Specific chemical behavior of Nd^{II} and Dy^{II} iodides in reactions with aromatic compounds

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Benzene, toluene, *tert*-butylbenzene, or biphenyl virtually do not react with NdI_2 (**1**) or DyI_2 (**2**) in THF at −20 °C but appreciably accelerate the reactions of these salts with solvents, resulting in LnI_3 and intractable mixtures of products of the general composition [LnI(H)(R)(THF)] (R are fragments of the THF molecule). The same effect is induced by the addition of diphenylmercury or tetraphenyltin to solutions of **1** or **2**. Phenol easily oxidizes **1** and **2** to give at 0 °C the $PhOLnI_2(THF)_x$ complexes ($x = 3, 4$) in 55—95% yields. At −90 °C, iodide **2** is converted into a similar complex $PhODyI_2(THF)_4$, whereas **1** gives a mixture of $PhONdI_2(THF)_4$, $(PhO)_2NdI(THF)_5$, $NdI_3(THF)_3$, and [NdI(H)R(THF)]. A plausible pathway of the reactions including the intermediate formation of extremely reactive monovalent lanthanide iodides LnI is discussed.

Key words: neodymium, dysprosium, iodide, reduction, aromatic hydrocarbon.

The convenient methods for the synthesis of molecular iodides of divalent thulium,[1] dysprosium,[2] and neodymium[2] developed recently made these salts available for further structural and chemical studies. X-Ray diffraction analysis showed that the $TmI_2(DME)_3$ [1] and $NdI_2(THF)_5$ [3] molecules have a pentagonal-bipyramidal geometry, similar to that of samarium complexes $SmI_2(THF)_5$, $SmI_2(DME)(THF)_3$, and $SmI_2(DME)_2(THF)$.[4] In the crystal of the dysprosium analog $DyI_2(DME)_3$, two conformers were found,[5] one with linear and one with bent I—Dy—I fragment. Comparison of the electrode potentials of Sm, Tm, Dy, and Nd (E_0 (Ln^{3+}/Ln^{2+}) = −1.55, −2.3, −2.45, and −2.62 V, respectively[6]) leads to the suggestion that the reductive properties of divalent metal iodides markedly increase on passing from samarium to thulium, dysprosium, and neodymium. This assumption is confirmed by the substantial decrease in the stability of solutions of LnI_2 in THF (*i.e.*, acceleration of reactions with the solvent) in the series $SmI_2 > TmI_2 > DyI_2 > NdI_2$.[7] Note that lanthanide iodides LnI_x (Ln = Sc, Y, La, Ce, Pr, $x = 1.8—2.3$) containing the metal in the +3 oxidation state exhibit relatively low reactivities.[8] These compounds, possessing metal-type conduction, are designated by the general formula $(Ln^{3+})(e^-)(I^-)_x$. Comparison of the reducing capacities of SmI_2 and TmI_2 in the cross-coupling of ketones and alkyl halides[9] showed that in the case of thulium iodide, the reaction time is markedly shorter and the product yield is higher. Our studies into the reactivity of TmI_2 toward alcohols, namely, 3,6-di(*tert*-butyl)pyrocatechol, 3,6-di(*tert*-butyl)benzo-1,2-quinone,[10a] cyclooctatetraene, acenaphthylene,[10b] and calix[4]arene[10c] also demonstrated high reducing capacity of this salt. The chemical properties of iodides **1** and **2** have scarcely been studied, although indirect data attest to a very high reactivity of these substances.[2] This has been confirmed[5] by the data that DyI_2 readily reduces naphthalene to the dianion in dimethoxyethane (DME) to give the $C_{10}H_8DyI(DME)_2$ complex and adds at the triple bond of diphenylacetylene to give, after hydrolysis, *cis*-stilbene. The addition of $C_6H_5CH_2CH_2Cl$ to cyclohexanone in the presence of DyI_2 occurs at −45 °C, whereas TmI_2 reacts only at 60 °C.

This paper deals with the unusual behavior of THF solutions of NdI_2 (**1**) and DyI_2 (**2**) in the presence of aromatic hydrocarbons and their derivatives. The results were interpreted by assuming a set of reactions that include the formation, under certain conditions, of extremely potent reducing agents, monovalent metal iodides LnI.

Results and Discussion

Both iodides **1** and **2** are insoluble in benzene or toluene and do not react with these hydrocarbons. The solvated salts $NdI_2(THF)_5$ and $DyI_2(THF)_5$ are also insoluble in aromatic solvents but, when placed in benzene at −10 °C, the crystals of these compounds acquire a dark-brown color and collapse over a period of 10 to 20 min. When benzene is added in any ratio (even in trace amounts) to a solution of **1** or **2** in THF at −30 °C, the

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initial violet (Nd) or khaki-green (Dy) color of the solution changes to dark-brown after several minutes and the compound $LnI_3(THF)_3$ precipitates. The amount of the triiodide formed corresponds to a half of LnI_2 used in the reaction.

Apart from $LnI_3(THF)_3$, compound **A** having identical properties in both cases was isolated from the reaction mixture as a brown noncrystalline pyrophorous powder soluble in THF and DME and partially soluble in ether, benzene, and toluene, but insoluble in hexane. The metal and iodine contents in substance **A** correspond to the formal composition $LnI(THF)_x$ (Ln = Nd, $x = 3$; Ln = Dy, $x = 2$). The atomic magnetic moment of the neodymium derivative (3.4 μ_B) corresponds to Nd^{III}. Its IR spectrum contains only bands for coordinated THF molecules (1010 and 860 cm^{-1}) and low-intensity bands at 1350, 1300, 1240, 1180, 1070, 910, 850, 650, and 540 cm^{-1}, which can be assigned to vibrations of the Ln—H, Ln—O—CH_2—, Ln—CH=CH_2, or —CH=CH—CH=CH— groups. The spectrum of the dysprosium product $\mathbf{A}_{Dy}$ differs only by a somewhat lower intensity of the bands at 1010 and 860 cm^{-1}. According to GLC and ^1H NMR spectroscopy, the volatile products of reactions of **1** and **2** with stoichiometric amounts of benzene contained >80% of the initial C_6H_6.

Since neither X-ray diffraction nor NMR spectroscopy (the latter, due to the presence of the paramagnetic metal) is applicable to the study of compound **A**, indirect chemical routes were employed to identify this product. Hydrolysis of $\mathbf{A}_{Nd}$ was found to give only $NdI(OH)_2$, THF, H_2, and benzene in 1 : 1.1 : 1.2 : 0.07 ratio. In addition, chromatographic analysis of the volatile fraction showed the presence of minor amounts of four other products, which could not be identified. The separation of inorganic and volatile components left a brown thick metal-free material; according to IR and ^1H NMR spectroscopy, this was a mixture of oligomers of cleaved THF. After oxidation of $\mathbf{A}_{Nd}$ with dry air, only THF and slight amounts of benzene were found in volatile products. The evolution of H_2 in the hydrolysis of **A** may indicate the presence of Ln—H groups. To confirm this assumption, the product $\mathbf{A}_{Dy}$ was made to react with Et_3GeBr. Previously, we found[11] that lanthanide hydride complexes $LnH_2(THF)_3$ (Ln = Sm, Eu, Yb) readily reduce triethylgermanium bromide to give Et_3GeH. The products of reaction of Et_3GeBr with **A** were found to contain triethylgermane, which confirms the presence of Ln—H groups in the compound.

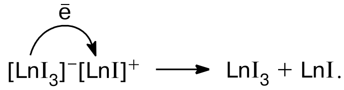
Thus, the elemental analysis, the IR spectrum, and the products formed in reactions with H_2O, O_2, and Et_3GeBr indicate that substance **A** contains the LnI, LnH, and LnR groups (R are monomeric or oligomeric fragments of cleaved THF) and coordinated THF. The ratio of these groups corresponds to the composition $[LnI(H)R(THF)_x]$ (Nd, $x = 2$; Dy, $x = 1$). Fractional solubility of **A** in various solvents attests that this is not a single compound but is, apparently, a mixture of $[LnI(H_2)(THF)_x]$, $[LnI(H)R(THF)_x]$, and $[LnI(R)R'(THF)_x]$ complexes. These compounds may result from the reaction of LnI_2 only with the solvent. Note that lanthanide derivatives containing Ln—H and Ln—C bonds are commonly colored brown.[12] The small amount of benzene found in the hydrolysis products obtained from **A** may be due either to its incomplete removal during vacuum drying or to the presence in **A** of Ln—C_6H_5 groups resulting from the reaction of benzene with lanthanide iodide. The fact that THF containing traces of aromatic compounds can be completely purified when treated with iodides **1** and **2** supports the latter assumption.

Similar transformations, *i.e.*, the formation of LnI_3 and brown $[LnI(H)R(solv.)_x]$ products, take place when the reactions are carried out in DME or when other aromatic compounds such as toluene, $Bu^tC_6H_5$, diphenyl, stilbene, Ph_2Hg, or Ph_4Sn are added to solutions of **1** and **2**. Meanwhile, aliphatic hydrocarbons, diethyl ether, or even $(Me_3Si)_2NH$, which contains an active hydrogen atom, have no influence on the solutions of the iodides studied.

The cleavage of the solvent by iodides **1** and **2**, which proceeds with remarkable ease in the presence of the above-mentioned aromatic compounds, cannot be explained by a direct reaction between LnI_2 and THF because without additives, solutions of these salts can be stored under the given conditions for 24 h without noticeable changes. At room temperature, they lose color after 5—7 h due to the reaction of LnI_2 with the ether group of the solvent, resulting in slightly colored products such as $ROLnI_2$.[2] It is also unlikely that the sharp increase in the reducing capacity of **1** and **2** in the presence of benzene and other similar substrates is related to a change in the reduction mechanism from inner-sphere to outer-sphere, which is proposed in some cases for interpreting the reactivity of SmI_2.[13] In our opinion, the unusual behavior of Nd^{II} and Dy^{II} diiodides in solutions is due to the ability of lanthanide halides to exist as two forms, neutral LnX_m and ionic $\{[LnX_{m+1}]^-[LnX_{m-1}]^+\}$ forms. In the case of trivalent lanthanide salts, the existence of both the LnX_3 and $\{[LnX_4]^-[LnX_2]^+\}$ forms has been proved reliably by X-ray diffraction data for dozens of compounds (see, for example, Ref. 14). The reactivity and the catalytic activity of compounds were found to be related to the structures of molecules.[14b,e] In solutions, the two forms are in equilibrium, which is confirmed by the formation of either neutral or ionic salt, depending on the synthesis or isolation conditions.[14e,f] Only neutral structures of the $LnX_2(solv.)_x$ type are known for divalent lanthanides;[1,3—5] however, it is reasonable to suggest that these salts, in particular, diiodides **1** and **2**, can also exist in solutions as $[LnI_3]^-[LnI]^+$ ion pairs.

$$2\,LnI_2 \rightleftharpoons [LnI_3]^-[LnI]^+. \qquad (1)$$

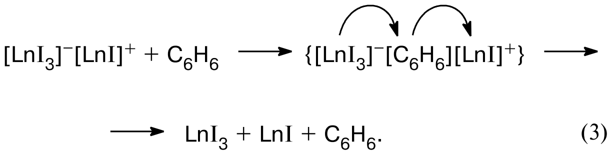
The coordinated solvent molecules are not shown in reaction (1) for the sake of simplicity, although their participation in these processes is of crucial importance. Reaction (1) proceeds as transfer of the I^- ion (*i.e.*, the iodine atom bearing an electron), between metal atoms. However, one may suggest that transfer of an electron alone, without a iodine atom can take place in the $\{[LnI_3]^-[LnI]^+\}$ ion pair under certain conditions. This transfer would give rise to two neutral products, namely, LnI_3 and an unusual metal(I) monoiodide LnI.



$$[LnI_3]^-[LnI]^+ \longrightarrow LnI_3 + LnI. \qquad (2)$$

Apparently, the formation of highly stable triiodide LnI_3 (which is actually observed in many reactions involving NdI_2, DyI_2, and TmI_2) apart from the metastable LnI makes reaction (2) thermodynamically feasible. The properties of monovalent lanthanide iodides are unknown;* however, it is reasonable to expect that they would exhibit an exceptionally high reducing capacity and, hence, a very low regioselectivity. In a THF/C_6H_6 mixture, an attack by LnI would be mainly directed at the THF molecules, because they are incorporated in the metal coordination sphere and, therefore, they are more easily accessible. Due to the low regioselectivity, the monoiodide attacks not only the most "reactive" C—O bond but also the C—H and C—C bonds to give a number of LnI(H)R type products, where R are fragments of the THF molecule including H atoms or THF oligomers. Apparently, partial exit of LnI from the reaction cage results in benzene metallation to give LnI(H)Ph or $LnI(Ph)_2$.

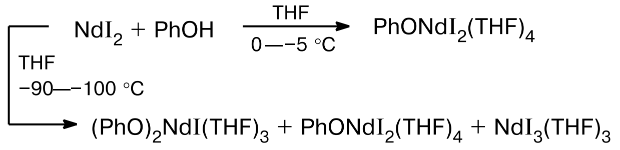
Since without benzene the reaction of **1** or **2** with the solvent occurs slowly to give the diiodide complexes like $ROLnI_2$,[2] one can conclude that the role of the substrate is to initiate generation of the iodides LnI. In our opinion, an aromatic compound incorporated in an intermediate like $\{[LnI_3][C_6H_6][LnI]\}$ provides the transport of an electron from the $[LnI_3]^-$ anion to the $[LnI]^+$ cation. After formation of neutral iodides LnI_3 and LnI, the substrate is liberated unchanged.



$$[LnI_3]^-[LnI]^+ + C_6H_6 \longrightarrow \{[LnI_3]^-[C_6H_6][LnI]^+\} \longrightarrow LnI_3 + LnI + C_6H_6. \qquad (3)$$

Note that a number binuclear lanthanide complexes with a bridging aromatic ligand have been reported, for example, $[K([18]\text{-crown-}6)(\eta^2\text{-}C_6H_6)_2]\{[La\{C_5H_3\text{-}Bu^t{}_2\text{-}1,3\}_2]_2(\mu\text{-}C_6H_6)\}$,[16a] $[K([18]\text{-crown-}6)][\{Nd[C_5H_3(SiMe_3)_2\text{-}1,3]_2\}_2(\mu\text{-}C_6H_6)]$;[16b] and $[LaI_2(THF)_3]_2(\mu\text{-}C_{10}H_8)$.[16c] Thus, benzene and other noncondensed aromatic compounds are involved in these reactions like a sort of catalysts that promote the transformation of single-electron reducing agents **1** and **2** into two-electron reducing agents LnI and the subsequent oxidation of these species by the solvent.

The assumed pattern of transformations taking place upon the addition of aromatic compounds to solutions of **1** or **2** in THF and DME allows one to interpret the unusual change in the route of reaction of **1** with phenol at lower temperatures. We found that at temperatures of −5 to 0 °C, both iodides in THF solutions react with PhOH in the same way to give the corresponding $PhOLnI_2(THF)_x$ phenoxides (x = 3, 4) in good yields. However, at temperatures of −90 to −100 °C, the neodymium and dysprosium derivatives react along different pathways. Whereas a solution of iodide **2** gradually loses color (as observed at 0 °C, but very slowly), in the case of **1**, within several minutes after the addition of phenol, the color of the mixture changes to dark-brown and the NdI_3 precipitate is formed. On subsequent warming-up to room temperature, the solution color turns to light-blue. In this case, the diphenoxide $(PhO)_2NdI(THF)_3$ (yield 46%) and $NdI_3(THF)_3$ were isolated from the reaction mixture together with $PhONdI_2(THF)_4$.



The reaction of **1** with Bu^tOH is accompanied by gradual decoloration, irrespective of the temperature, and affords only the monoalkoxide $Bu^tONdI_2(THF)_4$.

In terms of the proposed set of reactions of **1** or **2** with aromatic hydrocarbons (reactions (1)—(3)), the change in the reaction pathway upon a decrease in the temperature, found for the reaction of **1** with phenol, can be explained by switching of the attack by NdI_2 from the OH group (at 0 °C) to the Ph group (at −90 °C). Apparently, a decrease in the temperature has virtually no influence on the formation of the reactive complex of the diiodide with the benzene ring $\{[NdI_3][C_6H_5OH][NdI]\}$. This also does not influence the subsequent intramolecular electron transfer or reactions of the generated NdI monoiodide with the solvent and the phenol OH group, but sharply decelerates the direct reaction between the same OH

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* Previously,[15] the formal oxidation state 1+ for Group III metals was found only for scandium in the $[(\eta^5\text{-}Bu^t{}_2P_3C_2)Sc]_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-}Bu^t{}_3P_3C_3)$ complex prepared by cryogenic synthesis from Sc vapors and $Bu^tC\equiv P$.

group and the NdI_2 diiodide. The formation of the $(PhO)_2NdI(THF)_3$ diphenoxide observed at low temperatures is, apparently, due to two processes, namely, the reaction of phenol with the generated NdI monoiodide and the reaction of phenol with the $[NdI(H)R(THF)_x]$ complexes, resulting from cleavage of THF according to the scheme given above. The reaction of **1** with *tert*-butyl alcohol involves no aromatic compounds; therefore, NdI is not formed and no brown coloring or NdI_3 precipitate appears.

When dysprosium iodide **2** reacts with phenol, no intermediate $\{[DyI_3][C_6H_5OH][DyI]\}$ complex seems to form either at 0 °C or at low temperature, as indicated by the absence of the DyI_3 precipitate or the typical brown coloring of the reaction mixture. The $PhODyI_2(THF)_4$ phenoxide, which results from single-electron reduction of phenol, is formed in this case in 96% yield. The reaction of TmI_2 follows a similar pathway.[10a]

Thus, the reduction of substrates with Nd^{II} and Dy^{II} iodides can be either a single-electron or a formally two-electron process. Upon the addition of noncondensed aromatic compounds, characterized by low electron affinities, to solutions of **1** or **2** in THF, the reduction mechanism switches to the two-electron version and the reducing capacity of the iodides sharply increases. Compounds of the R_2LnI type become the major reaction products. The assumption that diiodides **1** and **2** exist in solutions in the ionic form $[LnI_3]^-[LnI]^+$ provides an interpretation for specific chemical properties of these salts. The electron transfer from the anion to the cation, which occurs under certain conditions, results in the generation of LnI monoiodides. The reduction potential of these species, as indicated by their reactions with the solvent, exceeds substantially those of alkali metals.

Experimental

All operations on the synthesis and isolation of compounds were carried out *in vacuo* using standard Schlenk equipment. Solutions of **1** and **2** were transferred into reaction vessels through glass connecting tubes, their contact with rubber tubes being avoided. The solvents, THF and DME, were refluxed over NaOH and over sodium metal and, finally, immediately prior to use, they were kept for 15 min over **1** or **2**. From the resulting solutions of iodides, the solvent was fed to the reaction vessel by vacuum condensation. Commercial benzene, toluene, Bu^tPh, diphenyl, stilbene, hexane, diethyl ether, cyclohexane, and silazane were purified by known procedures and dried at the final stage over a sodium mirror. The reagents Et_3GeBr, Et_3GeH, Ph_2Hg, and Ph_4Sn were synthesized by known procedures.[17—19]

Infrared spectra were recorded on Specord M80 and Perkin Elmer 577 instruments; the samples were prepared as mineral oil mulls. NMR spectra were recorded on a Bruker DPX 200 instrument. The GLC analysis of volatile products was performed on a Tsvet-530 chromatograph. Magnetic measurements were carried out at room temperature as described previously.[20] Due to the instability of organolanthanide compounds in air and the formation of carbides upon their combustion, the data of elemental C,H analysis are poorly reproducible; therefore, the compounds obtained were analyzed only for metal and iodine by complexometry.

The LnI_2 diodides (Ln = Nd, Dy) were prepared by burning a mixture of lanthanide metal with iodine according to a previously developed procedure.[2] Previously, we found that the precipitate left after the extraction of the combustion products with tetrahydrofuran or dimethoxyethane, which consists of LnI_2, LnI_3, and excess metal, affects appreciably the stability and the reactivity of the resulting solutions. Therefore, prior to the addition of substrates, solutions of **1** and **2** were centrifuged and decanted from the insoluble fraction at −30 °C. The amount of the diiodide taken in the reaction was found as the difference between the weights of LnI_2 before and after solvent extraction followed by drying the precipitate *in vacuo* at 100 °C.

Reaction of the diiodide 1 with benzene. Benzene (0.1 g, 1.28 mmol) was added at −20 °C to a violet suspension of iodide **1** (0.632 g, 1.51 mmol) in 40 mL of THF. Over a period of 5 min, the color of the mixture changed to dark-brown, compound **1** completely dissolved but a light-blue $NdI_3(THF)_3$ precipitate appeared (0.448 g, 0.604 mmol). Gas evolution was noted. After 30 min, the mixture was centrifuged, the solution was separated from the precipitate, and the solvent together with volatile products was removed by vacuum condensation. GLC and ^1H NMR analyses of the volatile products showed the presence of only THF and benzene (0.081 g, 81%). The brown waxy material left after the removal of the volatile products was dissolved in 5 mL of THF and 15 mL of hexane were added. The brown precipitate was separated from the mother liquor by centrifuging and dried *in vacuo* to give 0.45 g of brown pyrophoric powder **A**, μ_{eff} 3.4 μ_B (293 K). IR (Nujol), ν/cm^{-1}: 1340 m, 1250 m, 1180 m, 1150 w, 1070 m, 1010 s, 910 m, 860 s, 850 sh, 650 m. According to complexometry, substance **A** contained I (25.90%) and Nd (31.03%) and also THF (GLC, after hydrolysis) in a THF/Nd ratio of 2.06 (for $NdI(THF)_3$, calculated (%): I, 26.03; Nd, 30.63).

Reaction of 2 with benzene. Under conditions described in the previous procedure, benzene (0.312 g, 4.0 mmol) was added to iodide **2** (1.06 g, 2.55 mmol) in 40 mL of THF to give $DyI_3(THF)_3$ (0.97 g, 1.28 mmol) and a brown solid $\mathbf{A_{Dy}}$ (0.625 g), containing 36.93% dysprosium and 28.84% iodine (for $DyI(THF)_2$, calculated (%): Dy, 37.48; I, 29.27). GLC analysis of volatile products showed the presence of 0.28 g (90%) of benzene.

Hydrolysis of product A(Nd). A 90% aqueous solution of methanol (2 mL) was added to neat compound $\mathbf{A_{Nd}}$ (0.776 g). Vigorous evolution of H_2 was observed (24 mL, 1.07 mmol; identified by GLC). The resulting suspension was centrifuged and the solution was separated from the precipitate. The precipitate was washed with THF and dried *in vacuo* to give 0.675 g (1.39 mmol) of $NdI(OH)_2(THF)_{2.5}$. Found (%): I, 27.90; Nd, 29.03. $C_{10}H_{22}INdO_{4.5}$. Calculated (%): I, 26.14; Nd, 29.71. The removal of the volatile products by vacuum condensation at 100 °C left a brown resinous material (0.01 g). ^1H NMR ($CDCl_3$), δ: 5.36 (br.s, 4 H, CH); 4.96 (br.s, 4 H, CH); 3.69 (t, 2 H, CH_2); 3.24 (t, 2 H, CH_2); 2.19 (s, 6 H, CH_2); 2.03 (br.s, 18 H, CH_2); 1.59 (br.s, 42 H, CH_2); 1.27 (s, 42 H, CH_2); 0.88 (m, 18 H, CH_2). GLC analysis of the volatile products showed the presence of THF (0.113 g, 1.57 mmol), benzene (9 mg, 0.1 mmol), and traces of four unidentified compounds.

Oxidation of A_{Nd} with air. A 40 mL-tube containing A_{Nd} (207 mg) was carefully filled with dry air at –20 °C. The brown powder **A** immediately turned into a light-yellow waxy product. According to GLC, the volatile products separated from the reaction mixture by vacuum condensation at 100 °C contained THF (23 mg), benzene (0.5 mg), and three unidentified compounds (total amount 0.5 mg).

Reaction of A_{Dy} with Et_3GeBr. Bromo(triethyl)germane (0.55 g, 2.3 mmol) was added to a suspension of A_{Dy} (1.0 g) in 1 mL of THF. The mixture was stirred for 10 h at ~20 °C and the precipitate was separated by centrifuging. GLC analysis of the solution showed the presence of 132 mg (36%) of Et_3GeH.

Reaction of 1 with phenol at 0 °C. A solution of phenol (0.19 g, 2.0 mmol) in 10 mL of THF was added with stirring at 0 °C to iodide **1** (0.738 g, 1.85 mmol) in 30 mL of THF. The precipitate of **1** immediately dissolved and the color of the mixture changed from violet to light-blue. Gas evolution was observed. The solution was concentrated to 15 mL and allowed to stand for 12 h at −12 °C. The resulting light-blue crystals were separated by decanting off the mother liquor, washed with 10 mL of cold THF, and dried *in vacuo* at ~20 °C to give 0.597 g (41%) of $PhONdI_2(THF)_4$; m.p. 140—145 °C (dec.). IR (Nujol), ν/cm^{-1}: 3050 m, 1600 m, 1500 s, 1490 s, 1270 s, 1070 w, 1030 s, 910 m, 870 s, 770 m, 700 m, 590 m. Found (%): I, 32.02; Nd, 18.87. $C_{22}H_{37}I_2NdO_5$. Calculated (%): I, 32.56; Nd, 18.50. Hexane (20 mL) was added to the mother liquor. The precipitate thus formed (0.51 g, 35%) was washed with hexane and dried *in vacuo*. The iodine and neodymium contents, the IR spectrum, and the decomposition point of the precipitate were identical to those presented above for $PhONdI_2(THF)_4$. The total yield was 1.107 g (76%).

Reaction of 1 with phenol at −100 °C. A suspension of iodide **1** (0.59 g, 1.48 mmol) in 20 mL of THF was cooled to −100 °C, and phenol (0.16 g, 1.70 mmol) was added. After 3 min, the violet color of the mixture changed to brown. Slight gas evolution and precipitation of grayish-blue NdI_3 were observed. The mixture was heated to room temperature; as this took place, the solution gradually became light-blue. After settling, the solution was decanted from the precipitate. By vacuum condensation of the solvent, the solution was concentrated to 10 mL and cooled to −12 °C. After 2 days, the precipitated blue crystals of $(PhO)_2NdI(THF)_3$ were separated. Yield 0.229 g (46%). After recrystallization from THF, the substance melted with decomposition at 145 °C. IR (Nujol), ν/cm^{-1}: 3050 m, 1600 m, 1500 m, 1490 s, 1270 s, 1000 s, 910 m, 850 s, 760 m, 690 m, 660 m, 590 m. Found (%): I, 22.40; Nd, 21.16. $C_{24}H_{34}INdO_5$. Calculated (%): I, 18.84; Nd, 21.41. The grayish-blue precipitate was extracted with ether (2×20 mL). The ether was removed and the residue was recrystallized from a THF—ether mixture to give 0.129 g (11%) of $PhONdI_2(THF)_4$ as light-bluish crystals. The IR spectrum of the complex was identical to the spectrum of the product obtained at 0 °C. Found (%): I, 32.20; Nd, 18.63. $C_{22}H_{37}I_2NdO_5$. Calculated (%): I, 32.56; Nd, 18.50. The light-blue crystals (0.21 g, 37%) remaining after the extraction with ether were identified as $NdI_3(THF)_3$ (IR spectrum; the I and Nd contents).

Reaction of 2 with phenol. Phenol (0.1 g, 1.06 mmol) was added at −100 °C to a green suspension of **2** in 12 mL of THF. The color of the mixture almost did not change over a period of 20 min. During the subsequent 2 h, the mixture was warmed up to −15 °C and kept at this temperature for 20 min. During warming-up, the mixture gradually decolorized and, after completion of the reaction, the solution became light-straw-colored. Compound **2** completely dissolved and $PhODyI_2(THF)_3$ precipitated as a colorless finely crystalline solid, which was separated from the solution by decantation, recrystallized from THF, and dried *in vacuo* at room temperature. Yield 0.5 g (97%); m.p. 110 °C (dec.). IR (Nujol), ν/cm^{-1} : 3050 m, 1590 m, 1295 s, 1210 s, 1160 m, 1070 w, 1010 s, 910 m, 860 s, 770 s, 695 m, 560 m. Found (%): I, 35.60; Dy, 21.97. $C_{18}H_{29}I_2DyO_4$. Calculated (%): I, 34.98; Dy, 22.39.

Reaction of 1 with *tert*-butanol. A solution of Bu^tOH (0.41 g, 5.53 mmol) in 15 mL of THF was added at 0 °C to iodide **1** (3.01 g, 3.97 mmol) in 50 mL of THF. After 15 min, the reaction was over and the mixture acquired a light-blue color. The solution was concentrated to 10 mL and cooled to −15 °C. The light-blue crystals of $Bu^tONdI_2(THF)_4$ (2.33 g, 77%) formed after 10 h were separated by decantation, washed with cold THF, and dried *in vacuo*; m.p. 94—95 °C. IR (Nujol), ν/cm^{-1} : 1070, 1040, 1000, 900, 870, 840 (sh). Found (%): I, 32.94; Nd, 18.57%. $C_{20}H_{41}I_2NdO_5$. Calculated (%): I, 34.41; Nd, 18.99.

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