Russian Chemical Bulletin, International Edition, Vol. 55, No. 3, pp. 451—456, March, 2006

Acenaphthylene-1,2-diamine radical cation. Molecular structure of the $[(\text{dpp-BIAN})H_2]^{\bullet+}[X]^-$ complex ($(\text{dpp-BIAN})H_2$ is *N*,*N*′-bis(2,6-diisopropylphenyl)-acenaphthylene-1,2-diamine; X = Cl or I)

I. L. Fedushkin,★ *N. M. Khvoinova, A. Yu. Baurin, and G. K. Fukin*

G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences,
49 ul. Tropinina, 603950 Nizhny Novgorod, Russian Federation.
Fax: +7 (831 2) 62 7497. E-mail: igorfed@imoc.sinn.ru

Oxidation of *N*,*N*′-bis(2,6-diisopropylphenyl)acenaphthylene-1,2-diamine $(\text{dpp-BIAN})H_2$ with silicon tetrachloride or mercury(II) chloride affords the $[(\text{dpp-BIAN})H_2]^{\bullet+}[Cl]^-$ compound. The corresponding iodine derivative, $[(\text{dpp-BIAN})H_2]^{\bullet+}[I]^-$, was prepared by hydrolysis of the reaction products of the magnesium complex $(\text{dpp-BIAN})Mg(THF)_3$ with tetraiodosilane. X-ray diffraction study demonstrated that the $[(\text{dpp-BIAN})H_2]^{\bullet+}$ radical cation in these compounds chelates the corresponding halide anion.

Key words: acenaphthylene-1,2-diamines, diamines, oxidation, radical cations, chelation of halide ions, X-ray diffraction study, ESR spectroscopy.

In the last decade, acenaphthene-1,2-diimines (BIAN) have been widely used as ligands in coordination chemistry. Transition metal complexes with diimine ligands are efficient catalysts for alkyne hydrogenation,[1] carbon—carbon bond formation,[2] cycloisomerization,[3] hydrosilylation,[4] polymerization of alkenes[5] and acrylic monomers,[6] and copolymerization of CO_2 and methylenecyclopropene,[7] of ethylene and norbornene,[8] and of CO and styrene.[9] The so-called Brookhart catalysts,[10] *viz.*, acenaphthene-1,2-diimine complexes of transition metals, are the most well-known olefin polymerization catalysts. The π-acceptor properties of acenaphthene-1,2-diimines in metal complexes induce an electron deficiency at the metal atom, which is responsible for high reactivity of these complexes toward organic compounds.

In our recent studies,[11—16] we have demonstrated that main-group metals, unlike transition metals, can form complexes with different anionic forms of BIAN ligands. We used primarily 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-BIAN). A remarkable property of the dpp-BIAN ligand is that it shows variable "oxidation states" in complexes with main-group metals. Diimine dpp-BIAN can be reduced with alkali metals in ethereal media to the mono-, di-, tri-, and tetraanions to form the $(\text{dpp-BIAN})M_n(Et_2O)_n$ salts (M = Li or Na; n = 1—4).[11] In tetrahydrofuran, alkaline-earth metals reduce dpp-BIAN only to the dianion to give the monomeric $(\text{dpp-BIAN})M(THF)_n$ complexes (M = Mg, Ca, Sr, or Ba; n = 2—4).[12] Reduction of dpp-BIAN with metallic aluminum in the presence of its halides in toluene or Et_2O affords the radical-anionic compound $(\text{dpp-BIAN})AlCl_2$ and the dianionic products $(\text{dpp-BIAN})AlI(Et_2O)$ and $(\text{dpp-BIAN})AlCl(Et_2O)$, respectively.[13] We synthesized aluminum alkyl complexes with both the radical-anionic and dianionic dpp-BIAN ligands by the exchange reactions of the corresponding sodium derivatives of dpp-BIAN with alkylaluminum halides.[14] The reactions of sodium salts of dpp-BIAN with the dioxane complex of $GeCl_2$ gave the divalent germanium compounds (dpp-BIAN)Ge[15] and (dpp-BIAN)GeCl.[16]

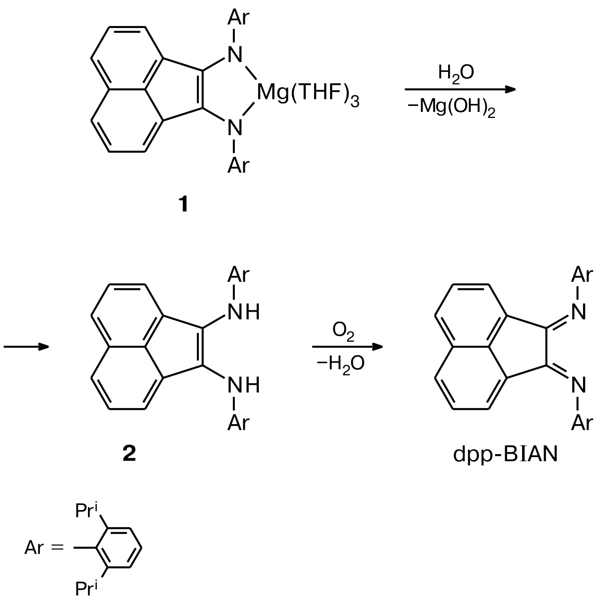
Using the $(\text{dpp-BIAN})Mg(THF)_3$ complex (**1**) with the dianionic dpp-BIAN ligand as an example, we demonstrated that acenaphthene-1,2-diimine complexes of main-group metals have specific reactivity toward various organic compounds. Complex **1** acts as a one-electron reducing agent for organic halides[17] and aromatic ketones.[18] The reactions of **1** with compounds containing a labile hydrogen atom, for example, with aliphatic ketones,[19] nitriles,[12b] and phenylacetylene,[20] involve the addition of these substrates to the complex through protonation of one nitrogen atom of the dpp-BIAN ligand to give, respectively, enolate, ketimide, and phenylethynyl derivatives. Hydrolysis of complex **1** *in vacuo* yields acenaphthylene-1,2-diamine $(\text{dpp-BIAN})H_2$ (**2**),[21] which is immediately transformed into acenaphthene-1,2-diimine dpp-BIAN when exposed to atmospheric oxygen (Scheme 1).

Recently,[16a] we have observed the transformation of the dpp-BIAN radical anion into the $(\text{dpp-BIAN})H_2$ radi-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, pp. 436—440, March, 2006.

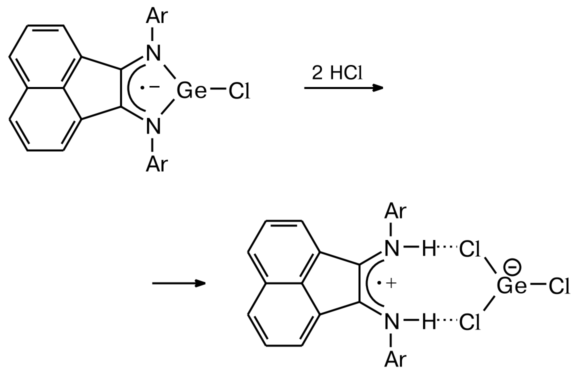
1066-5285/06/5503-0451

Scheme 1



cal cation in the reaction of (dpp-BIAN)GeCl with HCl (Scheme 2).

Scheme 2

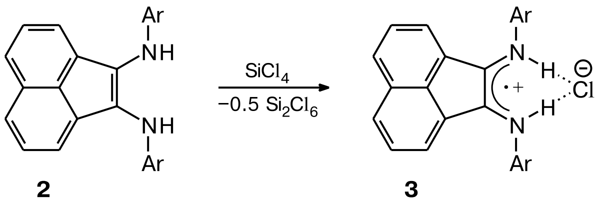


In the present study, we performed oxidation of acenaphthylene-1,2-diamine (dpp-BIAN)H$_2$ with mercury(II) and silicon(IV) chlorides giving rise to the radical-cationic derivative [(dpp-BIAN)H$_2$]$^{\bullet+}$[Cl]$^-$ (**3**). The iodine analog [(dpp-BIAN)H$_2$]$^{\bullet+}$I$^-$ (**4**) was synthesized by the reaction of compound **1** with SiI$_4$ followed by hydrolysis.

Results and Discussion

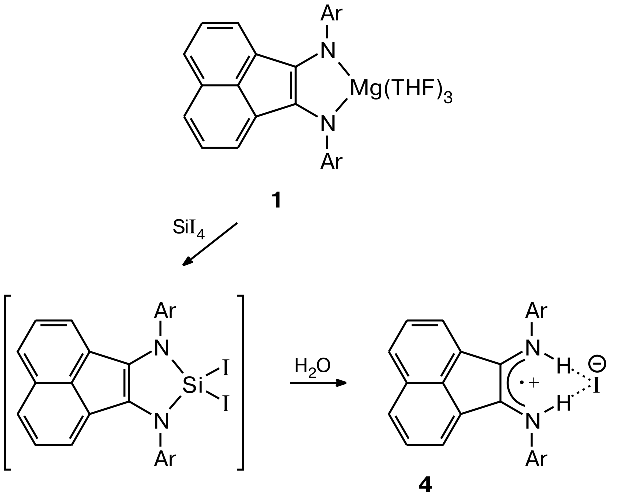
Synthesis of [(dpp-BIAN)H$_2$]$^{\bullet+}$[Cl]$^-$ (3) and [(dpp-BIAN)H$_2$]$^{\bullet+}$I$^-$ (4). After the addition of an excess of SiCl$_4$ to a solution of diamine **2** in tetrahydrofuran at room temperature, the color of the reaction mixture changed from violet to red and then to green. After removal of the solvent and volatile products *in vacuo*, compound **3** was obtained in 57% yield as dark-green prismatic crystals by crystallization of the solid residue from benzene (Scheme 3). An analogous transformation occurs in the reaction of diamine **2** with mercury(II) chloride.

Scheme 3



Compound **2** reacts with neither iodine nor mercury iodide. However, iodine analog of **3**, *viz.*, the [(dpp-BIAN)H$_2$]$^{\bullet+}$I$^-$ compound (**4**), was generated by hydrolysis of the reaction mixture, which was obtained in the reaction of complex **1** with SiI$_4$ (Scheme 4).

Scheme 4



This result was surprising. We expected that the reaction of compound **1** with SiI$_4$ would afford the (dpp-BIAN)SiI$_2$ compound. The latter, in turn, could serve as the starting reagent for the synthesis of silylene (dpp-BIAN)Si, which is a silicon analog of germylene (dpp-BIAN)Ge synthesized earlier.[15] Unfortunately, we failed to isolate the primary product of this reaction in individual form. Apparently, the [(dpp-BIAN)H$_2$]$^{\bullet+}$I$^-$ compound (**4**) is formed as a result of the transformations presented in Scheme 4. The silicon derivative (tms-BIAN)SiCl$_2$ (tms is trimethylsilyl) analogous to the intermediate presented in Scheme 4 was prepared in the crystalline state by the reaction of the dilithium salt of 1,2-bis[(trimethylsilyl)imino]acenaphthene[22] with $SiCl_4$.

Compound **4** was isolated in 42% yield as dark-green crystals by crystallization from benzene. Compounds **3** and **4** were characterized by elemental analysis, ESR spectroscopy, and IR spectroscopy. The ESR spectra of compounds **3** and **4** are identical and are septets, whose hyperfine structure is determined by splitting of the unpaired electron in the $[(dpp\text{-}BIAN)H_2]^{\bullet+}$ radical cation on two equivalent nitrogen nuclei and two equivalent protons (a_N = 0.52, a_H = 0.50 mT, g = 2.0030). The parameters of both signals are similar to those observed in the ESR spectra of the $[(dpp\text{-}BIAN)H_2]^{\bullet+}[GeCl_3]^-$ and $[\{(dpp\text{-}BIAN)H_2^{\bullet+}\}_2(Cl^-)]^+[GeCl_3]^-$ compounds (a_N = 0.53 mT, a_H = 0.48 mT, g = 2.0031).[16] In the IR spectra of compounds **2** and **3**, N—H stretching bands are observed in the 3300—3000 cm^{-1} region. These bands are virtually identical to the corresponding bands in the spectrum of the $[\{(dpp\text{-}BIAN)H_2^{\bullet+}\}_2(Cl^-)]^+[GeCl_3]^-$ compound containing two $[(dpp\text{-}BIAN)H_2]^{\bullet+}$ radical cations, which chelate the Cl^- anion (X-ray diffraction data, see Ref. 16).

The structures of compounds **3** and **4** were established by X-ray diffraction study of single crystals grown from benzene (Figs 1 and 2, respectively). The crystallographic data, details of X-ray data collection, and parameters of the structure refinement are given in Table 1. Selected bond lengths and bond angles in molecules **3** and **4** are listed in Table 2. The corresponding parameters for $[(dpp\text{-}BIAN)H_2]^{\bullet+}[GeCl_3]^-$ (**5**)[16] and the Na complex with the $(dpp\text{-}BIAN)^{\bullet-}$ radical anion (**6**)[11a] are given in Table 2 for comparison.

In molecules **3** and **4**, the $[(dpp\text{-}BIAN)H_2]^{\bullet+}$ radical cation chelates the corresponding halide anion. The H(1) and H(2) atoms were at the nitrogen atoms located from difference Fourier maps at distances of 0.92 and 0.96 Å in molecule **3** and 0.84 and 0.85 Å in molecule **4**. It should be noted that the nitrogen atoms have a trigonal planar geometry (sp^2 hybridization) rather than a pyramidal geometry typical of amines. In the trigonal planar structure, the lone electron pair of each nitrogen atom efficiently interacts with the p_z orbitals of the C(1) and C(2) atoms, due to which the unpaired electron is delocalized over the π system involving the N(1)—C(1)—C(2)—N(2) atoms. Earlier, the structure of only one acenaphthylene-1,2-diamine, *viz.*, *N,N′*-bis(2-biphenyl)acenaphthylene-1,2-diamine $[(dph\text{-}BIAN)H_2]$, has been established by X-ray diffraction.[21] Although the N—H distances in $(dph\text{-}BIAN)H_2$ (0.92(3) and 0.86(3) Å) are similar to the corresponding distances in compounds **3** and **4** and the nitrogen atoms also have a trigonal planar geometry, the C—N and C—C distances in the N(1)—C(1)—C(2)—N(2) fragment in molecules **3** and **4** substantially differ from those in $(dph\text{-}BIAN)H_2$. In $(dph\text{-}BIAN)H_2$, the C(1)—N(1), C(2)—N(2), and C(1)—C(2) distances (1.395(3), 1.400(3), and 1.369(3) Å, respectively) are similar to the corresponding distances in metal complexes with the dph-BIAN dianion.[15a,23]

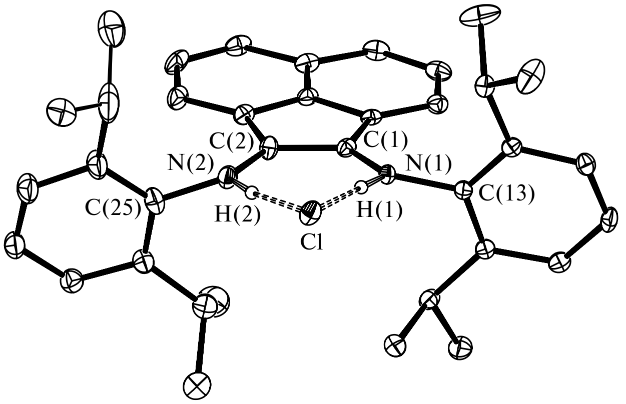


Fig. 1. Molecular structure of $[(dpp\text{-}BIAN)H_2]^{\bullet+}[Cl]^-$ (**3**) represented by thermal ellipsoids at the 30% probability level. The hydrogen atoms, except for those at the nitrogen atoms, are omitted.

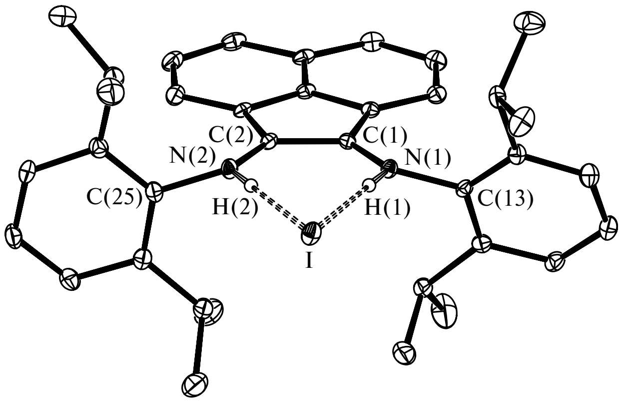


Fig. 2. Molecular structure of $[(dpp\text{-}BIAN)H_2]^{\bullet+}[I]^-$ (**4**) represented by thermal ellipsoids at the 30% probability level. The hydrogen atoms, except for those at the nitrogen atoms, are omitted.

In fact, $(dph\text{-}BIAN)H_2$ can be considered as a complex of the $(dph\text{-}BIAN)^{2-}$ dianion with two H^+ cations. In compounds **3** and **4**, the C(1)—N(1), C(2)—N(2), and C(1)—C(2) distances (see Table 2) are similar to the corresponding distances in metal complexes with the $(dpp\text{-}BIAN)^{\bullet-}$ radical anion.[11a,12b,13,14a,16a] In other words, the $[(dpp\text{-}BIAN)H_2]^{\bullet+}$ radical cation can be prepared by the addition of two protons to the $[(dpp\text{-}BIAN)]^{\bullet-}$ radical anion.

The average distances between the H(1) and H(2) atoms, on the one hand, and the halogen atoms, on the other hand, in compounds **3** and **4** are 2.13 and 2.62 Å, respectively. The difference between these distances is substantially larger than the difference between the atomic radii (R_{Cl} = 1.0 Å, R_I = 1.4 Å)[24] and ionic radii (R_{Cl} = 1.81 Å, R_I = 2.20 Å)[24] of the chlorine and iodine atoms.

Table 1. Crystallographic parameters, details of X-ray diffraction data collection, and characteristics of the structure refinement of compounds **3** and **4**

Parameter	**3**	**4**
Molecular formula	$C_{36}H_{42}ClN_2$	$C_{36}H_{42}IN_2$
Molecular weight	538.17	629.62
Crystal system	Orthorhombic	Orthorhombic
T/K	100	100
Space group	$P2_12_12_1$	$P2_12_12_1$
a/Å	10.6190(10)	11.2074(5)
b/Å	12.3809(11)	12.2367(5)
c/Å	23.600(2)	23.6897(11)
V/Å^3	3102.8(5)	3248.8(2)
Z	4	4
ρ_{calc}/g cm^{-3}	1.152	1.287
μ/mm^{-1}	0.149	1.011
F(000)	1156	1300
Crystal dimensions/mm	0.15×0.12×0.10	0.35×0.16×0.04
Scan range, θ/deg	1.73—25.01	1.72—26.50
Indices of measured reflections	$-12 \le h \le 12$ $-14 \le k \le 14$ $-28 \le l \le 27$	$-14 \le h \le 14$ $-15 \le k \le 15$ $-29 \le l \le 29$
Number of observed reflections	24365	28989
Number of independent reflections (R_{int})	5476 (0.0836)	6729 (0.0469)
Absorption correction SADABS (max/min)	0.9852/0.9780	0.9607/0.7186
Number of parameters in refinement	378	520
Number of restrictions	34	0
GOOF (F^2)	1.032	1.007
R_1/wR_2 ($I > 2\sigma(I)$)	0.0636/0.1384	0.0279/0.0535
R_1/wR_2 (based on all reflections)	0.0887/0.1505	0.0351/0.0551
$\Delta\rho$ (max)/$\Delta\rho$ (min) /e Å^3	0.632/–0.457	0.718/–0.267

Table 2. Selected bond lengths (d) and bond angles (ω) in compounds **3**, **4**, $[(\text{dpp-BIAN})H_2]^{\bullet+}[GeCl_3]^-$ (**5**),[16] and $(\text{dpp-BIAN})^{\bullet-}Na^+$ (**6**)[11a]

Parameter	**3**	**4**	**5**	**6**
Bond		d/Å		
N(1)—H(1)	0.92(6)	0.84(3)	0.86(3)	—
N(2)—H(2)	0.96(6)	0.85(3)	0.92(3)	—
Hal—H(1)*	2.12(5)	2.64(2)	—	—
Hal—H(2)*	2.14(5)	2.60(2)	—	—
N(1)—C(1)	1.334(5)	1.332(3)	1.344(2)	1.324(2)
N(2)—C(2)	1.332(5)	1.324(3)	1.326(2)	1.333(2)
C(1)—C(2)	1.435(5)	1.441(3)	1.447(3)	1.446(2)
N(1)—C(13)	1.439(5)	1.438(3)	1.454(2)	1.411(2)
N(2)—C(25)	1.441(5)	1.456(3)	1.441(2)	1.406(2)
Angle		ω/deg		
H(1)—Hal—H(2)*	56.6(7)	48.9(4)	—	—
Hal—H(1)—N(1)*	174.0(7)	176.6(4)	—	—
Hal—H(2)—N(2)*	172.5(7)	177.2(4)	—	—

* Hal = Cl (**3**, **5**) or I (**4**).

To summarize, we demonstrated that acenaphthylene-1,2-diamine can be oxidized to the radical cation with some reagents, for example, with $SiCl_4$ and $HgCl_2$. We believe that the radical-cationic salts $[(\text{dpp-BIAN})H_2]^{\bullet+}[Cl]^-$ (**3**) and $[(\text{dpp-BIAN})H_2]^{\bullet+}I^-$ (**4**) can be used as reagents for hydrochlorination and hydroiodination of organic compounds. In addition, we plan to use compounds **3** and **4** for the synthesis of main-group metal complexes with the dpp-BIAN ligand in nonsolvating media by deprotonation of the $[(\text{dpp-BIAN})H_2]^{\bullet+}$ radical cation with organolithium, -magnesium, and -aluminum compounds.

Experimental

Compounds **1** and **2** are very sensitive to atmospheric oxygen and moisture, whereas compounds **3** and **4** are slowly oxidized with atmospheric oxygen only in solution to form diimine dpp-BIAN. All operations associated with the synthesis, isolation, and identification of compounds **3** and **4** were carried out *in vacuo* using the Schlenk technique. Compound **1** was synthesized according to a procedure described earlier.[12a] Tetrahydrofuran and benzene were dried over sodium benzophenone ketyl and withdrawn by vacuum condensation immediately before use. The IR spectra of compounds **3** and **4** were recorded on a FSM-1201 Fourier-transform spectrometer (Monitoring Ltd.) in Nujol mulls. The ESR spectra were measured on a Bruker ER 200D-SRC instrument.

***N,N′*-Bis(2,6-diisopropylphenyl)acenaphthylene-1,2-diamine radical cation chloride (3). Method *A* (from (dpp-BIAN)H_2 and $SiCl_4$).** Methanol (0.1 g, 3.1 mmol) was added to a solution of complex **1**, which was prepared from diimine dpp-BIAN (0.5 g, 1 mmol) in THF (30 mL). The color of the reaction mixture immediately changed from green to violet, which is indicative of the formation of diamine (dpp-BIAN)H_2 (**2**). The precipitate that formed was filtered off. Tetrachlorosilane (0.5 g, 2.9 mmol) was added to the cooled filtrate. The reaction mixture turned green within a few minutes. The solvent was removed *in vacuo*, and the residue was dissolved in benzene (20 mL). Crystallization from benzene afforded compound **3** in a yield of 0.3 g (57%) as dark-green, almost black, crystals, m.p. 188 °C (decomp.). Found (%): C, 80.28; H, 7.78. $C_{36}H_{42}ClN_2$ (M 538.17). Calculated (%): C, 80.34; H, 7.87. IR, ν/cm^{-1}: 3234 w, 3111 w, 3061 w, 1965 w, 1899 w, 1834 w, 1657 w, 1619 m, 1584 m, 1534 s, 1488 m, 1361 w, 1330 m, 1292 w, 1257 w, 1188 m, 1150 w, 1104 w, 1061 m, 1042 w, 977 w, 938 m, 850 w, 831 v.s, 804 v.s, 777 v.s, 757 m, 669 w, 611 m, 573 w, 534 m, 504 w, 477 w.

Method *B* (from (dpp-BIAN)H_2 and $HgCl_2$). Mercury chloride (0.26 g, 0.96 mmol) was added to a solution of diamine (dpp-BIAN)H_2 (**2**), which was prepared according to the above-described procedure. The reaction mixture was vigorously stirred for 5 min, during which it turned green. The solvent was removed *in vacuo*, and the residue was dissolved in benzene (20 mL). Crystallization from benzene afforded compound **3** (0.29 g, 54%) as dark-green, almost black, crystals. The

IR spectrum of this product is identical to the above-described spectrum.

***N,N´*-Bis(2,6-diisopropylphenyl)acenaphthylene-1,2-diamine radical cation iodide (4).** Silicon tetraiodide (0.5 g, 0.93 mmol) was added to a solution of complex **1**, which was prepared from diimine dpp-BIAN (0.5 g, 1 mmol) in THF (30 mL). The color of the reaction mixture immediately changed from green to crimson-red. After the addition of H_2O (0.4 g, 22 mmol) to the resulting solution, the reaction mixture immediately turned green. After removal of the solvent, the residue was dried *in vacuo* for 30 min. Compound **4** (0.24 g, 38%) was isolated as dark-green, almost black, crystals from benzene, m.p. 176 °C (decomp.). Found (%): C, 68.51; H, 6.70. $C_{36}H_{42}IN_2$ (M 629.62). Calculated (%): C, 68.67; H, 6.72. IR, ν/cm^{-1}: 3215 w, 3080 w, 3042 w, 1965 w, 1896 w, 1831 w, 1611 m, 1588 m, 1523 s, 1426 w, 1361 w, 1323 w, 1292 w, 1254 w, 1184 m, 1146 w, 1107 w, 1061 m, 1042 w, 984 w, 934 m, 850 w, 831 v.s, 804 v.s, 773 v.s, 754 m, 684 w, 611 m, 569 w, 531 m, 504 w, 477 w.

X-ray diffraction study of compounds 3 and 4. X-ray diffraction data sets were collected on a Bruker AXS SMART APEX diffractometer at 100 K (ω-φ-scanning technique, Mo-Kα radiation, λ = 0.71073 Å, graphite monochromator) at 173 K. Absorption corrections were applied using the SADABS program.[25] The structures were solved by direct methods using the SHELXS97 program package[26] and refined by the full-matrix least-squares method against F^2 with the use of the SHELXL97 program package.[27] All nonhydrogen atoms were refined anisotropically. The hydrogen atoms were placed in idealized positions (U_{iso} = 0.08 Å^3). The atomic coordinates were deposited with the Cambridge Structural Database.

This study was financially supported by the Russian Foundation for Basic Research (Project No. 05-03-32643), the Council on Grants of the President of the Russian Federation (Program for State Support of Leading Scientific Schools of the Russian Federation, Grant NSh-58.2003.3), and the Federal Agency for Science and Innovations of the Ministry of Education and Science of the Russian Federation (State Contract 2006-RI-19.0/001/206).

References

1. M. W. van Laren and C. J. Elsevier, *Angew. Chem., Int. Ed.*, 1999, **38**, 3715.
2. (a) R. van Belzen, H. Hoffmann, and C. J. Elsevier, *Angew. Chem., Int. Ed.*, 1997, **36**, 1743; (b) G. A. Grasa, R. Singh, E. D. Stevens, and S. P. Nolan, *J. Organomet. Chem.*, 2003, **687**, 269.
3. A. Heumann, L. Giordano, and A. Tenaglia, *Tetrahedron Lett.*, 2003, **44**, 1515.
4. J. W. Sprengers, M. de Greef, M. A. Duin, and C. J. Elsevier, *Eur. J. Inorg. Chem.*, 2003, 3811.
5. (a) E. Cherian, E. B. Lobkovsky, and G. W. Coates, *Chem. Commun.*, 2003, **20**, 2566; (b) F. Al-Abaidi, Z. Ye, and S. Zhu, *Macromol. Chem. Phys.*, 2003, **204**, 1653; (c) V. Fassina, C. Ramminger, M. Seferin, R. S. Mauler, R. F. de Souza, and A. L. Monteiro, *Macromol. Rapid Commun.*, 2003, **24**, 667; (d) M. D. Leatherman, S. A. Svejda, L. K. Johnson, and M. Brookhart, *J. Am. Chem. Soc.*, 2003, **125**, 3068.
6. I. Kim, J.-M. Hwang, J. K. Lee, C. S. Ha, and S. I. Woo, *Macromol. Rapid Commun.*, 2003, **24**, 508.
7. D. Takeuchi, A. Yasuda, and K. Osakada, *Dalton Trans.*, 2003, 2029.
8. J. Kiesewetter and W. Kaminsky, *Chem. Eur. J.*, 2003, **9**, 1750.
9. B. Binotti, C. Carfagna, C. Zuccaccia, and A. Macchioni, *Chem. Commun.*, 2005, 92.
10. (a) B. S. Williams, M. D. Leatherman, P. S. White, and M. Brookhart, *J. Am. Chem. Soc.*, 2005, **127**, 5132; (b) J. Merna, J. Cihlar, M. Kucera, A. Deffieux, and H. Cramail, *Eur. Polym. J.*, 2005, **41**, 303; (c) W. Liu and M. Brookhart, *Organometallics*, 2004, **23**, 6099; (d) D. H. Camacho, E. V. Salo, J. W. Ziller, and Z. Guan, *Angew. Chem., Int. Ed.*, 2004, **43**, 1821.
11. (a) I. L. Fedushkin, A. A. Skatova, V. A. Chudakova, and G. K. Fukin, *Angew. Chem., Int. Ed. Engl.*, 2003, **42**, 3294; (b) I. L. Fedushkin, A. A. Skatova, V. A. Chudakova, V. K. Cherkasov, G. K. Fukin, and M. A. Lopatin, *Eur. J. Inorg. Chem.*, 2004, 388.
12. (a) I. L. Fedushkin, A. A. Skatova, V. A. Chudakova, G. K. Fukin, S. Dechert, and H. Schumann, *Eur. J. Inorg. Chem.*, 2003, 3336; (b) I. L. Fedushkin, A. G. Morozov, O. V. Rassadin, and G. K. Fukin, *Chem. Eur. J.*, 2005, **11**, 5749.
13. A. N. Lukoyanov, I. L. Fedushkin, M. Hummert, and H. Schumann, *Izv. Akad. Nauk, Ser. Khim.*, 2006, No. 3, 409 [*Russ. Chem. Bull., Int. Ed.*, 2006, **55**, No. 3].
14. (a) H. Schumann, M. Hummert, A. N. Lukoyanov, and I. L. Fedushkin, *Organometallics*, 2005, **24**, 3891; (b) A. N. Lukoyanov, I. L. Fedushkin, M. Hummert, and H. Schumann, *Z. Anorg. Allg. Chem.*, 2006, **632**, No. 819.
15. I. L. Fedushkin, A. A. Skatova, V. A. Chudakova, N. M. Khvoinova, A. Yu. Baurin, S. Dechert, M. Hummert, and H. Schumann, *Organometallics*, 2004, **23**, 3714.
16. (a) I. L. Fedushkin, N. M. Khvoinova, A. Yu. Baurin, G. K. Fukin, V. K. Cherkasov, and M. P. Bubnov, *Inorg. Chem.*, 2004, **43**, 7807; (b) I. L. Fedushkin, N. M. Khvoinova, A. Yu. Baurin, V. A. Chudakova, A. A. Skatova, V. K. Cherkasov, G. K. Fukin, and E. V. Baranov, *Izv. Akad. Nauk, Ser. Khim.*, 2006, 71 [*Russ. Chem. Bull., Int. Ed.*, 2006, **55**, No. 1].
17. (a) I. L. Fedushkin, A. A. Skatova, A. N. Lukoyanov, V. A. Chudakova, S. Dechert, M. Hummert, and H. Schumann, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 2641 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 2751]; (b) I. L. Fedushkin, V. M. Makarov, E. C. E. Rosenthal, and G. K. Fukin, *Eur. J. Inorg. Chem.*, 2006, 827.
18. I. L. Fedushkin, A. A. Skatova, V. K. Cherkasov, V. A. Chudakova, S. Dechert, M. Hummert, and H. Schumann, *Chem. Eur. J.*, 2003, **9**, 5778.
19. I. L. Fedushkin, A. A. Skatova, G. K. Fukin, M. Hummert, and H. Schumann, *Eur. J. Inorg. Chem.*, 2005, 2332.
20. I. L. Fedushkin, N. M. Khvoinova, A. A. Skatova, and G. K. Fukin, *Angew. Chem., Int. Ed.*, 2003, **42**, 5223.
21. I. L. Fedushkin, V. A. Chudakova, S. Dechert, M. Hummert, and H. Schumann, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 2634 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 2744].

22. I. L. Fedushkin, N. M. Khvoinova, A. V. Piskunov, G. K. Fukin, M. Hummert, and H. Schumann, *Izv. Akad. Nauk, Ser. Khim.*, 2006, No. 5 [*Russ. Chem. Bull., Int. Ed.*, 2006, **55**, No. 5].
23. I. L. Fedushkin, V. A. Chudakova, A. A. Skatova, N. M. Khvoinova, Yu. A. Kurskii, T. A. Glukhova, G. K. Fukin, S. Dechert, M. Hummert, and H. Schumann, *Z. Anorg. Allg. Chem.*, 2004, **630**, 501.
24. S. S. Batsanov, *Eksperimental´nye osnovy strukturnoi khimii* [*Experimental Fundamentals of Structural Chemistry*], Izd-vo standartov, Moscow, 1986, p. 238 (in Russian).
25. G. M. Sheldrick, *Empirical Absorption Correction Program*, Universität Göttingen, Göttingen (Germany), 1996.
26. G. M. Sheldrick, *Program for Crystal Structure Solution*, Universität Göttingen, Göttingen (Germany), 1990.
27. G. M. Sheldrick, *Program for Crystal Structure Refinement*, Universität Göttingen, Göttingen (Germany), 1997.

Received December 20, 2005;
in revised form March 9, 2006