1586 *Russian Chemical Bulletin, International Edition, Vol. 60, No. 8, pp. 1586—1590, August, 2011*

Reduction of the groups C=O and C=N with neodymium and dysprosium diiodide hydrides

M. E. Burin,** *A. A. Logunov, N. O. Druzhkov, G. K. Fukin, and M. N. Bochkarev

G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences,
49 ul. Tropinina, 603950 Nizhny Novgorod, Russian Federation.
Fax: +7 (831) 462 7497. E-mail: mboch@iomc.ras.ru

Neodymium diiodide hydride under mild conditions adds at the carbonyl group of benzophenone to give (diphenylmethoxy)(diiodo)neodymium(III) of the formula $I_2Nd(OCHPh_2)(THF)_4$. In reactions of NdI_2H and DyI_2H with *N*-(2,6-diisopropylphenyl)-9,10-phenanthrenequinonimine, the system of conjugated C=N and C=O groups of the quinone is reduced. The resulting *o*-aminophenanthrolate complexes are structurally characterized by X-ray diffraction.

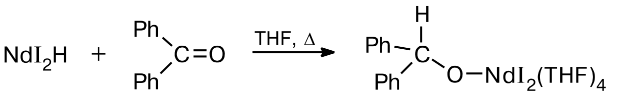
Key words: neodymium diiodide hydride, dysprosium diiodide hydride, ketones, imines, reduction, X-ray diffraction analysis.

In the synthesis of organic derivatives of rare-earth metals, common starting reagents include free lanthanides, halides LnX_2 and LnX_3 (X = Cl and I), or their hydrates.[1—7] Other inorganic compounds such as oxides Ln_2O_3, hydrides LnH_3, and carboxylates $Ln(RCO_2)_3$ are not employed, though being accessible, as sources of rare earth metals in the organolanthanide synthesis because of their low reactivity. Recently, we have found[8] that neodymium(III) and dysprosium(III) diiodide hydrides (NdI_2H and DyI_2H, respectively) can serve as promising lanthanide reagents. These compounds, which are directly prepared from diiodides LnI_2 and hydrogen, react with alcohols, phenol,[8] cyclopentadienylpotassium,[9] and potassium naphthalene[10] under mild conditions to give the corresponding complexes containing, apart from the Ln—I bonds, the Ln—OR, Ln—Cp, and Ln—$C_{10}H_8$ bonds, respectively. In a search for other possible applications of NdI_2H and DyI_2H, here we studied the reactivities of these compounds toward some carbonyl- and imino-containing substrates.

Results and Discussion

Heating of an equimolar mixture of benzophenone and NdI_2H in THF at 60 °C for 2 h (Scheme 1) produced a reddish violet solution. Subsequent workup involving concentration and addition of diethyl ether afforded adduct **1** as air-unstable colorless crystals. According to X-ray diffraction data, complex **1** results from the addition of the hydride fragment Nd—H of the starting diiodide hydride to the carbonyl group of benzophenone.

Scheme 1



1

The coordination polyhedron of the Nd atom is a distorted pentagonal bipyramid made up of four THF molecules and the I(2) atom in the equatorial plane and the diphenylmethoxy ligand $OCHPh_2$ and the I(1) atom in the axial positions (Fig. 1, Table 1). The angle Nd(1)—O(1)—C(1) (170.4(2)°) and the Nd(1)—O(1) bond length (2.111(2) Å) are typical of rare earth metal

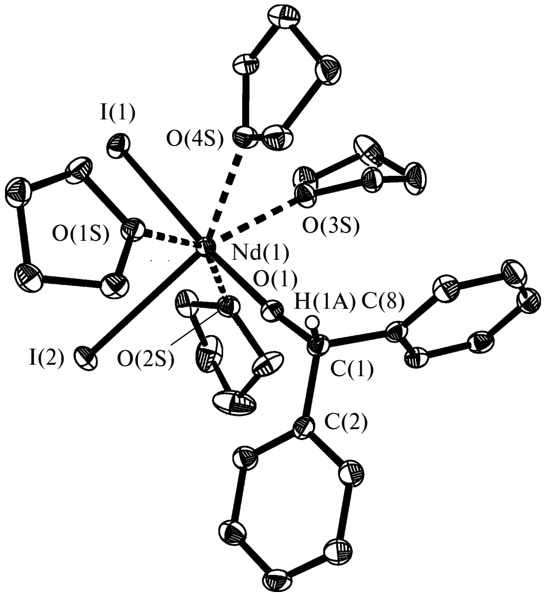


Fig. 1. Molecular structure of the complex $I_2Nd(OCHPh_2)$—$(THF)_4$ (**1**).

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1562—1565, August, 2011.

Table 1. Selected bond lengths (*d*) and bond angles (ω) in structure **1**

Bond	*d*/Å	Angle	ω/deg
Nd(1)—O(1)	2.111(2)	C(2)—C(1)—C(8)	110.8(3)
O(1)—C(1)	1.376(4)	O(1)—C(1)—C(2)	114.3(3)
Nd(1)—O(1S)	2.495(2)	O(1)—C(1)—C(8)	110.0(3)
Nd(1)—O(2S)	2.493(2)	C(1)—O(1)—Nd(1)	170.4(2)
Nd(1)—O(3S)	2.536(2)	O(1)—Nd(1)—I(1)	174.51(6)
Nd(1)—O(4S)	2.520(2)	O(1)—Nd(1)—I(2)	95.40(6)
Nd(1)—I(1)	3.1752(3)		
Nd(1)—I(2)	3.2054(3)		

alkoxides.[11—14] The C(1)—O(1) bond length (1.376(4) Å) in the diphenylmethoxy ligand is comparable with an analogous bond in the complex $Yb(OCHPh_2)_2(OAr)(HMPA)_2$ (1.369 Å).[11]

Dysprosium diiodide hydride reacts with benzophenone in a similar way, yielding a fine crystalline light yellow product. According to elemental analysis and IR spectroscopic data, this compound can be formulated as $(I_2DyOCHPh_2)_2(THF)$. However, we failed to obtain its crystals suitable for X-ray diffraction experiments.

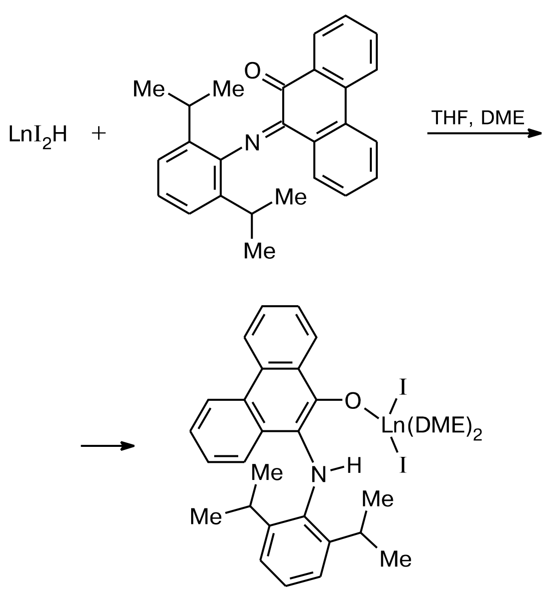
Reactions of NdI_2H and DyI_2H with 9,10-phenanthrenequinonimine in THF occurred under more drastic conditions: even exposure to ultrasound at 70 °C for 7 days provided only 40—50% conversion of the starting hydride. During the reaction, the initial green solutions characteristic of the neutral ligand turned reddish brown. By adding DME, we isolated yellow crystals of complexes **2** and **3** in 77 and 86% yields, respectively (Scheme 2). Note that the reaction in boiling acetonitrile resulted in complete dissolution of the starting iodide hydrides in 6 h. However, the yields of products **2** and **3** in this case did not exceed 50% (probably because of intense side processes).

Both compounds are very unstable in air; they are well soluble in THF but virtually insoluble in hexane.

According to X-ray diffraction data, complexes **2** and **3** are isostructural Nd^{III} and Dy^{III} aminophenanthrolate diiodides with a distorted pentagonal-bipyramidal coordination of the Ln cation. The equatorial plane consists of the O atoms of the DME molecules and the aminophenanthrolate ligand, while the iodide anions are in the axial positions (Fig. 2, Table 2).

Complexes **2** and **3** are first representatives of a novel class, namely, lanthanide aminophenanthrolates. Their closest semiquinonimine analogs **4** and **5** have been obtained recently[15] from appropriate diiodides LnI_2 and 9,10-phenanthrenequinonimine (Scheme 3).

Scheme 2



2, 3

Ln = Nd (**2**), Dy (**3**)

Interestingly, the complexes of both groups show monodentate coordination of the ligands. In view of compounds **4** and **5**, this is unusual for iminoquinone complexes. As a consequence, the geometrical parameters of the fragments Ln—L are similar. For instance, the angles Ln(1)—O(1)—C(1) in products **2** and **3** (172.1(2)° and 172.50(16)°, respectively) are smaller only by 4° than the corresponding angles in complexes **4** and **5**, while the angles O(1)—C(1)—C(2) and C(1)—C(2)—N(1) in complexes **2**—**5** vary within 1°. However, the pairs of complexes **2**, **3** and **4**, **5** differ substantially in nature. In complexes **4** and **5**, one ligand is neutral and is coordinated to the metal center, while the other is 9,10-phenanthrenesemiquinonimine with the unpaired electron at the C_{meta} atom of the central ring of the phenanthrene fragment. In complexes **2** and **3**, the phenanthrolate ligand contains the substituent $2,6-Pr^i_2C_6H_3NH$ at the C(2) atom. The protonation of the N(1) atom in these complexes is evident from both X-ray diffraction data and IR spectra (an absorption band at 3315—3320 cm^{-1}).

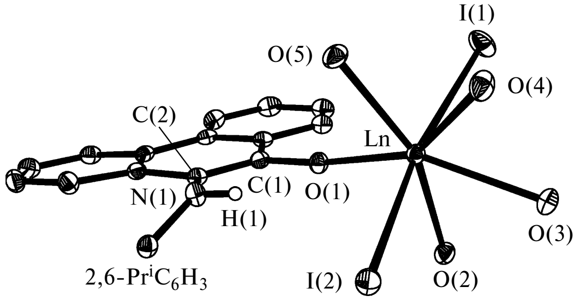


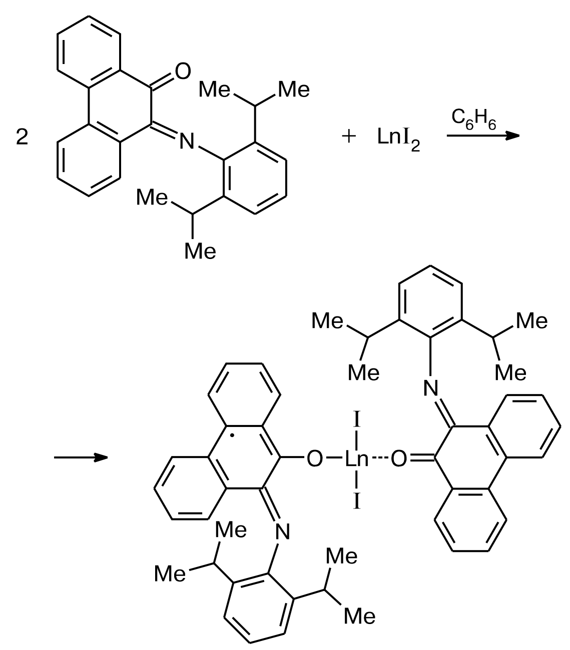
Fig. 2. Molecular structures of the complexes $LnI_2LH(DME)_2$ (Ln = Nd (**2**), Dy (**3**)). For the coordinated DME molecules, the O atoms are shown only.

Table 2. Selected bond lengths (*d*) and bond angles (ω) in structures **2** and **3**

Bond	*d*/Å	
	2	**3**
Ln(1)—O(1)	2.155(2)	2.085(2)
Ln(1)—O(2)	2.507(2)	2.434(2)
Ln(1)—O(3)	2.526(2)	2.441(2)
Ln(1)—O(4)	2.545(2)	2.463(2)
Ln(1)—O(5)	2.512(2)	2.439(2)
Ln(1)—I(1)	3.0849(3)	3.0042(2)
Ln(1)—I(2)	3.1055(3)	3.0281(2)
C(1)—O(1)	1.343(4)	1.342(3)
C(1)—C(2)	1.384(4)	1.389(4)
C(2)—N(1)	1.398(4)	1.391(3)
N(1)—C(15)	1.429(4)	1.437(3)

Angle	ω/deg	
	2	**3**
O(1)—Ln(1)—I(1)	96.77(6)	96.40(5)
O(1)—Ln(1)—I(2)	93.33(6)	93.27(5)
O(1)—Ln(1)—O(2)	79.92(8)	78.62(7)
O(1)—Ln(1)—O(3)	145.82(8)	145.90(7)
O(2)—Ln(1)—O(3)	65.98(8)	67.37(6)
Ln(1)—O(1)—C(1)	172.1(2)	172.50(16)
O(1)—C(1)—C(2)	119.5(3)	119.3(2)
C(1)—C(2)—N(1)	116.8(3)	116.9(2)
C(2)—N(1)—C(15)	128.1(3)	127.8(2)

Scheme 3



4, 5

Ln = Nd (**4**), Dy (**5**)

The magnetic moment of product **2** (3.3 μ_B) corresponds to that of the Nd^{3+} cation (μ_{eff} = 3.68 μ_B);[16] *i.e.*, the metal undergoes no redox transformations during this complexation reaction.

Attempted addition of NdI$_2$H and DyI$_2$H to the C=O (carbon monoxide), C=C (styrene), C≡C (phenylacetylene and diphenylacetylene), and N=N bonds (azobenzene) were unsuccessful: even upon exposure of the reaction mixture to ultrasound at 70 °C for many hours, the starting reactants were recovered intact.

To sum up, we found that NdI$_2$H and DyI$_2$H readily add at the C=O bond of benzophenone to give the corresponding alkoxide diiodides I$_2$LnOCHPh$_2$. Under more drastic conditions (ultrasound, 70 °C), the same iodide hydrides react with *N*-(2,6-diisopropylphenyl)-9,10-phenanthrenequinonimine in THF, yielding lanthanide complexes of a novel type, namely, (*o*-aminophenanthrolato)(diiodo)neodymium and (*o*-aminophenanthrolato)(diiodo)dysprosium.

Experimental

Reactions were carried out using standard Schlenk equipment to prevent any contact with atmospheric oxygen or moisture. The solvent THF and DME were dried and stored over Na/benzophenone and distilled *in vacuo* immediately before use. Iodide hydrides NdI$_2$H and DyI$_2$H and *N*-(2,6-diisopropylphenyl)-9,10-phenanthrenequinonimine were prepared as described earlier.[8,17] IR spectra were recorded on a FSM-1201 FTIR spectrometer in the 4000—400 cm^{-1} range. Magnetic measurements were effected according to a known procedure.[18]

X-ray diffraction studies were carried out on a Bruker AXS SMART APEX diffractometer (Mo-Kα radiation, graphite monochromator, φ—ω scan mode) at 100 K. The structures were solved by the direct methods and refined anisotropically by the full-matrix least-squares method on F^2 for all non-hydrogen atoms with the SHELXTL program package.[19] Absorption corrections were applied using the SADABS program.[20] The hydrogen atoms were located geometrically and refined isotropically using a riding model. The crystallographic parameters and the data collection statistics for structures **1**—**3** are summarized in Table 3.

Reduction of benzophenone with NdI$_2$H. A solution of benzophenone (0.35 g, 1.92 mmol) in THF (4 mL) was added to a suspension of NdI$_2$H (0.768 g, 1.92 mmol) in THF (10 mL). The reaction mixture was stirred at 60 °C for 2 h. The resulting reddish violet solution was filtered; the greater part of the solvent was removed from the vessel *in vacuo* and collected in a cooled trap. Then diethyl ether (10 mL) was slowly added to the reddish violet concentrate by diffusion under reduced pressure. The colorless crystalline precipitate that formed was washed with THF and dried *in vacuo*. The yield of product **1** was 0.35 g (20%). Found (%): C, 39.84; H, 5.65. C$_{29}$H$_{43}$O$_5$NdI$_2$. Calculat-

Table 3. Crystallographic parameters and the data collection statistics for complexes **1**—**3**

Parameter	**1**	**2**	**3**
Molecular formula	$C_{29}H_{43}I_2NdO_5$	$C_{36}H_{51}I_2NNdO_6$	$C_{36}H_{51}DyI_2NO_6$
Molecular weight	869.67	991.82	1010.08
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2(1)/c$	$P2(1)/c$	$P2(1)/c$
a/Å	9.4197(4)	11.7045(8)	11.6620(6)
b/Å	17.9246(7)	12.9607(9)	12.8756(7)
c/Å	19.4114(8)	26.7027(18)	26.543(1)
β/deg	95.480(1)	101.133(1)	101.331(1)
V/Å^3	3262.5(2)	3974.5(5)	3907.8(4)
Z	4	4	4
d_{calc}/g cm^{-3}	1.771	1.658	1.717
μ/mm^{-1}	3.517	2.901	3.533
F(000)	1692	1952	1976
Crystal dimensions/mm	0.16×0.11×0.07	0.32×0.18×0.10	0.30×0.10×0.09
θ_{max}/deg	27.50	26.00	26.50
Number of measured/independent reflections	30723/7461	33319/7798	24206/8094
R_{int}	0.0263	0.0236	0.0241
$S(F^2)$	1.055	1.085	1.067
R factor ($I > 2\sigma(I)$)			
R_1	0.0349	0.0294	0.0292
wR_2	0.0811	0.0702	0.0688
R factor for all reflections			
R_1	0.0482	0.0342	0.0349
wR_2	0.0853	0.0725	0.0709
Residual electron density, (max/min)/e Å^{-3}	2.217/—0.591	1.875/—1.195	2.079/—1.000

ed (%): C, 40.04; H, 4.95. IR (Nujol, KBr), ν/cm^{-1}: 1458 s, 1378 m, 1367 m, 1317 w, 1270 m, 1182 w, 1172 m, 1037 m, 1032 m, 1019 m, 927 w, 911 w, 754 m, 735 s, 698 s, 655 m, 603 m, 544 w.

Reduction of *N*-(2,6-diisopropylphenyl)-9,10-phenanthrenequinonimine with NdI_2H. Tetrahydrofuran (8 mL) was added to a mixture of NdI_2H (0.45 g, 1.12 mmol) and the quinonimine (0.41 g, 1.12 mmol). The suspension was heated in an ultrasound bath at 70 °C for five days. The resulting reddish brown solution was decanted from the precipitate of the starting iodide hydride NdI_2H (0.24 g) and concentrated *in vacuo*. The solid residue was washed with hexane (2×10 mL). The resulting brown powder was dissolved in THF (1 mL) and DME (5 mL) was added. The yellow crystals of complex **2** that formed were separated by decantation, washed with cold DME, and dried *in vacuo*. The yield was 0.40 g (77% with respect to the consumed NdI_2H); m.p. >180 °C (decomp.); $\mu_{eff} = 3.3\ \mu_B$. One crystal was used in an X-ray diffraction experiment. Found (%): C, 43.61; H, 5.10. $C_{36}H_{51}I_2NNdO_6$. Calculated (%): C, 43.59; H, 5.14. IR (Nujol, KBr), ν/cm^{-1}: 3321 m, 1569 s, 1296 m, 1174 w, 1113 m, 1075 s, 1033 s, 1007 m, 969 m, 927 m, 848 m, 749 m, 669 m, 641 w.

Reduction of 9,10-phenanthrenequinonimine with DyI_2H. Complex **3** was obtained from DyI_2H (0.45 g, 1.08 mmol) and the quinonimine (0.40 g, 1.09 mmol) as described above for complex **2**. The yield was 0.38 g (86% with respect to the consumed DyI_2H), yellow crystals, m.p. >120 °C (decomp.). The unreacted DyI_2H (0.27 g) was recovered. Found (%): C, 42.65; H, 5.31. $C_{36}H_{51}I_2NDyO_6$. Calculated (%): C, 42.81; H, 5.05. IR (Nujol, KBr), ν/cm^{-1}: 3317 s, 1603 m, 1575 s, 1517 w, 1488 w, 1206 m, 1190 w, 1178 w, 1119 s, 1076 s, 1031 s, 1012 s, 975 m, 932 m, 856 s, 788 m, 753 m, 696 m, 675 m.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 10-03-00190).

References

1. F. T. Edelmann, D. M. M. Freckmann, H. Schumann, *Chem. Rev.*, 2002, **102**, 1851.
2. H. Schumann, J. A. Meese-Marktscheffel, L. Esser, *Chem. Rev.*, 1995, **95**, 865.
3. A. Krief, A.-M. Laval, *Chem. Rev.*, 1999, **99**, 745.
4. W. J. Evans, *Coord. Chem. Rev.*, 2000, **206—207**, 263.
5. F. G. N. Cloke, *Chem. Soc. Rev.*, 1993, **22**, 17.
6. W. J. Evans, B. L. Davis, *Chem. Rev.*, 2002, **102**, 2119.
7. M. N. Bochkarev, L. N. Zakharov, G. S. Kalinina, *Organoderivatives of Rare Earth Elements*, Kluwer Academic Publishers, Dordrecht, 1995.
8. M. N. Bochkarev, A. A. Logunov, M. E. Burin, *Izv. Akad. Nauk, Ser. Khim.*, 2007, 1887 [*Russ. Chem. Bull., Int. Ed.*, 2007, **56**, 1953].
9. M. E. Burin, A. A. Logunov, G. K. Fukin, M. N. Bochkarev, *J. Coord. Chem.*, 2009, **62**, 3134.
10. M. E. Burin, A. A. Logunov, V. I. Faerman, M. N. Bochkarev, *Izv. Akad. Nauk, Ser. Khim.*, 2011, 1560 [*Russ. Chem. Bull., Int. Ed.*, 2011, **60**, 1591].

11. Z. Hou, A. Fujita, Y. Zhang, T. Miyano, H. Yamazaki, Y. Wakatsuki, *J. Am. Chem. Soc.*, 1998, **120**, 754.
12. M. Kritikos, M. Moustiakimov, M. Wijk, G. Westin, *J. Chem. Soc., Dalton Trans.*, 2001, 1931.
13. D. M. Barnhart, D. L. Clark, J. C. Huffman, R. L. Vincent, J. G. Watkin, *Inorg. Chem.*, 1993, **32**, 4077.
14. S. Mathur, M. Veith, H. Shen, S. Hüfner, M. H. Jilavi, *Chem. Mater.*, 2002, **14**, 568.
15. M. N. Bochkarev, A. A. Fagin, N. O. Druzhkov, V. K. Cherkasov, M. A. Katkova, G. K. Fukin, Y. A. Kurskii, *J. Organomet. Chem.*, 2010, **695**, 2774.
16. W. J. Evans, M. A. Horzbor, *J. Organomet. Chem.*, 1987, **326**, 299.
17. G. A. Abakumov, V. K. Cherkasov, N. O. Druzhkov, Yu. A. Kurskii, G. K. Fukin, L. G. Abakumova, T. N. Kocherova, *Synth. Commun.*, 2006, **36**, 3241.
18. A. V. Protchenko, M. N. Bochkarev, *Prib. Tekh. Eksp.*, 1990, **1**, 194 [*Sov. Instr. Exp. Tech.* (*Engl. Transl.*), 1990, **1**].
19. G. M. Sheldrick, *SHELXTL v. 6.12, Structure Determination Software Suite*, Bruker AXS, Madison, Wisconsin, USA.
20. G. M. Sheldrick, *SADABS v. 2.01, Bruker/Siemens Area Detector Absorption Correction Program*, Bruker AXS, Madison, Wisconsin, USA.

Received December 15, 2010