. The reaction ceased after 1—3 s to form NdI_2 as a friable glassy black-brown substance. Found (%): I, 63.23; Nd, 36.77. I_2Nd. Calculated (%): I, 63.76; Nd, 36.24, μ_{eff} = 2.9 μ_B. A white film of NdI_3 (0.15 g, 10%) was deposited on the cold walls of the ampule.

Note: simultaneous heating of the whole system or a considerable increase in the loading can result in explosion.

The ampule was carefully shaken and tapped to grind the alloy obtained. The substance was removed into another ampule and condensed with 50 mL THF. A dark-violet solution formed on heating to room temperature and stirring. After settling, the solution was decanted to remove the precipitate of nondissolved iodides (NdI_2, NdI_3) and metal excess. The solvent was removed by condensation *in vacuo* to a volume of 2 mL. The dark-violet crystalline precipitate of compound **2** that formed was separated from the mother liquor by decanting and dried *in vacuo* to obtain the desired compound in 12% yield (0.42 g). Found (%): I, 38.07; Nd, 21.00. $C_{12}H_{30}I_2NdO_6$. Calculated

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(%): I, 37.97; Nd, 21.58. μ_{eff} = 2.8 μ_B (293 K). IR (Nujol), ν/cm^{-1}: 2930, 2879, 1453, 1409, 1189, 1095, 1060, 1035, 860, 548, 480. UV-Vis (DME), λ_{max}/nm: 515. On fast heating, compound **2** decomposes at temperatures above 50 °C.

Compounds **2—4** were obtained and isolated similarly. For **1** found (%): I, 37.01; Nd, 18.83. $C_{20}H_{40}I_2NdO_5$. Calculated (%): I, 33.46; Nd, 19.01. For **3** found (%): Dy, 20.16; I, 33.24. $C_{20}H_{40}DyI_2O_5$. Calculated (%): Dy, 20.95; I, 32.67. For **4** found (%): Dy, 22.80; I, 37.36. $C_{12}H_{30}DyI_2O_6$. Calculated (%): Dy, 23.66; I, 36.96.

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Alkylation of naphthalene and toluene by ethylene in naphthalene/alkali metal systems in THF

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We have previously[1,2] found that a reversible hydrogen transfer occurs between naphthalene rings of sodium naphthalene, as well as between sodium naphthalene and THF molecules, in the naphthalene/sodium system in THF at room temperature. Benzene, toluene, ethylene, and even methane undergo similar reactions of exchange of hydrogen atoms with the C—H bonds of naphthalene rings. Taking into account so high an efficiency of this system in C—H bond activation, we studied the possibility of using such systems for the alkylation of hydrocarbons by ethylene under mild conditions. In this work, we report on the first examples of these reactions found by us.

Experiments were carried out at room temperature and atmospheric pressure according to the standard procedure. The amount of naphthalene was 3 mmol, and the volume of THF was 1.5 mL (reaction time 24 h). Alkali metal (Li, Na, or K) was taken, as a rule, in a twofold molar excess with respect to naphthalene. The products formed were analyzed by GLC and GC-MS.

In a typical experiment, sodium (0.138 g, 6 mmol), naphthalene (0.384 g, 3 mmol), and THF (1.5 mL) were placed in a Schlenk tube under an argon atmosphere, and the mixture was stirred under an ethylene atmosphere on a magnetic stirrer at room temperature. A gradual absorption of ethylene was observed in the course of the reaction, and 1-ethylnaphthalene appeared in the solution. After 24 h, the amount of absorbed ethylene was 0.73 moles per mole of naphthalene, and the yield of 1-ethylnaphthalene was 37% based on naphthalene. Along with 1-ethylnaphthalene, small amounts (~3%) of its two dihydro derivatives were also found. The change of THF for 1,2-dimethoxyethane and a decrease in the molar ratio of Na to naphthalene from 2 : 1 to 1 : 1 decreased substantially the efficiency of alkylation. When the reaction was carried out in the presence of 15-crown-5, the products of naphthalene alkylation were formed as traces only.

The naphthalene/potassium system in THF exhibits even higher activity in naphthalene alkylation by ethyl-

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