Russian Chemical Bulletin, International Edition, Vol. 53, No. 12, pp. 2751—2762, December, 2004

Reactions of (dpp-BIAN)Mg(thf)$_3$ complex (dpp-BIAN is 1,2-bis{(2,6-diisopropylphenyl)imino}acenaphthene) with halogen-containing reagents

I. L. Fedushkin,[a]* A. A. Skatova,[a] A. N. Lukoyanov,[a] V. A. Chudakova,[a]
S. Dechert,[b] M. Hummert,[b] and H. Schumann[b]

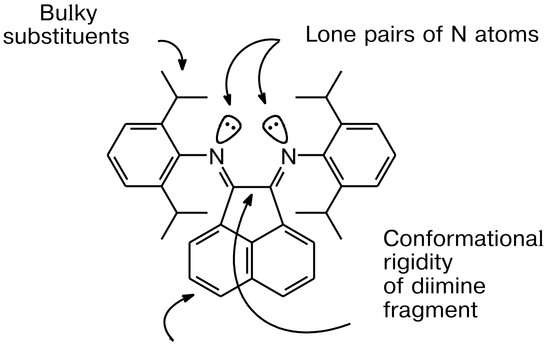
[a]G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences,
49 ul. Tropinina, 603950 Nizhnii Novgorod, Russian Federation.
Fax: +7 (831 2) 12 7497. E-mail: igorfed@imoc.sinn.ru
[b]Technical University of Berlin,
D-10623 Berlin, Germany.*
Fax: +49 (30) 3142 2168

The reactions of the acenaphthenediimine complex (dpp-BIAN)Mg(thf)$_3$ (**1**) (dpp-BIAN is 1,2-bis{(2,6-diisopropylphenyl)imino}acenaphthene) with various chlorine-, bromine-, and iodine-containing reagents afforded the unsymmetrical compounds [(dpp-BIAN)MgCl(thf)]$_2$ (**6**), [(dpp-BIAN)MgBr(thf)]$_2$ (**7**), and (dpp-BIAN)MgI(DME) (**8**). The reaction of complex **1** with Me_3SiCl in THF is accompanied by the cleavage of the THF molecule to form [{dpp-BIAN$(CH_2)_4OSiMe_3$}MgCl]$_2$ (**9**), in which the trimethylsilanyloxybutyl group is bound to one of the carbon atoms of the diimine fragment. The reaction of complex **1** with $Me_2NCH_2CH_2Cl$ in THF produces the [dpp-BIAN(H)$(CH_2)_2NMe_2$] compound (**10**) containing no magnesium. Paramagnetic complexes **6**—**8** were characterized by ESR spectroscopy. Diamagnetic compounds **9** and **10** were studied by ^{1}H and ^{13}C NMR spectroscopy. The molecular structures of complexes **6**—**10** were established by X-ray diffraction analysis. In the crystalline state, compounds **6**, **7**, and **9** exist as halogen-bridged dimers. In all magnesium derivatives, BIAN serves as a chelate ligand.

Key words: magnesium, diimine ligands, dianion, reduction, radical anion.

Transition metal complexes with 1,3-diaza-1,4-butadiene ligands, in particular, acenaphthene-1,2-diimine (BIAN) derivatives, have attracted attention due to a number of interesting chemical properties of these complexes. These compounds exhibit catalytic activity in alkyne hydrogenation,[1] C—C bond formation,[2,3] cycloisomerization,[4] and, particularly, in polymerization of various olefins[5—9] and acrylic monomers,[10] and copolymerization of CO_2 with methylenecyclopropane[11] and of ethylene with norbornene.[12]

Recently, we have begun studies aimed at developing new reactions of organic molecules with acenaphthenediimine complexes of main-group metals. At that moment, neither main-group metal complexes with BIAN ligands nor compounds containing BIAN in the anionic form were known. Acenaphthene-1,2-diimines have the following distinguishing features as the ligands: (1) conformational rigidity of the chelating diimine fragment; (2) presence of the lone electron pairs of the nitrogen atoms serving as centers of metal-atom coordination and proton-acceptor centers; (3) presence of the π-system, which can act as an electron reservoir.



1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-BIAN)

Recently,[13,14] we have synthesized and characterized alkali and alkaline-earth metal complexes with various

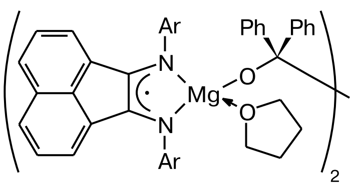
---

* Institute für Chemie der Technischen Universität Berlin, Straße der 17 Juni 135, D-10623 Berlin, Germany.

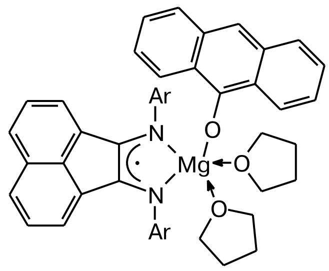
Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2641—2651, December, 2004.

reduced forms of 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-BIAN). Reduction of dpp-BIAN with alkali metals (Li, Na) in solvating solvents allowed us to prepare four anionic (dpp-BIAN)$^{n-}$ forms (n = 1, 2, 3, and 4) for the first time. Each anionic form was isolated in the crystalline state and characterized by X-ray diffraction analysis. The mononuclear (dpp-BIAN)$^{2-}$M^{2+}(thf)$_n$ complexes (M = Mg, n = 3; M = Ca, n = 4) were synthesized in nearly quantitative yields by reduction of dpp-BIAN with Mg or Ca metal in THF.[15] The synthesis of two new BIAN ligands, *viz.*, 1,2-bis[(2,5-di-*tert*-butylphenyl)imino]acenaphthene (dtb-BIAN) and 1,2-bis[(2-diphenyl)imino]acenaphthene (dph-BIAN), and their complexes with magnesium and calcium was documented.[16] The exchange reactions of $GeCl_2(C_4H_8O_2)$ with magnesium derivatives of the above three BIAN ligands afforded germylenes (dpp-BIAN)Ge, (dtb-BIAN)Ge, and (dph-BIAN)Ge, which were structurally characterized.[17]

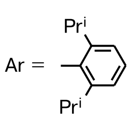
It was found that the (dpp-BIAN)Mg(thf)$_3$ complex (**1**) readily reduces benzophenone, resulting in oxidation of the dpp-BIAN dianion to the radical anion and the formation of the corresponding pinacolate [(dpp-BIAN)$^{\bullet-}$Mg(thf)]$_2$[μ-$O_2C_2Ph_4$] (**2**).[18] By contrast, the reaction of **1** with 9(10H)-anthracenone involves deprotonation of its phenol tautomer giving rise to the anthryl-9-oxy derivative (dpp-BIAN)$^{\bullet-}$Mg($OC_{14}H_9$)(thf)$_2$ (**3**).[18]



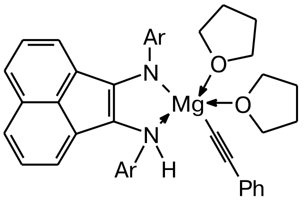
2



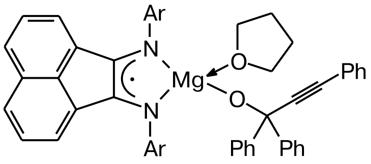
3



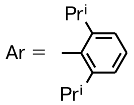
In the reaction of complex **1** with phenylacetylene, the latter binds to complex **1** to give the phenylethynyl derivative [dpp-BIAN(H)]Mg(C≡CPh)(thf)$_2$ (**4**). The insertion of benzophenone into **4** is accompanied by abstraction of the H atom and oxidation of the dpp-BIAN ligand to the radical anion giving rise to the alkoxide (dpp-BIAN)$^{\bullet-}$Mg[OC(Ph$_2$)CCPh](thf) (**5**).[19]



4



5

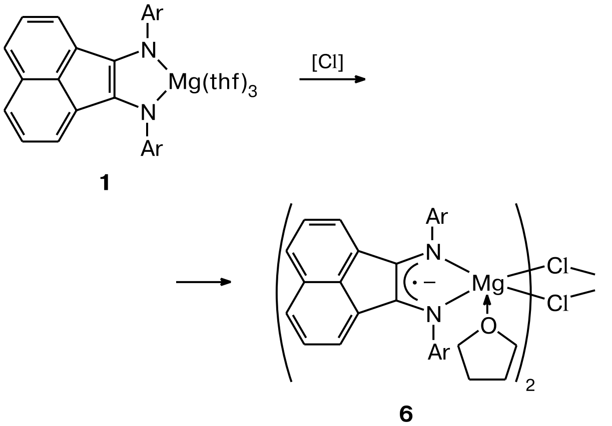


As part of our continuing studies, we investigated the reactions of complex **1** with halogen-containing reagents. In the present study, we found a new type of reactions of complex **1**, which can be classified as the oxidative addition of a halogen-containing substrate to the C—N—Mg group.

Results and Discussion

Oxidation of (dpp-BIAN)Mg(thf)$_3$ (1) to (dpp-BIAN)MgCl(thf) (6). The reactions of complex **1** with such reagents as CuCl, $HgCl_2$, $CHCl_3$, $SiCl_4$, or Ph_3SnCl in a THF solution lead to oxidation of the dpp-BIAN dianion to the radical anion giving rise to (dpp-BIAN)MgCl(thf) (**6**) in 72% yield (Scheme 1).

Scheme 1



[Cl] = CuCl, $HgCl_2$, $CHCl_3$, $SiCl_4$, Ph_3SnCl

The first two reactions give finely dispersed Cu and Hg metals, respectively. The reaction with Ph_3SnCl yields Ph_6Sn_2 as the second product. We failed to isolate and identify the by-product formed in the reaction with $SiCl_4$.

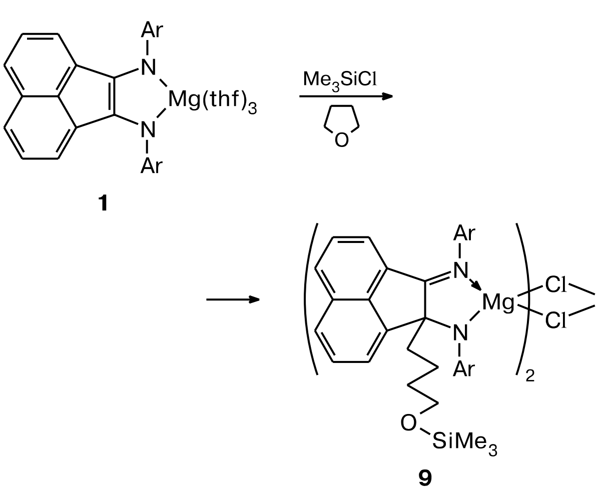
We believe that this reaction affords hexachlorodisilane as a silicon-containing product. After removal of the solvent from the reaction mixture, we obtained a resinous product, which gradually solidified. Crystallization of this product from diethyl ether afforded compound **6** as dark-red (almost black) prismatic crystals. Compound **6** was identified by elemental analysis and IR and ESR spectroscopy. The crystal structure of **6** was established by X-ray diffraction analysis. Complex **6** is paramagnetic both in the crystalline state and solution. At room temperature, the ESR spectrum of a solution in toluene has a signal (quintet, $g = 2.0048$, $A_N = 0.42$ mT), whose parameters indicate that the unpaired electron in molecule **6** is localized on the dpp-BIAN ligand. Analogous spectra were recorded[14] for the (dpp-BIAN)M compounds (M = Li, Na).

Reaction of (dpp-BIAN)Mg(thf)$_3$ (1) with 1,2-dibromo-1,2-diphenylethane. After the addition of 1,2-dibromo-1,2-diphenylethane (0.5 equiv.) to a solution of complex **1** in THF, the reaction mixture virtually immediately turned red. After removal of the solvent and crystallization from diethyl ether, the (dpp-BIAN)MgBr(thf) compound (**7**) was isolated as dark-red prismatic crystals. The IR spectrum of complex **7** is virtually identical to the spectrum of complex **6**. The ESR signal of compound **7**, unlike that of compound **6**, appears as a sextet (toluene, 293 K, $g = 2.0045$, $A_N = 0.44$, $A_{Br} = 0.2$ mT), which is indicative of splitting of the unpaired electron not only on two N atoms of the BIAN ligand but also on the Br atom.

Oxidation of (dpp-BIAN)Mg(thf)$_3$ (1) with iodine. After the addition of iodine (0.5 equiv.) to a solution of complex **1** in THF, the color of the reaction mixture immediately changed from green to red. The replacement of the solvent by 1,2-dimethoxyethane and then by toluene allowed us to isolate the (dpp-BIAN)MgI(DME) compound (**8**) from a concentrated toluene solution as orange-red crystals in 76% yield. The ESR spectrum of complex **8**, unlike that of complex **6**, has eight lines (octet, $g = 2.0022$, $A_N = 0.44$, $A_I = 0.27$ mT) associated with splitting of the unpaired electron on two N atoms (^{14}N, $I = 1$, 99.6%) and on the I atom (^{127}I, $I = 5/2$, 100%).

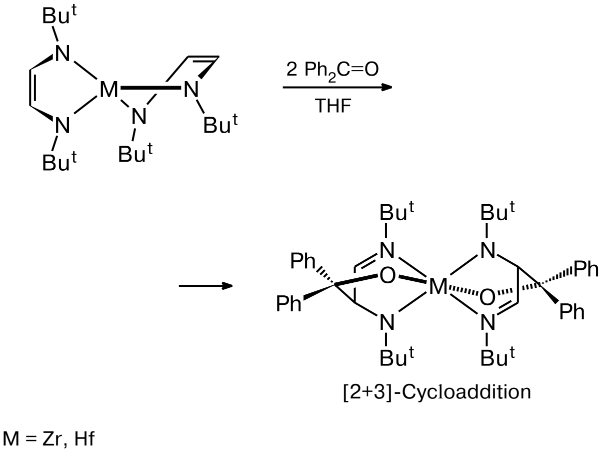
Reaction of (dpp-BIAN)Mg(thf)$_3$ (1) with Me$_3$SiCl. The reaction proceeds somewhat slower than the above-described processes and requires heating of the mixture over a short period of time. As in the above reactions, the color of the solution changed from green to red, although the color was visually less intense. A resinous product obtained after removal of the solvent *in vacuo* is readily soluble in hexane. After repeated removal and addition of hexane, compound **9** was isolated in the crystalline state. Apparently, this workup provides more complete removal of THF. Recrystallization of the finely crystalline powder from benzene or toluene afforded compound **9** as large pink prismatic crystals. The absence of the ESR signal in the spectrum of compound **9** suggests that the reaction with Me$_3$SiCl, unlike that with SiCl$_4$, did not lead to oxidation of the dpp-BIAN dianion to the radical anion. The composition and structure of compound **9** were established by ^{1}H, ^{13}C, and ^{1}H—^{1}H COSY NMR spectroscopy and X-ray diffraction analysis. The reaction of **1** with Me$_3$SiCl involves the cleavage of the THF molecule and the attachment of the Cl atom to the Mg atom. The cleavage of THF gives an electrophilic species, which attacks the C atom of the diimine fragment (nucleophilic center of complex **1**) to form [{dpp-BIAN(CH$_2$)$_4$OSiMe$_3$}MgCl]$_2$ (**9**) (Scheme 2).

Scheme 2



The cleavage of THF with trimethylchlorosilane in the presence of magnesium metal was documented.[20] Refluxing of a mixture of Mg (0.5 mol), Me$_3$SiCl (1.0 mol), and THF (2.0 mol) for 175 h followed by hydrolysis of the reaction mixture afforded 4-trimethylsilylbutanol HO(CH$_2$)$_4$SiMe$_3$ in 40% yield.[20] It is known[21] that phosphorus halides also cleave THF in the presence of magne-

Scheme 3



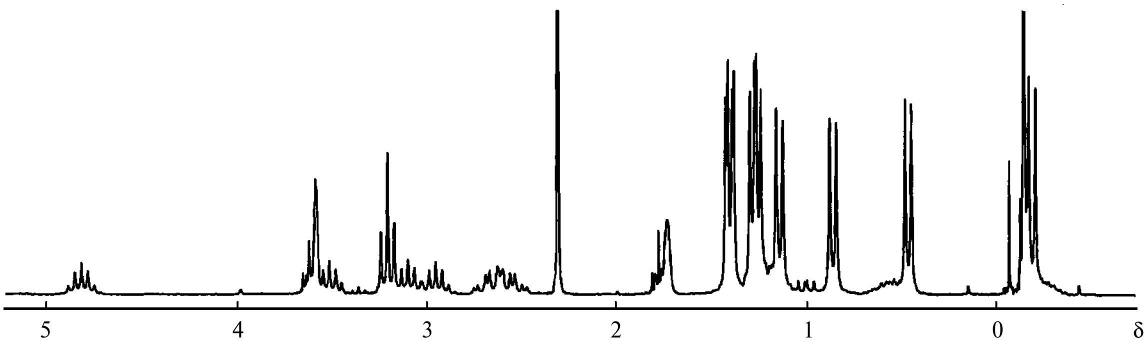


Fig. 1. ^{1}H NMR spectrum of complex **9** (200 MHz, THF-d$_8$, 295 K). The region of the signals for aromatic protons is omitted.

sium metal. The THF ring opening in the reaction with the Grignard reagent Ph_3CMgBr was described.[22] An analogous addition of an organic substrate to the imine C atom was observed in the reactions of Ti, Zr, and Sm complexes containing the 1,4-di-*tert*-butyl-1,3-diazadiene dianion with benzophenone (Scheme 3).[23] As mentioned above, the reaction of **1** with benzophenone gives pinacolate **2** instead of the [2+3]-cycloaddition product.

In a THF solution, dimer **9** is, apparently, transformed into the mononuclear complex containing coordinated THF molecules. In the ^{1}H NMR spectrum (Fig. 1), the coordinated THF molecules give broadened signals at δ 3.59 and 1.73. In compound **9**, all protons of the dpp-BIAN fragment are nonequivalent, which is reflected in the presence of four signals for the methine protons (septets at δ 4.82, 3.52, 3.10, and 2.96) and eight signals for the methyl protons of four isopropyl groups (doublets at δ 1.40, 1.39, 1.27, 1.25, 1.13, 0.86, 0.46, and –0.20) in the NMR spectrum. The Me_3Si group is observed as a singlet at δ –0.15. The presence of the asymmetric C atom affects the protons of the CH_2 groups of the THF molecule located in the α positions with respect to the chiral center. These protons become diastereotopic and are observed in the spectrum as very broad signals at δ 0.55 and –0.25. In the ^{1}H—^{1}H COSY NMR spectrum, the protons of the OCH_2 group appear as a triplet at δ 3.21 and have a cross-peak with a signal at δ ~1.2, which overlaps with doublets. This signal belongs, apparently, to the protons of the CH_2 group in the γ position with respect to the chiral center. The corresponding protons of the β-CH_2 group are observed in the spectrum as a quintet of doublets at δ 2.62.

When changing the solvent from THF-d$_8$ to C_6D_6, a second set of signals appears in the spectrum, which is evidence for the presence of two different forms of complex **9**. As an illustration, Fig. 2 shows the region of the spectrum, where the methine protons of the isopropyl groups are observed.

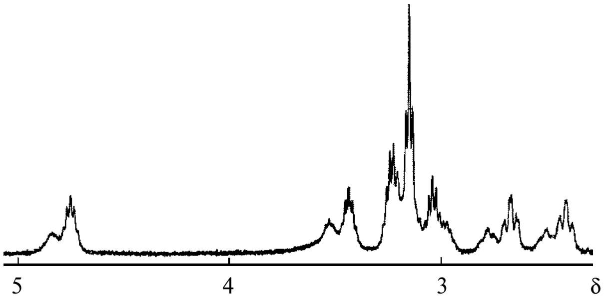


Fig. 2. Region of the ^{1}H NMR spectrum of complex **9** (200 MHz, C_6D_6, 295 K) containing signals for the methine protons.

Presumably, the appearance of two forms of complex **9** in a C_6D_6 solution is associated with partial dissociation of the dimer into monomers. Intramolecular coordination of the O atom of the side chain to the Mg atom may be the driving force for this process. To elucidate the possibility of the existence of a form with intramolecular coordination, we attempted to optimize the geometry of this form using the HyperChem program. The geometry of the molecule after optimization is shown in Fig. 3. As is

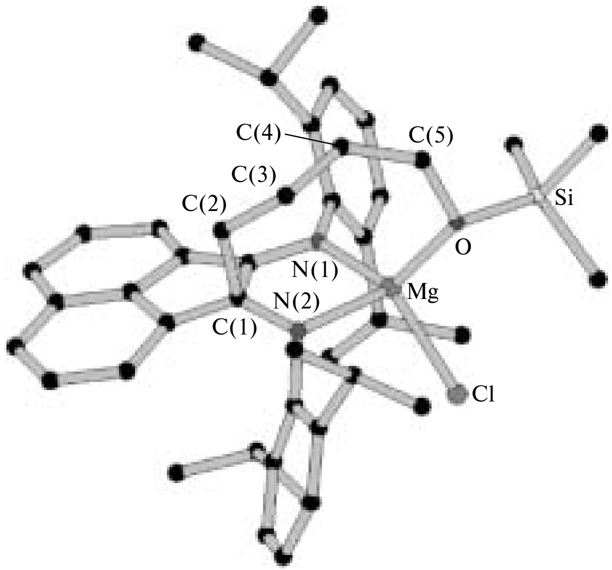
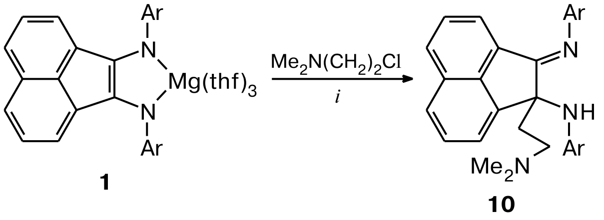


Fig. 3. Geometry optimization using the HyperChem 5.02 program for the isomer of $[\{(dpp\text{-}BIAN)(CH_2)_4OSiMe_3\}MgCl]_2$ (**9**) characterized by intramolecular coordination of the O atom to the Mg atom. The bond lengths (Å): C(1)—C(2), 1.52; C(2)—C(3), 1.54; C(3)—C(4), 1.53; C(4)—C(5), 1.55; C(5)—O, 1.44; Mg—O, 2.02.

Scheme 4



i. 1) THF, 2) hexane.

evident from the bond lengths, this geometry is unstrained and can occur in the absence of a coordinated solvent.

Reaction of (dpp-BIAN)Mg(thf)$_3$ (1) with 2-(dimethylamino)ethyl chloride. This reaction proceeds even slower than the reaction with Me$_3$SiCl. Refluxing of complex **1** with 2 equivs of Me$_2$NCH$_2$CH$_2$Cl in THF for 1 h followed by storage of the reaction mixture at room temperature for 2 days led to a change in the color of the reaction mixture from green to black-brown. Removal of the solvent and crystallization of the product from hexane afforded the dpp-BIAN(H)(CH$_2$)$_2$NMe$_2$ compound (**10**) containing no magnesium (Scheme 4). This fact can be attributable to the presence of an impurity of HCl or H$_2$O in Me$_2$NCH$_2$CH$_2$Cl used in the reaction, because 2-(dimethylamino)ethyl chloride was prepared by treating hydrochloride Me$_2$NCH$_2$CH$_2$Cl • HCl with sodium hydroxide.

In independent experiments, compound **10** was isolated as either pink-cream-colored prismatic crystals or yellow needle-like crystals in yields of up to 55%. However, the ^{1}H NMR spectra and the results of X-ray diffraction analysis of both types of crystals demonstrated that they are identical. The ^{1}H NMR spectrum of compound **10** in C$_6$D$_6$ is shown in Fig. 4.

The starting dpp-BIAN molecule has two mirror planes, one of which is perpendicular to the acenaphthene-diimine plane and passes along to the C—C bond between two six-membered rings, whereas another plane coincides with the plane of the diimine fragment. Since molecule **10**, like complex **9**, has no symmetry elements, we expected that the ^{1}H NMR spectrum of product **10** would be similar to that of complex **9**. However, the spectrum of compound **10** shows half as many signals in the aliphatic proton region as those observed in the spectrum of complex **9**. Two signals for the methine protons appear as partially overlapping septets at δ 3.56 and 3.42. Four doublets for the Me groups of the isopropyl fragments instead of the expected eight doublets are observed at δ 1.50, 1.40, 1.25, and 1.24. The methylene protons of the —CH$_2$—CH$_2$—NMe$_2$ fragment are observed as four triplets of doublets at δ 3.11, 2.99, 2.30, and 1.93, the first two of which correspond to the H atoms in the α position with

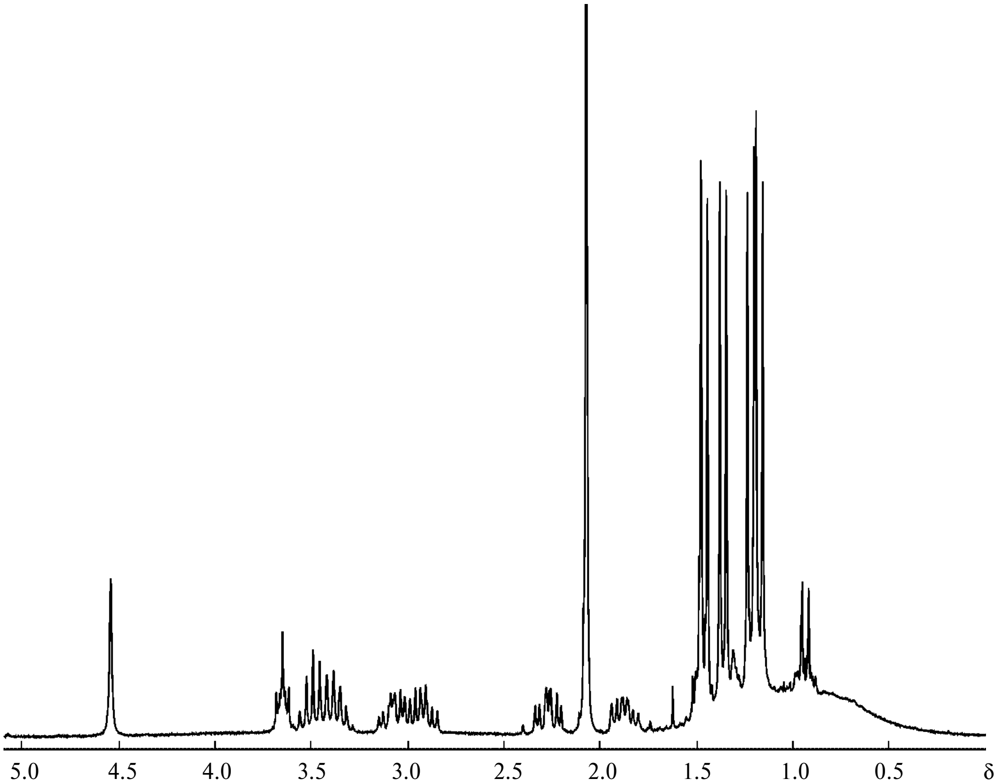


Fig. 4. ^{1}H NMR spectrum of complex **10** (200 MHz, C$_6$D$_6$, 295 K). The region of the signals for aromatic protons is omitted.

respect to the Me_2N group. The methyl protons of this group give a singlet at δ 2.10. The nonequivalence of all four protons in the $—CH_2—CH_2—$ fragment is, apparently, associated with the presence of the closely located chiral center and hindered rotation about the C—C bonds in the $—CH_2—CH_2—C^*$ chain. An analogous nonequivalence of four methylene protons in the $—CH_2—CH_2—NMe_2$ group was observed[24] in an ytterbium(II) complex, in which two $—CH_2—CH_2—NMe_2$ fragments of the Cp ring are coordinated to the Yb atom. The proton at the N atom gives a singlet at δ 4.58.

The absence of some signals in the ^1H NMR spectrum of compound **10** can be attributable to their strong broadening due to slow (on the NMR time scale) internal rotation of the aniline fragment. A close inspection of the ^1H NMR spectrum (see Fig. 4) revealed a rise of the zero line at δ 4.5—2.5 and, particularly, at δ 2.0—0. Since the C*—N and $N—C_{ipso}$ bonds are single and the N(H) atom, unlike the amido N atom in complex **9**, is not involved in the chelate ring closure, the aniline fragment can undergo free rotation.

Molecular structures of compounds 6—10. The structures of compounds **6—10** were established by X-ray diffraction analysis. The crystallographic data, characteristics of X-ray diffraction study, and details of the structure refinement are given in Table 1. Selected bond lengths and bond angles in molecules **6—8** and **9—10** are given in Tables 2 and 3, respectively. In the crystalline state, molecules **6** and **7** (Figs. 5 and 6, respectively) are isostructural and form dimers through the bridging Cl and Br atoms, respectively. Both molecules occupy inversion centers, which are located at the midpoint of the line between the metal atoms. In molecules **6** and **7**, the Mg atoms are in a tetragonal-pyramidal environment formed by two N atoms

Table 1. Crystallographic data, characteristics of X-ray diffraction study, and details of the structure refinement for complexes **6—10**

Parameter	**6**	**7**	**8**	**9**	**10**
Formula	$C_{80}H_{96}Cl_2Mg_2N_4O_2$	$C_{80}H_{96}Br_2Mg_2N_4O_2$	$C_{40}H_{50}IMgN_2O_2\cdot C_7H_8$	$C_{86}H_{114}Cl_2Mg_2N_4O_2Si_2\cdot 2(C_4H_8O)$	$C_{40}H_{51}N_3$
Molecular weight	1265.13	1354.09	788.10	1555.72	573.84
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2(1)/c$
a/Å	11.8029(2)	11.8686(2)	13.0319(3)	12.8568(2)	19.6854(3)
b/Å	12.7984(3)	12.7054(3)	17.9676(5)	14.4726(2)	9.1767(2)
c/Å	13.5344(2)	13.7066(3)	18.1171(4)	15.4449(1)	19.1463(4)
α/deg	91.8570(10)	91.4540(10)	93.715(1)	110.637(1)	90.00
β/deg	94.7330(10)	94.79	93.737(1)	113.613(1)	92.079(1)
γ/deg	116.5790(10)	116.4050(10)	96.736(1)	91.070(1)	90.00
V/Å^3	1816.66(6)	1840.25(7)	4192.67(18)	2421.06(5)	3456.45(12)
Z	1	1	4	1	4
ρ/g cm^{-3}	1.156	1.219	1.249	1.067	1.103
μ/mm^{-1}	0.155	1.166	0.814	0.152	0.064
F(000)	678	711	1640	840	1248
Crystal dimensions /mm	0.70×0.60×0.30	0.38×0.20×0.18	0.30×0.27×0.42	0.25×0.37×0.34	0.12×0.37×0.18
Scan range, θ/deg	1.51—25.00	1.49—26.50	1.13—27.50	1.53—25.00	1.04—23.31
Ranges of h, k, l indices	$-11 \le h \le 14$ $-15 \le k \le 14$ $-15 \le l \le 16$	$-14 \le h \le 11$ $-15 \le k \le 15$ $-17 \le l \le 17$	$-16 \le h \le 16$ $-18 \le k \le 23$ $-23 \le l \le 23$	$-15 \le h \le 15$ $-15 \le k \le 17$ $-18 \le l \le 13$	$-21 \le h \le 21$ $-10 \le k \le 10$ $-16 \le l \le 21$
Number of observed reflections	11242	13006	31708	14916	17403
Number of independent reflections	6327	7550	18900	8404	4989
R_{int}	0.1173	0.0642	0.0623	0.0761	0.1015
Goodness-of-fit on F^2	1.149	0.920	0.930	1.023	1.002
R_1/wR_2 ($I > 2\sigma(I)$)	0.0710/0.1698	0.0518/0.0889	0.0529/0.0881	0.0746/0.1708	0.0547/0.1153
R_1/wR_2 (based on all parameters)	0.0926/0.1923	0.1095/0.1047	0.1213/0.1078	0.1436/0.1978	0.1086/0.1395
Residual electron density/e Å^{-3}, ρ_{max}/ρ_{min}	0.406/−0.563	0.516/−0.573	0.905/−0.850	0.763/−0.301	0.264/−0.247

Table 2. Selected bond lengths (*d*) and bond angles (ω) in molecules **6**—**8**[a]

Parameter[b]	**6**	**7**	**8**
Bond		*d*/Å	
Mg—N(1)	2.123(3)	2.122(3)	2.104(3)
Mg—N(2)	2.130(3)	2.121(3)	2.117(3)
Mg—Hal(1)	2.4518(13)	2.6147(10)	2.7420(11)
Mg—Hal(1´)	2.4461(12)	2.6173(11)	—
Mg—O(1)	2.056(2)	2.056(3)	2.128(3)
Mg—O(2)	—	—	2.084(3)
Mg—Mg´	3.6034(19)	3.831(2)	—
Mg—C(1)	2.853(3)	2.851(3)	2.870(4)
Mg—C(2)	2.853(3)	2.846(3)	2.870(4)
C(1)—N(1)	1.339(4)	1.339(3)	1.336(4)
C(2)—N(2)	1.324(4)	1.335(4)	1.328(4)
C(1)—C(2)	1.445(4)	1.436(4)	1.438(5)
Angle		ω/deg	
O(1)—Mg—N(1)	101.97(10)	101.65(11)	93.92(11)
O(2)—Mg—N(1)	—	—	143.31(12)
O(1)—Mg—N(2)	102.02(10)	102.27(11)	149.33(11)
O(2)—Mg—N(2)	—	—	90.18(11)
N(1)—Mg—N(2)	80.83(10)	81.16(10)	80.29(11)
O(1)—Mg—Hal(1´)	98.80(8)	99.22(7)	—
O(1)—Mg—Hal(1)	98.22(8)	98.40(8)	95.28(7)
O(2)—Mg—Hal(1)	—	—	102.07(8)
Hal(1)—Mg—Hal(1´)	85.27(4)	85.87(3)	—
Mg—Hal(1)—Mg´	94.73(4)	94.13(3)	—

[a] In molecules **6**, **7**, and **8**, Hal = Cl, Br, and I, respectively.

[b] The primed atoms are related to the unprimed atoms by the symmetry operation $-x + 2$, $-y + 1$, $-z$.

and two halogen atoms in the base of the pyramid and the O atom of the THF molecule in the apex of the pyramid.

Table 3. Selected bond lengths (*d*) and bond angles (ω) in molecules **9** and **10**

Parameter	**9**	**10**
Bond	*d*/Å	
Mg—N(1)	1.945(3)	—
Mg—N(2)	2.111(3)	—
Mg—Cl	2.3510(16)	—
Mg—Cl´	2.3811(16)	—
Mg—C(1)	2.783(4)	—
Mg—C(2)	2.770(4)	—
Mg—Mg´	3.264(2)	—
Si—O(1)	1.645(3)	—
N(1)—H(1)	—	0.871(28)
N(1)—C(1)	1.476(4)	1.500(3)
N(2)—C(2)	1.284(5)	1.270(3)
C(1)—C(2)	1.542(5)	1.548(4)
C(1)—C(5)	1.526(5)	1.520(4)
C(1)—C(37)	1.563(5)	1.521(4)
C(38)—N(3)	—	1.461(3)
Angle	ω/deg	
N(1)—Mg—N(2)	85.48(13)	—
N(1)—Mg—Cl	126.15(11)	—
N(2)—Mg—Cl	118.52(11)	—
Cl—Mg—Cl´	92.80(5)	—
Mg—Cl—Mg´	87.20(5)	—
C(13)—N(1)—C(1)	117.8(3)	119.9(2)
C(2)—N(2)—C(25)	120.0(3)	119.9(2)
N(1)—C(1)—C(5)	120.0(3)	112.5(2)
N(1)—C(1)—C(2)	107.9(3)	102.0(2)
C(5)—C(1)—C(2)	101.8(3)	102.3(2)
N(1)—C(1)—C(37)	109.7(3)	112.3(2)
C(5)—C(1)—C(37)	108.2(3)	113.3(2)
C(2)—C(1)—C(37)	108.5(3)	113.5(2)

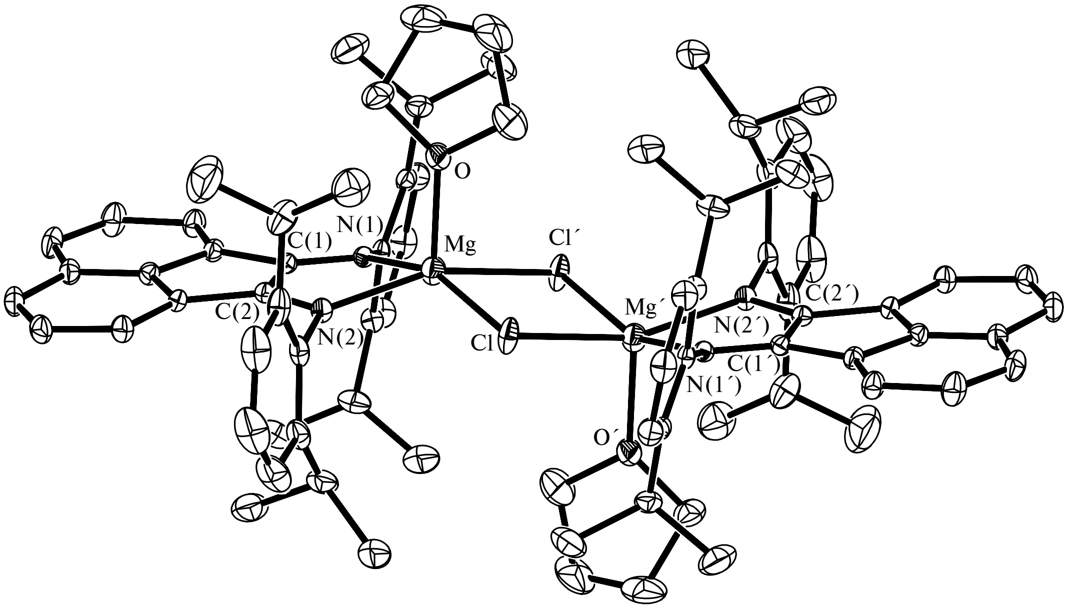


Fig. 5. Molecular structure of (dpp-BIAN)MgCl(thf) (**6**) with displacement ellipsoids drawn at the 30% probability level. The H atoms are omitted.

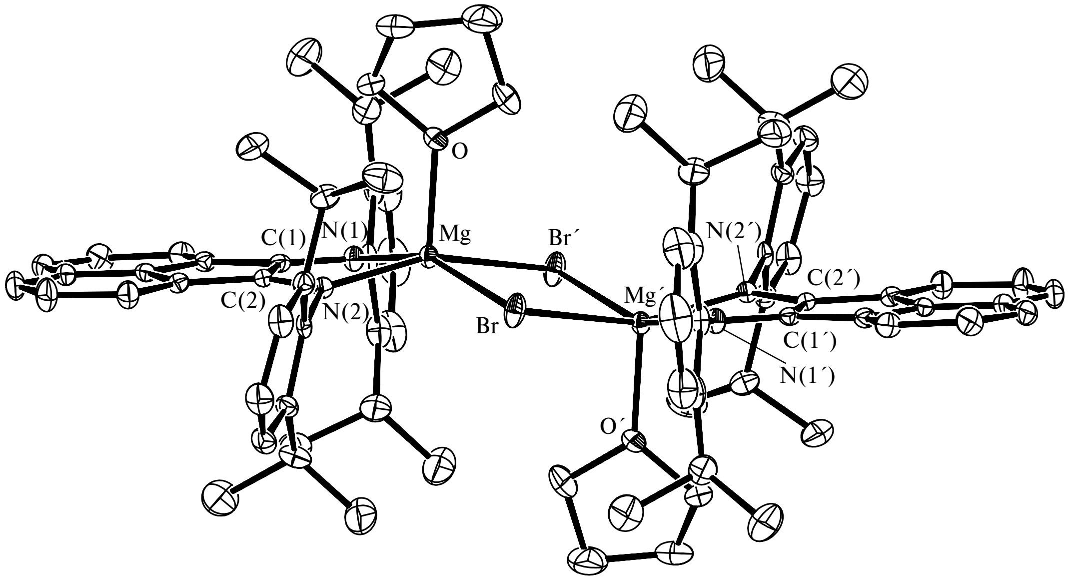


Fig. 6. Molecular structure of (dpp-BIAN)MgBr(thf) (**7**) with displacement ellipsoids drawn at the 30% probability level. The H atoms are omitted.

By contrast, the metal atom in the starting mononuclear complex **1** is in a trigonal-bipyramidal environment with one N atom and two O atoms in the equatorial plane and one N atom and one O atom in the axial positions. This is manifested in the differences in the Mg—N and Mg—O distances (Mg—O_{ax}, 2.224 Å; Mg—O_{eq}, 2.070 Å and 2.084 Å; Mg—N_{ax}, 2.105 Å; Mg—N_{eq}, 2.045 Å).[15] In molecules **6** and **7**, the Mg atoms deviate from the basal planes toward the apex by 0.096 and 0.088 Å, respectively. In both molecules, the Mg—N bond lengths are virtually identical [2.123(3) and 2.130(3) Å in **6**; 2.122(3) and 2.121(3) Å in **7**]. The Mg—O_{thf} distances in molecules **6** and **7** are 2.056 Å. As expected, the Mg—Br distances in molecule **7** [2.6173(11) and 2.6147(10) Å] are ~0.16 Å longer than the Mg—Cl distances in molecule **6** [2.4461(12) and 2.4518(13) Å]. Unlike **6** and **7**, molecule **8** (Fig. 7) exists as a monomer in which the Mg atom is coordinated to two N atoms of the BIAN ligand, two O atoms of the DME molecule, and the I atom. Small differences in the Mg—N(1) [2.104(3) Å] and Mg—N(2) [2.117(3) Å] bond lengths and, particularly, in the Mg—O(1) [2.128(3) Å] and Mg—O(2) [2.084(3) Å] bond lengths can be attributable to distortion of the geometry of the molecule toward the trigonal bipyramid. In molecule **8**, the Mg—I bond length is 2.7420(11) Å. In complexes **6**—**8**, the Mg—N distances are noticeably longer than those in complex **1**, which indicates that the interaction between the cation and the BIAN ligand is weakened in going from dianion **1** to radical anions **6**—**8**. Along with the results of ESR spectroscopy, the geometry of the diimine fragment of molecules **6**—**8** suggests that the reactions under study are accompanied by oxidation of the dianion to the radical anion. For example, the short N—C bonds [1.274(2) and 1.275(2) Å] and the long C—C bond [1.528(2) Å] are observed in the diimine fragment of neutral 1,2-bis[(2-diphenyl)imino]acenaphthene (dph-BIAN).[16] Taking into account the symmetry of the lowest unoccupied molecular orbital of the neutral BIAN molecule, two-electron reduction to the dianion should lead to elongation of the N—C bonds and shortening of the C—C bond. This is observed in the starting complex **1** [N(1)—C(1), 1.401(6) Å; N(2)—C(2), 1.378(7) Å; C(1)—C(2), 1.389(7) Å; the atomic numbering scheme corresponds to that presented in Figs 5—7].[15] One-electron oxidation of the BIAN dianion should lead to changes in the bond lengths to the values intermediate between those characteristic of $(\text{dpp-BIAN})^{2-}$ and $(\text{dpp-BIAN})^{0}$. This is actually observed in complexes **6**—**8** (see Table 2).

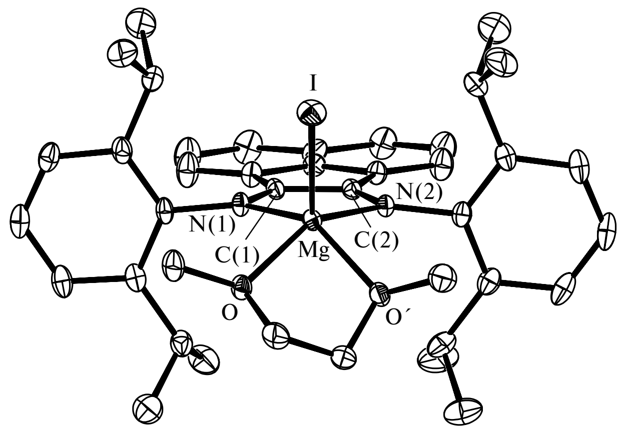


Fig. 7. Molecular structure of (dpp-BIAN)MgI(DME) (**8**) with displacement ellipsoids drawn at the 30% probability level. The H atoms are omitted.

Similar bond lengths in the BIAN radical anions are observed in the diimine fragments of complexes **2** and **3** [in **2**: N(1)—C(1), 1.324(4) Å; N(2)—C(2), 1.331(4) Å; C(1)—C(2), 1.457(5) Å; in **3**: N(1)—C(1), 1.334(7) Å; N(2)—C(2), 1.339(7) Å; C(1)—C(2), 1.432(6) Å].[18]

The structures of compounds **9** and **10** are shown in Figs 8 and 9, respectively. Selected bond lengths and bond angles in molecules **9** and **10** are given in Table 3. In spite of the fact that compound **10**, unlike **9**, contains no magnesium, the BIAN ligands in both molecules undergo similar transformations. The addition of electrophilic species to the BIAN ligand in the reactions of **1** with Me_3SiCl and $Me_2NCH_2CH_2Cl$ giving rise to a C—C bond results in the appearance of a chiral center at the C(1) atom in molecules **9** and **10**. Complex **9** exists as a centrosymmetric dimer (*Z* = 1). The C(1) atom in molecule **9** (see Fig. 8) has an *R* configuration, whereas the C(1´) atom has an *S* configuration. The unit cell of compound **10** contains two pairs of the molecules, *viz*., the *R* and *S* isomers (*Z* = 4). The *R* isomer of compound **10** is shown in Fig. 9. In compound **9**, each Mg atom is in a distorted tetragonal coordination formed by two bridging Cl atoms and two N atoms of the chelating amido/imino-BIAN ligand. The differences in the amido and imino functions of two N atoms are manifested in the differences in the bond lengths with the Mg atom. The Mg—N(1) amide bond [1.945(3) Å] is substantially shorter than the Mg—N(2) coordination bond [2.111(3) Å]. This functionality of the BIAN ligand differs from that in the above-described three ligands (dianion in **1**; radical anions in **2**, **3**, and **6—8**; amido/amine in **4**) and is, in fact, observed for the first time. As expected, a decrease in the coordination number of the Mg atom from five in compound **6** to four in complex **9** leads to shorten-

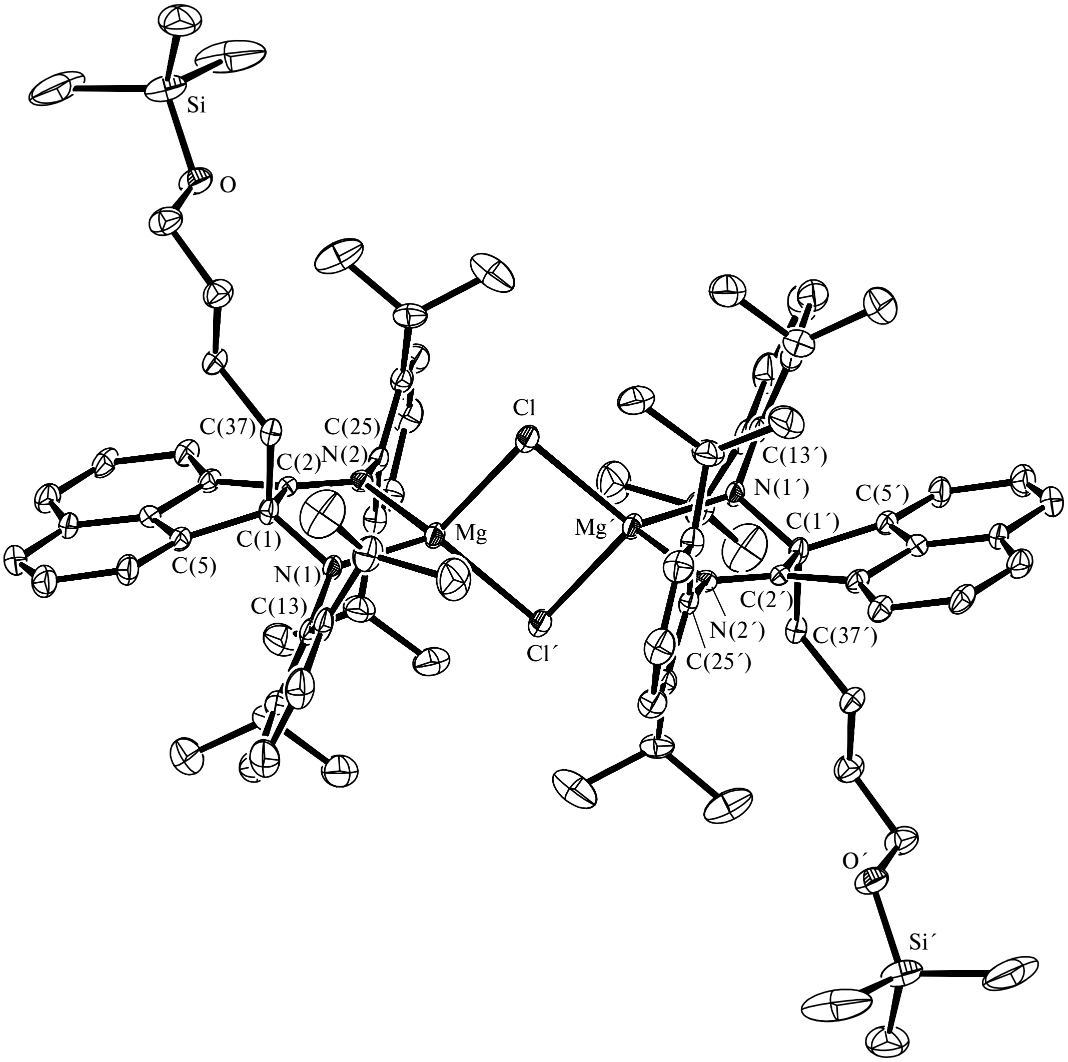


Fig. 8. Molecular structure of $[\{(dpp\text{-}BIAN)(CH_2)_4OSiMe_3\}MgCl]_2$ (**9**) with displacement ellipsoids drawn at the 30% probability level. The H atoms are omitted.

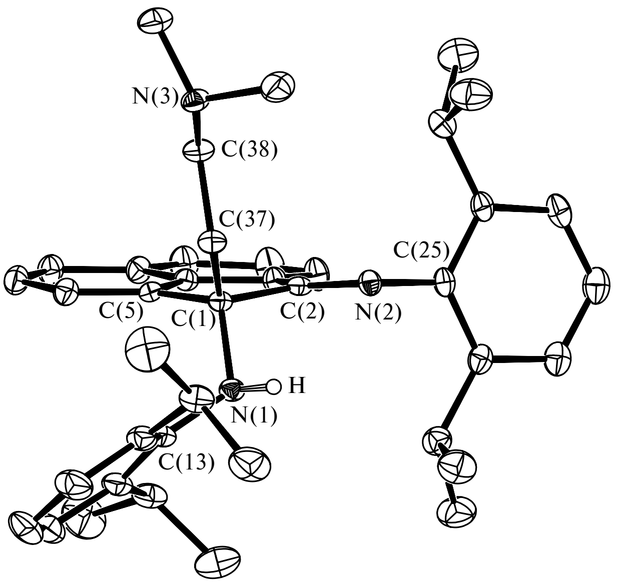


Fig. 9. Molecular structure of dpp-BIAN(H)$(CH_2)_2NMe_2$ (**10**) with displacement ellipsoids drawn at the 30% probability level. The H atoms are omitted.

ing of the Mg—Cl bonds in **9** [2.3510(16) and 2.3811(16) Å]. Similar bond lengths are observed in the Ar—N=C—C*—N(Mg,H)—Ar fragment of compounds **9** and **10**. For example, the N(2)—C(2) [**9**, 1.284(5) Å; **10**, 1.270(3) Å] and N(1)—C(1) [**9**, 1.476(4) Å; **10**, 1.500(3) Å] bond lengths in both compounds are close to the lengths of the carbon—nitrogen double and single bonds, respectively. In molecules **9** and **10**, the lengths of the newly formed C(1)—C(37) bonds are 1.563(5) and 1.521(4) Å, respectively.

To summarize, we found that the Mg complex with the dianionic acenaphthenediimine ligand (dpp-BIAN)Mg(thf)$_3$ can reduce various halogen-containing compounds, with the resulting oxidation of the BIAN ligand to the radical anion and formation of the unsymmetrical (dpp-BIAN)MgX complexes (X = Cl, Br, I). These compounds are of interest as the starting reagents for the synthesis of various derivatives with composition (dpp-BIAN)MgR (R is amide, alkoxide, alkyl, aryl, *etc.*). The exchange reactions of (dpp-BIAN)MgI with alkali metal amides and alkoxides produce the corresponding alkoxy and amido derivatives. The reactions of complex **1** with Me_3SiCl and $Me_2NCH_2CH_2Cl$ are accompanied by the addition of the alkyl group at the imine C atom of the ligand, which has not been observed earlier for diimine complexes of main-group metals.

Experimental

All compounds under study are sensitive to atmospheric oxygen and moisture and, hence, all operations associated with their synthesis, isolation, and identification were carried out *in vacuo* or under dry nitrogen using the Schlenk technique. 1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-BIAN) was prepared by condensation of acenaphthenequinone (Aldrich) and the corresponding aniline (Aldrich) in acetonitrile.[25] Complex **1** was synthesized according to a known procedure.[15] In all cases, a solution of complex **1** in THF was prepared from dpp-BIAN (0.5 g, 1.0 mmol) and an excess of Mg metal and was used in the reactions *in situ*. 2-(Dimethylamino)ethyl chloride was prepared by treating its hydrochloride $Me_2NCH_2CH_2Cl \cdot HCl$ (Aldrich) with solid NaOH followed by vacuum condensation. Trimethylchlorosilane was kept over CaH_2 during several hours and distilled *in vacuo* immediately before use. Tetrahydrofuran, 1,2-dimethoxyethane, diethyl ether, toluene, benzene, and hexane were dried, stored over sodium benzophenone ketyl, and distilled immediately before use. The yields of the products are given with respect to the amount of dpp-BIAN (1.0 mmol) used for the synthesis of complex **1**. The IR spectra were recorded on a Specord M-80 spectrometer (Nujol mulls). The NMR spectra were measured on Bruker DPX-200 and Bruker ARX-400 spectrometers; the chemical shifts are given in the δ scale relative to the chemical shifts of the residual protons and ^{13}C isotopes of deuterated solvents. The ESR spectra were recorded on a Bruker ESR 200D-SRC instrument (9.35 GHz).

Bis{1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthenide magnesium chloride tetrahydrofuranate} (6). Tetrachlorosilane (0.17 g, 1.0 mmol) was added to a solution of complex **1**, which was prepared from dpp-BIAN (0.5 g, 1.0 mmol) in THF. The reaction was accompanied by a rapid change in the color of the mixture from green to dark-red. The volatile products and solvent were removed *in vacuo*, and diethyl ether (30 mL) was added to the residue. Compound **6** was isolated from a concentrated solution in Et_2O as dark-red prismatic crystals in 72% yield (0.46 g). M.p. >245 °C (with decomp.). Reliable elemental analysis data were not obtained because of high sensitivity of compound **6** to atmospheric oxygen and moisture. IR, ν/cm^{-1}: 1640 m, 1520 s, 1430 s, 1305 w, 1250 m, 1170 w, 1100 w, 1020 s, 930 m, 880 m, 850 m, 805 w, 785 m, 750 s. ESR (toluene, 293 K): quintet, $g = 2.0048$, $A_N = 0.42$ mT.

Bis{1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthenide magnesium bromide tetrahydrofuranate} (7). 1,2-Dibromo-1,2-diphenylethane (0.145 g, 0.42 mmol) was added to a solution of complex **1**, which was prepared from dpp-BIAN (0.5 g, 1.0 mmol) in THF. The reaction was accompanied by a rapid change in the color of the mixture from green to dark-red. The volatile products and solvent were removed *in vacuo*, and diethyl ether (30 mL) was added to the residue. Compound **7** was isolated from a solution in Et_2O as dark-red prismatic crystals in 48% yield (0.39 g). M.p. >243 °C (with decomp.). Reliable elemental analysis data were not obtained because of very high sensitivity of compound **7** to atmospheric oxygen and moisture. IR, ν/cm^{-1}: 1640 w, 1520 s, 1430 s, 1305 w, 1250 m, 1170 w, 1100 w, 1020 s, 930 m, 880 m, 850 m, 805 w, 785 m, 750 s. ESR (toluene, 293 K): sextet, $g = 2.0045$, $A_N = 0.44$, $A_{Br} = 0.2$ mT.

1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthenide magnesium iodide dimethoxyethanate (8). Iodine (0.13 g, 0.5 mmol) was added to a solution of complex **1**, which was prepared from dpp-BIAN (0.5 g, 1.0 mmol) in THF. The reaction was accompanied by an immediate change in the color of the solution from green to red. The solvent was removed *in vacuo*, and the residue was dissolved in DME (25 mL). The solvent was again removed from the resulting solution *in vacuo*, and the residue was dissolved in toluene. Compound **8** was crystallized from a concentrated toluene solution (5 mL) as red-orange crystals in a yield of 0.60 g (76%), m.p. 195 °C. Reliable elemental analysis data were not obtained because of very high sensitivity of compound **8** to atmospheric oxygen and moisture. IR, ν/cm^{-1}: 1540 s, 1440 s, 1310 w, 1180 m, 1040 m, 850 m, 820 w, 760 m. ESR (toluene, 290 K): octet, g = 2.0022, A_N = 0.44, A_I = 0.27 mT.

Bis{(2,6-diisopropylphenyl)[2-(2,6-diisopropylphenylimino)-1-(4-trimethylsilanyloxybutyl)acenaphthen-1-yl]amidomagnesium chloride} (9). Trimethylsilyl chloride (0.86 g, 7.9 mmol) was added to a solution of complex **1** (which was prepared from dpp-BIAN (0.5 g, 1.0 mmol)) in THF. The reaction mixture was heated at 50—60 °C. In the course of the reaction, the solution gradually turned claret-colored. After 30 min, THF was removed from the reaction mixture *in vacuo* and hexane was added to the residue. Then the hexane was removed *in vacuo* and a new portion of hexane was again added to the residue. This operation was repeated two times. After removal of the hexane, the solid residue was dissolved in benzene (30 mL) and the solution was concentrated to 10 mL by heating (60 °C). Compound **9** was isolated from the benzene solution as pink crystals in a yield of 0.31 g (38%). M.p. 173—175 °C. Found (%): C, 70.08; H, 8.12. $C_{40}H_{51}N_3$ (573.84 g mol^{-1}). Calculated (%): C, 72.57; H, 8.42. IR, ν/cm^{-1}: 1640 m, 1620 m, 1250 m, 1100 w, 1080 w, 840 m, 780 w, 760 m, 680 m. ^{1}H NMR (200 MHz, THF-d$_8$, 20 °C), δ: 7.81 and 7.49 (both d, 1 H each, J = 7.8 Hz); 7.40—7.00 (m, 6 H); 6.90 (t, 1 H, J = 7.0 Hz); 6.75 (dd, 1 H, J = 7.8 Hz, J = 1.2 Hz); 6.17 and 6.10 (both d, 1 H each, J = 6.7 Hz); 4.82 (sept, 1 H, J = 6.8 Hz); 3.59 (s, 8 H, THF); 3.52, 3.10, and 2.96 (all sept, 1 H each, J = 6.8 Hz); 2.62 (m, 2 H); 1.60 (s, 8 H, THF); 1.40, 1.39, 1.27, 1.25, 1.13, and 0.86 (all d, 3 H each, J = 6.8 Hz); 0.55 (br.s, 1 H); 0.46 and –0.20 (both d, 3 H each, J = 6.8 Hz); –0.25 (br.s, 1 H). ^{13}C NMR (50 MHz, THF-d$_8$, 20 °C), δ: 193.12, 154.35, 151.26, 148.90, 145.77, 145.35, 140.79, 140.73, 140.36, 138.40, 132.28, 131.73, 130.94, 129.65, 128.89, 128.56, 127.37, 126.54, 126.02, 125.64, 124.74, 124.58, 123.30, 123.18, 122.80, 122.36, 77.54, 62.79, 52.43, 34.50, 29.39, 29.14, 28.44, 27.53, 27.34, 26.81, 26.36, 23.40, 21.89, 21.50, –0.52.

(2,6-Diisopropylphenyl)[2-(2,6-diisopropylphenylimino)-1-(2-dimethylaminoethyl)acenaphthen-1-yl]amine (10). 2-(Dimethylamino)ethyl chloride (0.22 g, 2.0 mmol) was added to a solution of complex **1**, which was prepared from dpp-BIAN (0.5 g, 1.0 mmol) in THF. The reaction mixture was refluxed for 1 h, after which the solution turned black-brown. Then the solvent was removed *in vacuo* and hexane was added to the residue. The solution was heated to 60 °C (5 min) and separated from hexane-insoluble products by centrifugation. After crystallization from hexane, compound **10** was obtained as pink-cream-colored crystals (m.p. 174—176 °C) or yellow crystals (m.p. 178—179 °C) in 55% yield. Pink-cream-colored crystals. Found (%): C, 82.14; H, 8.23. $C_{40}H_{51}N_3$ (573.84 g mol^{-1}). Calculated (%): C, 83.72; H, 8.96. IR, ν/cm^{-1}: 1650 s, 1240 m, 1180 m, 1000 m, 940 w, 890 w, 820 w, 770 m, 750 w. ^{1}H NMR (200 MHz, THF-d$_8$, 20 °C), δ: 7.86 and 7.73 (both d, 1 H each, J = 8.3 Hz); 7.37 (dd, 1 H, J = 8.3 Hz); 7.28—7.13 and 7.10 (both m, 3 H each); 6.62 and 6.55 (both d, 1 H each, J = 7.0 Hz); 4.31 (s, 1 H, N—H); 3.13 (sept, 1 H, J = 6.8 Hz); 2.98 (sept, 1 H, J = 7.0 Hz); 2.68 (m, 2 H); 2.06 (s, 6 H, NMe$_2$); 2.03 and 1.63 (both m, 1 H each); 1.25 (d, 3 H, J = 7.0 Hz); 1.08 (d, 3 H, J = 6.0 Hz); 1.01 (d, 3 H, J = 7.0 Hz); 0.91 (d, 3 H, J = 6.0 Hz). ^{13}C NMR (50 MHz, THF-d$_8$, 20 °C), δ: 174.67, 147.89, 142.01, 140.50, 139.75, 136.53, 136.49, 132.11, 131.82, 129.61, 128.36, 128.24, 125.92, 124.98, 124.56, 124.34, 124.06, 123.86, 123.34, 122.68, 71.47, 55.84, 45.68, 40.44, 29.36, 28.77, 28.12, 24.30, 24.23, 23.60, 23.50.

X-ray diffraction study of compounds 6—10. X-ray diffraction data were collected on a Siemens SMART CCD diffractometer (ω scanning technique, Mo-Kα radiation, λ = 0.71073 Å, graphite monochromator) at 173 K. The absorption correction was applied using the SADABS program.[26] The structures were solved by direct methods using the SHELXS-97 program package[27] and refined by the full-matrix least-squares method against F^2 using the SHELXL-97 program package.[28] All nonhydrogen atoms were refined anisotropically. The hydrogen atoms were placed in idealized positions (U_{iso} = 0.08 Å^3). The geometric parameters of the structures were analyzed using the PLATON program.[29] The atomic coordinates were deposited with the Cambridge Structural Database.

This study was financially supported by the Russian Foundation for Basic Research (Project No. 03-03-32246) and the Foundation for Support of National Science.

References

1. M. W. van Laren and C. J. Elsevier, *Angew. Chem., Int. Ed.*, 1999, **38**, 3715.
2. R. van Belzen, H. Hoffmann, and C. J. Elsevier, *Angew. Chem., Int. Ed.*, 1997, **36**, 1743.
3. G. A. Grasa, R. Singh, E. D. Stevens, and S. P. Nolan, *J. Organomet. Chem.*, 2003, **687**, 269.
4. A. Heumann, L. Giordano, and A. Tenaglia, *Tetrahedron Lett.*, 2003, **44**, 1515.
5. A. E. Cherian, E. B. Lobkovsky, and G. W. Coates, *Chem. Commun.*, 2003, **20**, 2566.
6. F. Al-Abaidi, Z. Ye, and S. Zhu, *Macromol. Chem. Phys.*, 2003, **204**, 1653.
7. V. Fassina, C. Ramminger, M. Seferin, R. S. Mauler, R. F. de Souza, and A. L. Monteiro, *Macromol. Rapid Commun.*, 2003, **24**, 667.
8. M. D. Leatherman, S. A. Svejda, L. K. Johnson, and M. Brookhart, *J. Am. Chem. Soc.*, 2003, **125**, 3068.
9. S. S. Ivanchev, G. A. Tolstikov, V. K. Badaev, N. I. Ivancheva, I. I. Oleinik, S. Ya. Khaikin, and I. V. Oleinik, *Vysokomol. Soedin., Ser. A*, *B*, 2002, **44**, 1478 [*Polym. Sci. USSR*, *Ser. A*, *B*, 2002, **44**, 931 (Engl. Transl.)].
10. I. Kim, J.-M. Hwang, J. K. Lee, C. S. Ha, and S. I. Woo, *Macromol. Rapid Commun.*, 2003, **24**, 508.
11. D. Takeuchi, A. Yasuda, and K. Osakada, *Dalton Trans.*, 2003, 2029.
12. J. Kiesewetter and W. Kaminsky, *Chem. — A Eur. J.*, 2003, **9**, 1750.
13. I. L. Fedushkin, A. A. Skatova, V. A. Chudakova, and G. K. Fukin, *Angew. Chem., Int. Ed.*, 2003, **42**, 3294.
14. I. L. Fedushkin, A. A. Skatova, V. A. Chudakova, V. K. Cherkasov, G. K. Fukin, and M. A. Lopatin, *Eur. J. Inorg. Chem.*, 2004, **2**, 388.
15. I. L. Fedushkin, A. A. Skatova, V. A. Chudakova, G. K. Fukin, S. Dechert, and H. Schumann, *Eur. J. Inorg. Chem.*, 2003, **18**, 3336.

16. 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.
17. 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.
18. I. L. Fedushkin, A. A. Skatova, V. K. Cherkasov, V. A. Chudakova, S. Dechert, M. Hummert, and H. Schumann, *Chem. — A Eur. J.*, 2003, **9**, 5778.
19. I. L. Fedushkin, N. M. Khvoinova, A. A. Skatova, and G. K. Fukin, *Angew. Chem., Int. Ed.*, 2003, **42**, 5223.
20. W. Steudel and H. Gilman, *J. Am. Chem. Soc.*, 1960, **82**, 6129.
21. A. Y. Garner and A. A. Tedeschi, *J. Am. Chem. Soc.*, 1962, **84**, 4734.
22. F. R. Jensen and R. L. Bedard, *J. Org. Chem.*, 1959, **24**, 874.
23. J. Scholz, H. Görls, H. Schumann, and R. Weimann, *Organometallics*, 2001, **20**, 4394.
24. I. L. Fedushkin, S. Dechert, and H. Schumann, *Organometallics*, 2000, **19**, 4066.
25. A. A. Paulovicova, U. El-Ayaan, K. Shibayama, T. Morita, and Y. Fukuda, *Eur. J. Inorg. Chem.*, 2001, 2641.
26. G. M. Sheldrick, *Empirical Absorption Correction Program*, Universität Göttingen, Göttingen (Germany), 1996.
27. G. M. Sheldrick, *Program for Crystal Structure Solution*, Universität Göttingen, Göttingen (Germany), 1990.
28. G. M. Sheldrick, *Program for Crystal Structure Refinement*, Universität Göttingen, Göttingen (Germany), 1997.
29. A. L. Spek, *PLATON A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht (Holland), 2000.

Received April 19, 2004;
in revised form October 8, 2004