Aluminum complexes with mono- and dianionic diimine ligands

A. N. Lukoyanov,[a] I. L. Fedushkin,[a]★ M. Hummert,[b] and H. Schumann[b]

[a]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
[b]Institute of Chemistry, Technical University of Berlin,
135 Strasse des 17 Juni, D-10623 Berlin, Germany.*
Fax: +49 (30) 3142 2168. E-mail: schumann@chem.tu-berlin.de

The metathesis reaction of the magnesium complex [(dpp-BIAN)$^{2-}$Mg^{2+}(THF)$_3$] (dpp-BIAN is 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) with one equivalent of AlCl$_3$ in toluene gave the [(dpp-BIAN)$^{2-}$AlCl$_2$]$^-$[Mg$_2$Cl$_3$(THF)$_6$]$^+$ complex (**1**). Reduction of dpp-BIAN with aluminum metal in the presence of AlCl$_3$ and AlI$_3$ in toluene and diethyl ether afforded the radical-anionic complex [(dpp-BIAN)$^-$AlCl$_2$] (**2**) and the dianionic complexes [(dpp-BIAN)$^{2-}$AlI(Et$_2$O)] (**3**) and [(dpp-BIAN)$^{2-}$AlCl(Et$_2$O)] (**4**), respectively. Compounds **1**—**4** were isolated in the crystalline state and characterized by IR spectroscopy and elemental analysis. The structures of compounds **1**—**3** were established by X-ray diffraction. Compound **2** was characterized by ESR spectroscopy. Compounds **3** and **4** were studied by ^{1}H and ^{13}C NMR spectroscopy.

Key words: aluminum, diimines, radical anion, dianion, X-ray diffraction study.

Transition metal complexes with 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-BIAN) are known[1—10] to be used for the preparation of catalysts for various organic reactions, including olefin polymerization catalysts. Recently, it has been found[11,12] that acenaphthene-1,2-diimines can be reduced by alkali metals to mono-, di-, tri-, and tetraanions. Alkaline-earth metals reduce dpp-BIAN only to the dianion,[13—15] and the resulting complexes show high specific reactivity toward such organic compounds as ketones,[16,17] nitriles,[18] alkyl halides,[19] and C—H acids.[20]

Derivatives of Group 13 elements with dpp-BIAN can be prepared by the reactions of metal halides with neutral dpp-BIAN.[21] In 2004, a gallium compound of composition (dpp-BIAN)$^-$GaI$_2$ with the radical-anionic acenaphthenediimine ligand was synthesized for the first time.[22] The low-valent compound "GaI," which was ultrasonically prepared from gallium and iodine in toluene, was used as the starting compound in this synthesis. Recently,[23] we have synthesized the nonsolvated dialkylaluminum derivatives [(dpp-BIAN)$^-$AlR$_2$] by the metathesis reaction of the sodium salt (dpp-BIAN)$^-$Na$^+$ with R$_2$AlHal (R = Me, Et, or Bu^i; Hal = Cl or Br).[23]

The aim of the present study was to develop new convenient procedures for the synthesis of aluminum complexes with diimine dpp-BIAN. New aluminum complexes with various reduced forms of dpp-BIAN were synthesized starting from aluminum metal and its halides.

Results and Discussion

Synthesis of the [(dpp-BIAN)$^{2-}$AlCl$_2$][Mg$_2$Cl$_3$(THF)$_6$] complex (1). The metathesis reaction of (dpp-BIAN)Mg(THF)$_3$ with one equivalent of AlCl$_3$ in THF followed by crystallization from toluene afforded the green [(dpp-BIAN)$^{2-}$AlCl$_2$][Mg$_2$Cl$_3$(THF)$_6$] complex (**1**), in which the ligand exists as the dianion, like that in the starting magnesium derivative (Scheme 1).

The reaction occurred at 80 °C and was completed within 5—10 min. After heating for a longer period of time, the product was completely decomposed, which was evidenced by a change in the color of the solution from green to violet.

The reaction product is unstable to atmospheric oxygen and moisture and is hydrolyzed to give dpp-BIAN(H)$_2$.[24] The IR spectrum of compound **1** shows absorption bands of coordinated tetrahydrofuran (1025 and 874 cm^{-1}), which is eliminated upon heating to 105 °C. Dissolution of compound **1**, which was isolated in the crystalline state, in THF or benzene results in its decomposition to form unidentified products. The crystal structure of compound **1** was established by X-ray diffraction (Fig. 1).

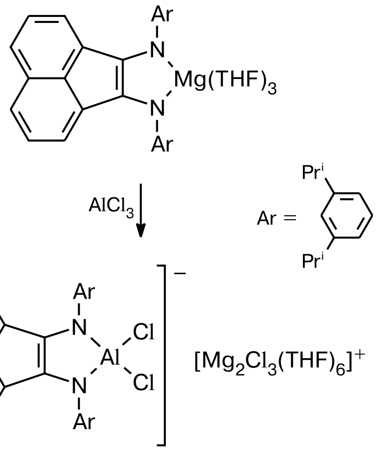
Selected bond lengths and bond angles are given in Table 1. The N—C and C—C bond lengths in the diimine

---

* Institut für Chemie der Technischen Universität Berlin, Straβe des 17 Juni, 135, D-10623 Berlin, Germany.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, pp. 409—415, March, 2006.

Scheme 1



1

fragment of compound **1** are much more similar to those in [(dpp-BIAN)$^{2-}$Na$_2$(Et$_2$O)$_3$] than to those in [(dpp-BIAN)$^-$Na]$_2$ (Table 2).[11] Hence, it can be concluded that the BIAN ligand in complex **1** is dianionic and the [(dpp-BIAN)$^{2-}$AlCl$_2$] fragment exists as the anion, which is a counterion to the [Mg$_2$Cl$_3$(THF)$_6$] cation.

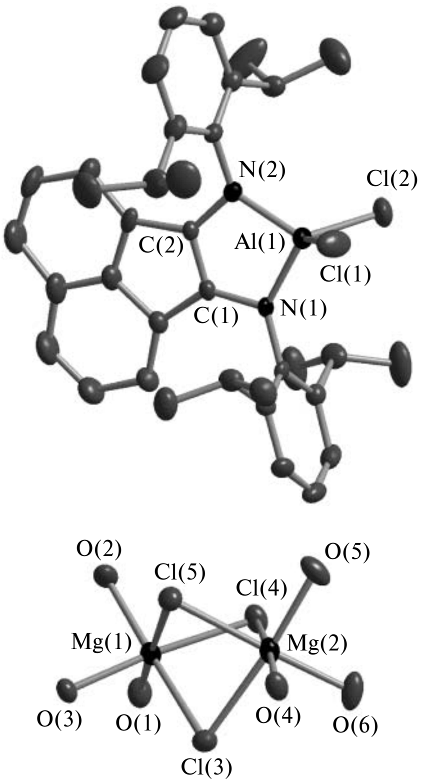


Fig. 1. Crystal structure of complex **1**. The hydrogen atoms and the carbon atoms of the tetrahydrofuran molecules are omitted. The atoms are represented by anisotropic displacement ellipsoids drawn at the 30% probability level.

Table 1. Selected bond lengths (*d*) and bond angles (ω) in compounds **1**—**3**

Parameter	1	2	3
Bond		*d*/Å	
Al—N(1)	1.844(4)	1.890(2)	1.833(6)
Al—N(2)	1.838(4)	1.888(2)	1.839(5)
C(1)—N(1)	1.396(6)	1.346(3)	1.394(8)
C(2)—N(2)	1.393(7)	1.341(3)	1.418(9)
C(1)—C(2)	1.364(8)	1.431(3)	1.390(11)
Al—Cl(1)	2.140(3)	2.116(1)	—
Al—Cl(2)	2.151(2)	2.109(1)	—
Al—I	—	—	2.509(3)
Al—O	—	—	1.891(6)
Mg(1)—Cl(3)	2.480(3)	—	—
Mg(1)—Cl(4)	2.507(2)	—	—
Mg(1)—Cl(5)	2.525(3)	—	—
Mg(2)—Cl(3)	2.517(2)	—	—
Mg(2)—Cl(4)	2.493(3)	—	—
Mg(2)—Cl(5)	2.479(2)	—	—
Angle		ω/deg	
N(1)—Al—N(2)	92.37(17)	89.19(9)	95.49(25)
Cl(1)—Al—Cl(2)	103.6(1)	108.74(4)	—
I—Al—O	—	—	106.02(17)

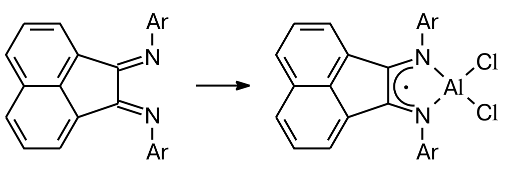
Table 2. Bond lengths in the diimine fragments in compounds **1**, **2**, **3**, [(dpp-BIAN)$^-$Na]$_2$ (**A**), and [(dpp-BIAN)$^{2-}$Na$_2$(Et$_2$O)$_3$] (**B**)

Compound	1	2	3	A	B
	(our data)			(Ref. 11)	
N—C	1.396(6)	1.346(3)	1.394(8)	1.3239(18)	1.387(4)
	1.393(7)	1.341(3)	1.418(9)	1.3326(19)	1.386(4)
C(1)—C(2)	1.364(8)	1.431(3)	1.390(11)	1.446(2)	1.402(4)

Synthesis of the [(dpp-BIAN)$^-$AlCl$_2$] complex (2). Aluminum metal does not react with dpp-BIAN in toluene, diethyl ether, or tetrahydrofuran. However, reduction of dpp-BIAN with aluminum metal in the presence of aluminum halides readily proceeds at room temperature both in toluene and diethyl ether. Mixing of dpp-BIAN with AlCl$_3$ in toluene rapidly affords [(dpp-BIAN)AlCl$_2$][AlCl$_4$] (see Ref. 21) as dark crystals poorly soluble in toluene. These crystals were dissolved by stirring the resulting mixture with aluminum for 5—10 h to give the (dpp-BIAN)$^-$AlCl$_2$ compound (**2**), which is readily soluble in toluene (Scheme 2).

The solution was separated from an excess of aluminum metal after complete dissolution of the initially formed dark crystals. Compound **2** was isolated from a toluene solution as green crystals. Compound **2** is paramagnetic and its ESR spectrum in solution is typical of

Scheme 2



2

Reagents and conditions: aluminum foil, $AlCl_3$, toluene.

aluminum compounds with the radical-anionic dpp-BIAN ligand.[23] The ESR spectrum (Fig. 2) shows splitting of the unpaired electron due to ^{27}Al (100%, $I = 5/2$), chlorine [^{35}Cl (75.77%, $I = 3/2$) and ^{37}Cl (24.23%, $I = 3/2$], ^{14}N (99.64%, $I = 1$), and ^{1}H (99.99%, $I = 1/2$) (Table 3).

As can be seen from a comparison of the ESR spectra of the [(dpp-BIAN)$^-$$AlCl_2$] and [(dpp-BIAN)$^-$$AlMe_2$] compounds, the replacement of the alkyl groups at the aluminum atom by the chlorine atoms leads to redistribution of the electron density throughout the molecule and its shift to the halogen atoms. This is evidenced by the hyperfine interaction between the unpaired electron and the chlorine nuclei and a decrease in the hyperfine coupling constants of the aluminum and nitrogen nuclei and hydrogens. The molecular structure of compound **2** was established by X-ray diffraction (Fig. 3).

A comparison of the geometric parameters of the diimine ligand with the corresponding parameters of [(dpp-BIAN)$^-$Na]$_2$ and [(dpp-BIAN)$^{2-}$$Na_2(Et_2O)_3$] (see Ref. 11 and Table 2) shows that complex **2** has the monoanionic dpp-BIAN ligand. Therefore, reduction of dpp-BIAN with aluminum metal in toluene in the presence of $AlCl_3$ gives rise to the radical anion.

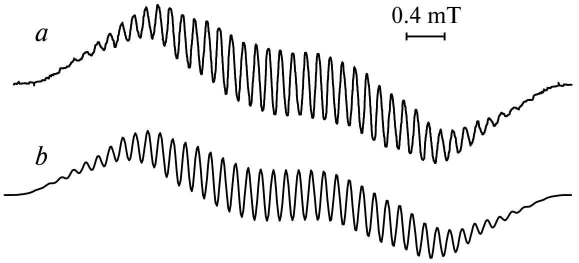


Fig. 2. ESR spectrum of compound **2** ($g = 2.0026$) in toluene (307 K) (*a*) and the stimulated spectrum (*b*) (parameters are given in Table 3).

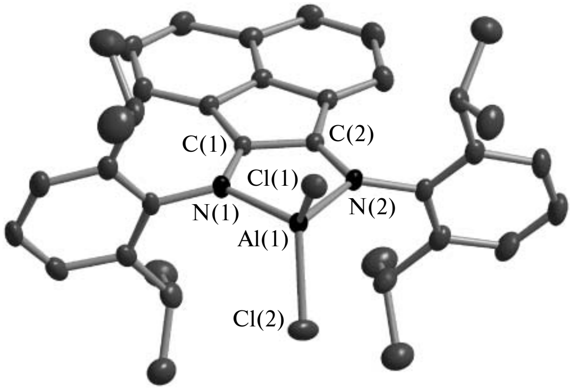


Fig. 3. Molecular structure of [(dpp-BIAN)$^-$$AlCl_2$] (**2**). The hydrogen atoms are omitted. The atoms are represented by anisotropic displacement ellipsoids drawn at the 30% probability level.

Synthesis of the [(dpp-BIAN)$^{2-}$AlHal(Et_2O)] complexes (Hal = I (3) or Cl (4)). In the presence of halides $AlHal_3$, reduction of dpp-BIAN with aluminum metal in diethyl ether occurs, like that in toluene, at

Table 3. Isotropic *g* factors and hyperfine splitting constants (*A*) for compounds **2**, [(dpp-BIAN)$^-$$AlMe_2$],[23] [(dpp-BIAN)$^-$MgI(DME)],[19] [(dpp-BIAN)$^-$GeCl],[25] and [{C_2H_2(N-Ph-2,6-Pr^i)$_2$}AlI_2] (see Ref. 26).

Compound	g_i	*A*/mT					ΔH/mT
		M[a]	^{14}N[b]	^{1}H[c]	^{1}H[d]	Hal[e]	
2	2.0026	0.515	0.38	0.13	0.10	0.125 (^{35}Cl) 0.104 (^{37}Cl)	0.12
[(dpp-BIAN)$^-$$AlMe_2$]	2.0031	0.60	0.46	0.14	0.10		
[(dpp-BIAN)$^-$MgI(DME)]	2.0022		0.44			0.27	
[(dpp-BIAN)$^-$GeCl]	2.0014	0.96	0.48	0.11	0.11	0.78 (^{35}Cl) 0.65 (^{37}Cl)	
[{C_2H_2(N-Ph-2,6-Pr^i)$_2$}AlI_2]	2.0038	0.285	0.67	0.59		0.04	

[a] M is ^{27}Al or ^{73}Ge.

[b] ^{14}N belongs to two equivalent nitrogen atoms.

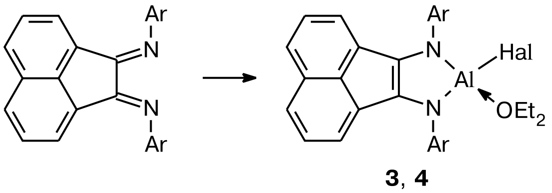
[c] ^{1}H belongs to two equivalent protons in the *ortho* positions of the naphthalene system (relative to the diimine fragment).

[d] ^{1}H corresponds to two equivalent protons in the *para* positions of the naphthalene system (relative to the diimine fragment).

[e] Hal belongs to the nuclei of the corresponding halogens (^{35}Cl and ^{37}Cl or ^{127}I) in the following compounds: **2**, for two equivalent chlorine atoms; [(dpp-BIAN)$^-$MgI(DME)], for one iodine atom; [(dpp-BIAN)$^-$GeCl], for one chlorine atom; and [{C_2H_2(N-Ph-2,6-Pr^i)$_2$}AlI_2], for two iodine atoms.

room temperature but affords compounds with the dianionic ligand, *viz.*, [(dpp-BIAN)$^{2-}$AlI(Et$_2$O)] (**3**) and [(dpp-BIAN)$^{2-}$AlCl(Et$_2$O)] (**4**) (Scheme 3).

Scheme 3



3, **4**

Hal = I (**3**); Cl (**4**)

Reagent conditions: aluminum foil, AlHal$_3$, Et$_2$O.

The reduction rate substantially depends on the activity of aluminum. In all cases, an aluminum foil was initially activated with iodine. After the disappearance of the iodine color, the solution containing AlI$_3$ was decanted from an excess of the metal, which was then used in the reactions with dpp-BIAN and AlHal$_3$. Depending on the activity of aluminum, the reduction time varies from 3 h to 2 days. The activity of aluminum remained rather high after its repeated use. In all cases, reduction of the newly added diimine is completed within tens of minutes. The completion of reduction was evidenced by the appearance of the blue color of the solution. No further chemical transformations occur in the reaction mixture upon prolonged (longer than 1 week) stirring at room temperature. The ethereal solutions were concentrated, after which compounds **3** and **4** were obtained as dark-blue plate-like crystals. Crystals of compound **3** suitable for X-ray diffraction study were grown from benzene. Complexes **3** and **4** in solution show almost identical behavior, which was studied by ^{1}H NMR spectroscopy.

The ^{1}H NMR spectrum of compound **3** in C$_6$D$_6$ (Fig. 4, *a*) shows signals of both coordinated (quartet at δ 3.82 and a triplet at δ 0.66) and free (quartet at δ 3.35 and a triplet at δ 1.12) diethyl ether molecules. Two signals for the methine protons (septets at δ 4.04 and 3.64) and four doublets for the methyl protons (δ 1.48, 1.25, 1.18, and 1.09) are indicative of the nonequivalence of the isopropyl substituents of the Ph groups. This is due both to the absence of free rotation of the Ph rings about the C$_{ipso}$—N bonds and the absence of exchange between the iodine atom and the diethyl ether molecule in the coordination sphere of the aluminum atom. By contrast, the spectrum of compound **3** in THF-d$_8$ (Fig. 4, *b*) shows only one signal for the methine protons (septet at δ 3.69) and two signals for the methyl protons (doublets at δ 1.26 and 1.06) of the isopropyl substituents. This is indicative of the fast (on the NMR time scale) dynamic exchange between the solvent molecules (THF-d$_8$) and the iodine atom.

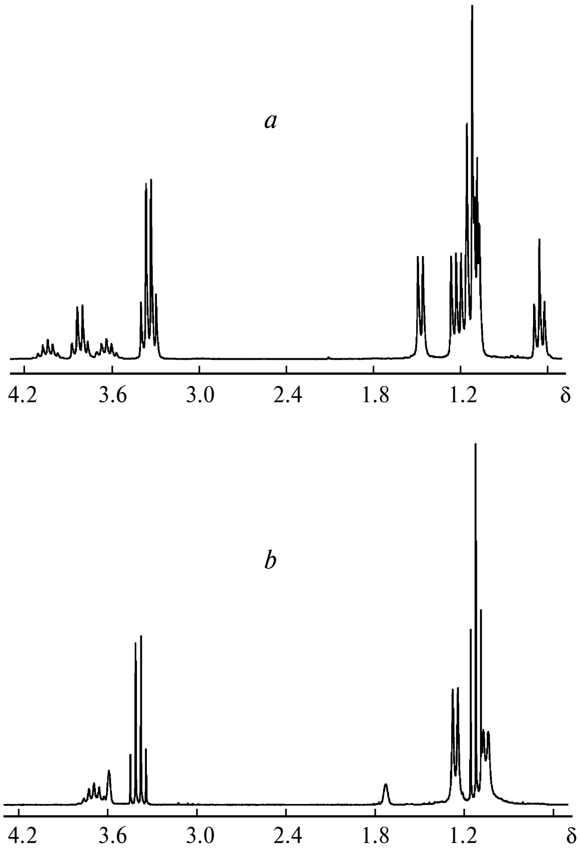


Fig. 4. ^{1}H NMR spectra (200 MHz, 293 K) of compound **3** in C$_6$D$_6$ (*a*) and THF-d$_8$ (*b*). The aromatic proton region is omitted.

The molecular structure of complex **3** is presented in Fig. 5. A comparison of the bond lengths and bond angles in the diimine fragments in compounds **2** and **3** demonstrated that the geometry of the diimine fragment in the

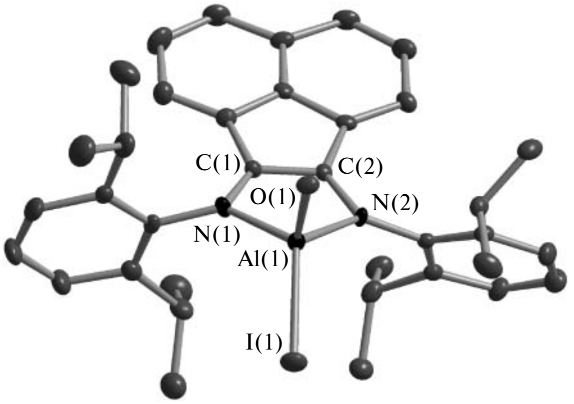


Fig. 5. Molecular structure of [(dpp-BIAN)$^{2-}$AlI(Et$_2$O)] (**3**). The hydrogen atoms and the carbon atoms of the diethyl ether molecules are omitted. The atoms are represented by anisotropic displacement ellipsoids drawn at the 30% probability level.

radical anion in complex **2** differs from that in the dpp-BIAN dianion in complex **3**. The N—Al distances in the aluminum complex with the dpp-BIAN dianion are also substantially shorter than the corresponding distances in the complex with the radical-anionic dpp-BIAN ligand (see Table 1).

Therefore, aluminum complexes with the mono- and dianionic acenaphthenediimine ligand dpp-BIAN, like those of alkali and alkaline-earth metals, can be synthesized by direct reduction of the ligand with aluminum metal in diethyl ether in the presence of aluminum halides. Unlike magnesium and calcium metals, reduction of dpp-BIAN can be performed in a nonsolvating medium (for example, in toluene). Regardless of the ratio of diimine to aluminum halide, only compounds of composition [(dpp-BIAN)$^-$AlHal$_2$] with the radical-anionic diimine ligand are formed in toluene, whereas only the [(dpp-BIAN)$^{2-}$AlHal(Et$_2$O)] complexes with the dpp-BIAN dianion are generated in diethyl ether. We developed convenient synthetic methods enabling the preparation of new alkyl, amide, and alkoxide derivatives of aluminum as organic synthons.

Experimental

Since the above-mentioned compounds, except for dpp-BIAN, are sensitive to atmospheric oxygen and moisture, all operations associated with their synthesis, isolation, and identification were carried out *in vacuo* using the Schlenk technique. Diimine dpp-BIAN was prepared by condensation of acenaphthenequinone and 2,6-diisopropylaniline (both from Aldrich) in acetonitrile. The [(dpp-BIAN)$^{2-}$Mg(THF)$_3$] complex was synthesized according to a known procedure.[13] Aluminum foil was cut into strips (30×5 mm) and activated with iodine in the corresponding solvents immediately before use. The solution of AlI$_3$ that formed was separated by decantation. Tetrahydrofuran, diethyl ether, benzene, and toluene were dried, stored over sodium benzophenone ketyl, and withdrawn by vacuum condensation immediately before use. The yields of the products given below were calculated based on the amount (1.0 mmol) of dpp-BIAN consumed in the syntheses of compounds **1**—**4**. The IR spectra were measured in Nujol mulls on a Magna System 750 spectrometer equipped with a DTGS detector. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX 200 instrument; the chemical shifts are given on the δ scale relative to the chemical shifts of the residual protons of deuterated solvents. The ESR signal of compound **2** was recorded on a Bruker ER 200D-SRC spectrometer relative to the signal of diphenyl picryl hydrazyl (DPPH, g = 2.0037).

1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthenide dichloroaluminate dimagnesium trichlorohexakis(tetrahydrofuranate) (1). Aluminum trichloride (0.2 g, 1 mmol) was added to a solution of the [(dpp-BIAN)$^{2-}$Mg(THF)$_3$] complex, which was prepared from dpp-BIAN (0.5 g, 1 mmol) in THF. The resulting green solution was heated at 80 °C for 10 min. Then all volatile components were removed *in vacuo*. The content of the ampoule was dissolved in toluene. The solution was heated at 80 °C and filtered off from the precipitate that formed. After storage for 8—10 h, green crystals of compound **1** were obtained in a yield of 0.75 g (63%). T.decomp. 105 °C. Found (%): C, 60,72; H, 7.41. C$_{60}$H$_{88}$AlCl$_5$Mg$_2$N$_2$O$_6$ (1186.17 g mol^{-1}). Calculated (%): C, 60.76; H, 7.48. IR, ν/cm^{-1}: 2718 w, 1907 w, 1772 w, 1612 w, 1589 m, 1511 s, 1359 w, 1344 m, 1255 m, 1211 w, 1192 m, 1176 m, 1137 m, 1108 m, 1058 w, 1025 s, 998 w, 923 s, 874 s, 810 s, 762 s, 729 m, 721 m, 695 w, 681 w, 662 m, 626 w, 620 w, 550 m, 539 s, 485 s, 474 s, 441 m.

1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthenidealuminum dichloride (2). A solution containing AlCl$_3$ (0.09 g, 0.67 mmol) and dpp-BIAN (0.5 g, 1 mmol) in toluene was added to a stripped aluminum foil. The reaction mixture was stirred for 12 h until the solution turned red-brown. Then the solution was separated from an excess of the foil by decantation. Crystallization from the resulting solution afforded compound **2** as green plate-like crystals in a yield of 0.49 g (83%). M.p. 264—267 °C. Found (%): C, 72.23; H, 6.59. C$_{36}$H$_{40}$N$_2$Cl$_2$Al (598.59 g mol^{-1}). Calculated (%): C, 72.17; H, 6.68. IR, ν/cm^{-1}: 3064 w, 2725 w, 2498 w, 1947 w, 1883 w, 1826 w, 1629 s, 1528 s, 1364 m, 1320 s, 1254 s, 1213 m, 1200 m, 1187 m, 1149 m, 1111 m, 1080 w, 1057 m, 1041 m, 953 m, 936 m, 902 m, 823 s, 805 s, 767 s, 724 m, 715 m, 622 w, 598 m, 523 s, 492 s. ESR (307 K, toluene): g = 2.002585; $A(^{35}\mathrm{Cl})$ = 0.125, $A(^{37}\mathrm{Cl})$ = 0.104 (2 Cl); $A(^{14}\mathrm{N})$ = 0.380 (2 N); $A(^{1}\mathrm{H})$ = 0.100 (2 H); $A(^{1}\mathrm{H})$ = 0.130 (2 H); $A(^{27}\mathrm{Al})$ = 0.515 mT (1 Al).

1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthenidealuminum iodide diethyl etherate (3). A solution containing AlI$_3$ (0.14 g, 0.33 mmol) and dpp-BIAN (0.5 g, 1 mmol) in diethyl ether was added to a stripped aluminum foil. The reaction mixture was stirred for 12 h until the solution turned bright-blue. Then the solution was separated from an excess of the foil by decantation. Volatile products were removed *in vacuo*, and the residue was dissolved in benzene. Crystallization afforded compound **3** as dark-blue plate-like crystals in a yield of 0.58 g (77.5%), m.p. 298—301 °C. Found (%): C, 66.58; H, 7.01. C$_{83}$H$_{103}$N$_4$O$_2$I$_2$Al$_2$ (1496.45 g mol^{-1}). Calculated (%): C, 66.62; H, 6.94. IR, ν/cm^{-1}: 3058 w, 2723 w, 1614 m, 1593 m, 1514 s, 1398 w, 1364 w, 1328 m, 1314 m, 1256 m, 1209 m, 1192 m, 1182 w, 1135 m, 1058 m, 1033 s, 1058 m, 1033 s, 1000 w, 966 w, 939 m, 928 s, 916 m, 887 s, 835 w, 813 c 806 m, 783 w, 763 s, 727 m, 686 s, 642 m, 629 m, 599 w, 551 m, 527 m, 517 w, 469 w, 434 m. ^{1}H NMR (200 MHz, THF-d$_8$, 20 °C), δ: 7.26 (s, 3 H); 7.17 (s, 6 H); 6.99 (d, 2 H, ^3J = 8.4 Hz); 6.77 (dd, 2 H, ^3J = 6.9 Hz, ^3J = 8.0 Hz); 5.84 (d, 2 H, ^3J = 6.9 Hz); 3.69 (sept, 4 H, ^3J = 6.9 Hz); 3.39 (q, 4 H, ^3J = 6.9 Hz); 1.26 (d, 12 H, ^3J = 6.9 Hz); 1.12 (t, 6 H, ^3J = 6.9 Hz); 1.06 (d, 12 H, ^3J = 6.9 Hz). ^{13}C NMR (400 MHz, THF-d$_8$, 20 °C), δ: 141.1, 134.0, 129.9, 126.7, 125.9, 124.6, 124.3, 123.0, 122.3, 121.0, 120.6, 115.1, 63.3, 25.6, 18.4, 12.6. ^{1}H NMR (200 MHz, C$_6$D$_6$, 20 °C), δ: 7.29 (m, 6 H); 7.07 (d, 2 H, ^3J = 8.2 Hz); 6.84 (dd, 2 H, ^3J = 6.9 Hz, ^3J = 8.2 Hz); 6.22 (d, 2 H, ^3J = 6.9 Hz); 4.04 (sept, 2 H, ^3J = 6.9 Hz); 3.82 (q, 4 H, ^3J = 7.1 Hz); 3.64 (sept, 2 H, ^3J = 6.9 Hz); 3.35 (q, ^3J = 7.1 Hz); 1.48 (d, 6 H, ^3J = 6.9 Hz); 1.25 (d, 6 H, ^3J = 6.9 Hz); 1.18 (d, 6 H, ^3J = 6.9 Hz); 1.12 (t, ^3J = 7.1 Hz); 1.09 (d, 6 H, ^3J = 6.9 Hz); 0.66 (t, 6 H, ^3J = 7.1 Hz).

1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthenidealuminum chloride diethyl etherate (4). A solution containing AlCl$_3$ (0.05 g, 0.33 mmol) and dpp-BIAN (0.5 g, 1 mmol) in diethyl ether was added to a stripped aluminum foil, and the reaction mixture was stirred for 12 h until the solution turned bright-blue. Then the solution was separated from an excess of the foil

Table 4. Crystallographic parameters, details of X-ray diffraction data collection, and characteristics of the structure refinement of compounds **1**, **2**, and **3**

Parameter	**1**	**2**	**3**
Molecular formula	$C_{60}H_{88}AlCl_5Mg_2N_2O_6$	$C_{36}H_{40}AlCl_2N_2$	$C_{83}H_{103}N_4O_2I_2Al_2$
Molecular weight	1186.17	598.58	1496.45
T/K	173(2)	173(2)	173(2)
Crystal system	Triclinic	Orthorhombic	Triclinic
Space group	$P\bar{1}$	$P2_12_12_1$	$P\bar{1}$
a/Å	12.2431(3)	11.1628(3)	10.7163(3)
b/Å	16.1250(5)	12.4990(3)	15.9205(4)
c/Å	16.6713(5)	24.1919(6)	25.5068(7)
α/deg	77.06	90	98.3830(10)
β/deg	86.4900(10)	90	93.6720(10)
γ/deg	89.3050(10)	90	103.9450(10)
V/Å^3	3201.65(16)	3375.35(15)	4155.95(19)
Z	2	4	2
d/g cm^{-3}	1.230	1.178	1.196
μ/mm^{-1}	0.308	0.244	0.822
F(000)	1264	1268	1554
Crystal dimensions/mm	0.43×0.36×0.10	0.48×0.44×0.41	0.43×0.28×0.08
Scan range, θ/deg	1.30—26.00	1.68—26.00	1.44—25.00
Indices of measured reflections	$-12 \le h \le 15$ $-19 \le k \le 17$ $-19 \le l \le 20$	$-9 \le h \le 13$ $-15 \le k \le 15$ $-28 \le l \le 29$	$-12 \le h \le 12$ $-15 \le k \le 18$ $-30 \le l \le 30$
Number of observed reflections	20952	23382	26634
Number of independent reflections	12291	6634	14608
R_{int}	0.1073	0.0981	0.1112
Goodness-of-fit (F^2)	0.862	1.013	0.985
R_1/wR_2 ($I > 2\sigma(I)$)	0.0704/0.1122	0.0487/0.0994	0.0662/0.1697
R_1/wR_2 (based on all parameters)	0.2297/0.1549	0.0668/0.1079	0.1376/0.2032
Residual electron density/e Å^3, ρ_{max}/ρ_{min}	0.320/−0.315	0.332/−0.267	1.776/−0.924

by decantation. Compound **4** was isolated as dark-blue plate-like crystals in a yield of 0.52 g (85%). T.decomp. 143—150 °C. Found (%): C, 75.40; H, 7.89. $C_{40}H_{50}N_2OClAl$ (637.29 g mol^{-1}). Calculated (%): C, 75.39; H, 7.91. IR, ν/cm^{-1}: 2723 w, 2671 w, 1670 w, 1613 w, 1591 m, 1545 w, 1462 s, 1310 m, 1255 m, 1207 w, 1180 w, 1150 w, 1132 w, 1111 w, 1088 w, 1088 w, 1058 w, 1044 w, 988 m, 939 m, 920 m, 872 m, 832 w, 814 m, 801 m, 758 s, 724 s, 686 w, 660 m, 623 w, 546 s, 505 m. ^{1}H NMR (200 MHz, THF-d$_8$, 20 °C), δ: 7.20 (s, 6 H); 7.04 (d, 2 H, ^3J = 8.3 Hz); 6.80 (dd, 2 H, ^3J = 6.8 Hz, ^3J = 8.3 Hz); 5.84 (d, 2 H, ^3J = 6.8 Hz); 3.70 (sept, 4 H, ^3J = 6.8 Hz); 3.40 (q, 4 H, ^3J = 7.0 Hz); 1.27 (d, 12 H, ^3J = 7.0 Hz); 1.13 (t, 6 H, ^3J = 7.0 Hz); 1.06 (d, 2 H, ^3J = 6.8 Hz). ^{1}H NMR (200 MHz, C_6D_6, 20 °C), δ: 7.38 (m, 6 H); 7.18 (d, 2 H, ^3J = 8.3 Hz); 6.95 (dd, 2 H, ^3J = 7.0 Hz, ^3J = 8.3 Hz); 6.33 (d, 2 H, ^3J = 6.8 Hz); 4.20 (sept, 2 H, ^3J = 6.8 Hz); 3.78 (sept, 2 H, ^3J = 6.8 Hz); 3.75 (q, 4 H, ^3J = 7.1 Hz); 3.35 (q, 4 H, ^3J = 7.1 Hz); 1.58 (d, 6 H, ^3J = 6.8 Hz); 1.35 (d, 6 H, ^3J = 6.8 Hz); 1.25 (d, 6 H, ^3J = 6.8 Hz); 1.21 (m, 12 H); 0.68 (t, 6 H, ^3J = 7.1 Hz). ^{13}C NMR (200 MHz, THF-d$_8$, 20 °C), δ: 146.48, 141.97, 135.46, 131.99, 126.47, 126.30, 124.97, 123.19, 122.92, 117.37, 65.36, 27.91, 24.46, 23.82, 14.74.

X-ray diffraction study of compounds 1—3. X-ray diffraction data sets were collected on a Siemens SMART CCD diffractometer (ω-scanning technique, MoKα radiation, λ = 0.71073 Å, graphite monochromator) at 173 K. Absorption corrections were applied using the SADABS program.[27] The structures were solved by direct methods using the SHELXS97 program package[28] and refined by the full-matrix least-squares method against F^2 with the use of the SHELXL97 program package.[29] All nonhydrogen atoms were refined anisotropically. The hydrogen atoms were placed in idealized positions (U_{iso} = 0.08 Å^3). The crystallographic data, details of X-ray diffraction study, and characteristics of the structure refinement for compounds **1—3** are given in Table 4.

We thank M. P. Bubnov for recording the ESR spectrum.

This study was financially supported by the Russian Foundation for Basic Research (Project No. 03-03-32246), the German Chemical Industry Fund (Fonds der Chemischen Industrie), and the German Research Society (die Deutsche Forschungsgemeinschaft, Graduiertenkolleg "Synthetische, mechanistische und reaktionstechnische Aspekte von Metallkatalysatoren").

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. 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. E. Cherian, E. B. Lobkovsky, and G. W. Coates, *Chem. Commun.*, 2003, **20**, 2566.
6. M. D. Leatherman, S. A. Svejda, L. K. Johnson, and M. Brookhart, *J. Am. Chem. Soc.*, 2003, **125**, 3068.
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. B. S. Williams, M. D. Leatherman, P. S. White, and M. Brookhart, *J. Am. Chem. Soc.*, 2005, **127**, 5132.
11. I. L. Fedushkin, A. A. Skatova, V. A. Chudakova, and G. K. Fukin, *Angew. Chem.*, *Int. Ed.*, 2003, **42**, 3294.
12. 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.
13. I. L. Fedushkin, A. A. Skatova, V. A. Chudakova, G. K. Fukin, S. Dechert, and H. Schumann, *Eur. J. Inorg. Chem.*, 2003, **18**, 3336.
14. 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.
15. I. L. Fedushkin, V. A. Chudakova, A. A. Skatova, and G. K. Fukin, *Heteroatom Chem.*, 2005, **16**, 663.
16. 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.
17. I. L. Fedushkin, A. A. Skatova, G. K. Fukin, M. Hummert, and H. Schumann, *Eur. J. Inorg. Chem.*, 2005, 2332.
18. I. L. Fedushkin, A. G. Morozov, O. V. Rassadin, and G. K. Fukin, *Chem. Eur. J.*, 2005, **11**, 5749.
19. 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].
20. I. L. Fedushkin, N. M. Khvoinova, A. A. Skatova, and G. K. Fukin, *Angew. Chem., Int. Ed.*, 2003, **42**, 5223.
21. H. A. Jenkins, C. L. Dumaresque, D. Vidovic, and J. A. C. Clyburne, *Can. J. Chem.*, 2002, **80**, 1398.
22. R. J. Baker, C. Jones, M. Kloth, and P. Mills, *New. J. Chem.*, 2004, **28**, 207.
23. H. Schumann, M. Hummert, A. N. Lukoyanov, and I. L. Fedushkin, *Organometallics*, 2005, **24**, 3891.
24. I. L. Fedushkin, V. A. Chudakova, G. K. Fukin, S. Dechert, M. Hummert, and H. Schumann, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 2634 [*Russ. Chem. Bull.*, *Int. Ed.*, 2004, **53**, 2744].
25. I. L. Fedushkin, N. M. Khvoinova, A. Yu. Baurin, G. K. Fukin, V. K. Cherkasov, and M. P. Bubnov, *Inorg. Chem.*, 2004, **43**, 7807.
26. R. J. Baker, R. D. Farley, C. Jones, M. Kloth, and D. M. Murphy, *J. Chem. Soc.*, *Dalton Trans.*, 2002, 3844.
27. G. M. Sheldrick, *Empirical Absorption Correction Program*, Universität Göttingen, 1996.
28. G. M. Sheldrick, *Program for Crystal Structure Solution*, Universität Göttingen, 1990.
29. G. M. Sheldrick, *Program for Crystal Structure Refinement*, Universität Göttingen, 1997.

Received July 27, 2005;
in revised form December 24, 2005