Reduction of aromatic ketones with the (dpp-BIAN)AlI(Et_2O) complex*

I. L. Fedushkin,[a]★ A. N. Lukoyanov,[a] G. K. Fukin,[a] 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) 62 9631. 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*

Reduction of benzophenone and 4,4′-bis(methoxy)benzophenone with the aluminum complex (dpp-BIAN)AlI(Et_2O) (**1**) containing the dianionic dpp-BIAN ligand (dpp-BIAN is 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) affords the pinacolate complexes [(dpp-BIAN)AlI]$_2$[μ-$O_2C_2Ph_4$] (**2**) and [(dpp-BIAN)AlI]$_2$[μ-$O_2C_2(C_6H_4OMe)_4$] (**3**), respectively, which undergo the pinacolone rearrangement upon prolonged storage in diethyl ether to form [(dpp-BIAN)AlI]$_2$O (**4**). The reaction of **1** with fluoren-9-one produces stable pinacolate (dpp-BIAN)Al[μ-$O_2(C_{13}H_8)_2$] (**7**) and the (dpp-BIAN)AlI_2 complex (**8**). Compounds **2—4**, **7**, and **8** were characterized by ESR spectroscopy. Hydrolysis products of compounds **2** and **3** were characterized by ^{1}H NMR spectroscopy. The structures of complexes **4** and **7** were established by X-ray diffraction.

Key words: aluminum, diimines, radical anion, X-ray diffraction study, electronic paramagnetic resonance.

In recent years, metal complexes with diimine ligands attracted interest due to their unique chemical properties. Based on this class of compounds, efficient catalysts were constructed for various chemical reactions, including alkyne hydrogenation,[1] carbon—carbon bond formation,[2] cycloisomerization,[3] hydrosilylation,[4] polymerization of olefins[5] and acrylic monomers,[6] copolymerization of ethylene and norbornene,[7] and copolymerization of CO_2 and methylenecyclopropene[8] and styrene.[9] Nowadays, acenaphthene-1,2-diimine (BIAN) derivatives of late transition metals (Brookhart catalysts) are the most efficient olefin polymerization catalysts.[10] The conformational rigidity of the BIAN ligand and its π-acceptor properties induce an electron deficiency at the metal atom, which is responsible for high reactivity of these complexes toward organic compounds.

In our studies of acenaphthene-1,2-diimine complexes with main-group metals, we used primarily 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-BIAN), which can easily be prepared by condensation of commercially available acenaphthenequinone and 2,6-diisopropylaniline in acetonitrile. An interesting feature of dpp-BIAN is that it has a variable oxidation state in complexes with main-group metals. Diimine dpp-BIAN can be reduced with alkali metals to the mono-, di-, tri-, and tetraanions to form salts (dpp-BIAN)$M_m(Et_2O)_n$ (M = Li or Na; m = 1—4).[11] Alkaline-earth metals reduce dpp-BIAN only to the dianion with the formation of the monomeric complexes (dpp-BIAN)M(THF)$_n$ (M = Mg, Ca, Sr, or Ba).[12] Reduction of dpp-BIAN with aluminum metal in the presence of $AlCl_3$ or AlI_3 in toluene or diethyl ether affords the radical-anionic complex (dpp-BIAN)$AlCl_2$ and the dianionic products (dpp-BIAN)AlCl(Et_2O) and (dpp-BIAN)AlI(Et_2O),[13] respectively. Alkyl derivatives of aluminum with both radical-anionic and dianionic dpp-BIAN ligands have been synthesized[14] by the exchange reactions of the corresponding sodium salts of dpp-BIAN with alkylaluminum halides.[14] Germylenes of composition (BIAN)Ge (see Ref. 15) and (dpp-BIAN)GeCl (see Ref. 16) were also prepared by the exchange reactions of sodium salts of three different acenaphthene-1,2-diimines with germanium dichloride.

The chemical properties of acenaphthene-1,2-diimine derivatives of main-group metals were studied in most detail for the (dpp-BIAN)Mg(THF)$_3$ complex. The latter serves as a one-electron reducing agent with respect to organic halides[17] and aromatic ketones.[18] The reactions of (dpp-BIAN)Mg(THF)$_3$ with organic compounds con-

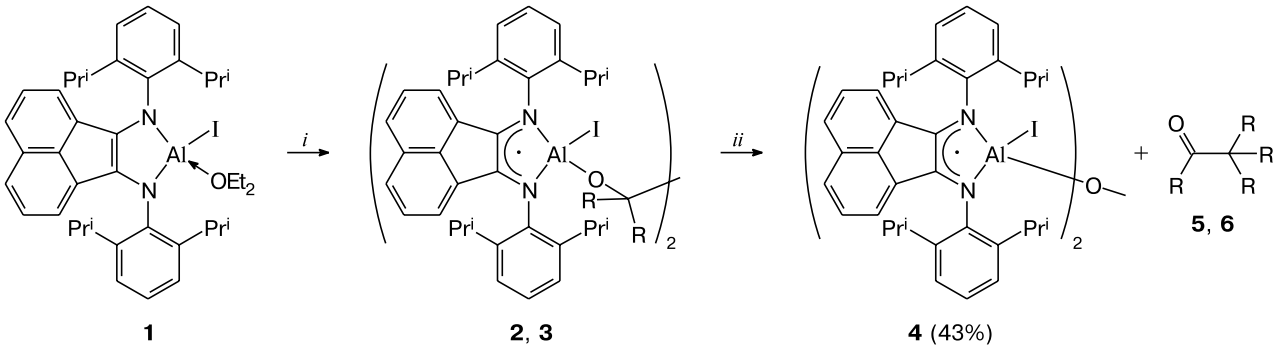
* dpp-BIAN is 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene.

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

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1134—1140, July, 2006.

1066-5285/06/5507-1177

Scheme 1



1 **2**, **3** **4** (43%)

i. $R_2C{=}O$, Et_2O, 1 min; *ii*. Et_2O.

R = Ph (**2**, **5**), *p*-$MeOC_6H_4$ (**3**, **6**)

taining 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 form the corresponding enolate, ketene imine, and phenylethynyl derivatives.

In the present work aimed at revealing the chemical properties of acenaphthene-1,2-diimine derivatives of aluminum, we examined the reactions of the (dpp-BIAN)AlI(Et_2O) complex with aromatic ketones. Reduction of aromatic ketones with the (dpp-BIAN)AlI(Et_2O) complex, unlike that with (dpp-BIAN)Mg$(THF)_3$, does not stop at the formation of pinacolates but affords pinacolone rearrangement products.

Results and Discussion

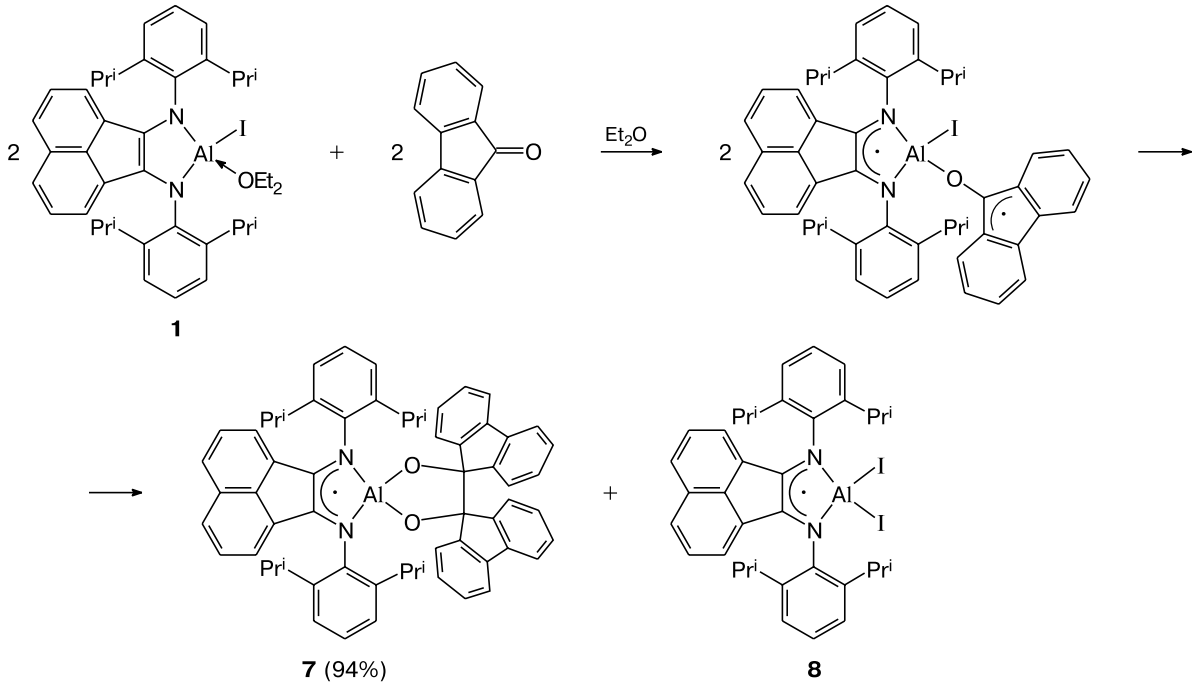
Reactions of the (dpp-BIAN)AlI(Et_2O) complex (1) with benzophenone, 4,4′-bis(methoxy)benzophenone, and fluoren-9-one. Compound **1** was prepared by reduction of diimine dpp-BIAN with aluminum metal in the presence of AlI_3 in diethyl ether according to a known procedure.[13] After the addition of equimolar amounts of the above-mentioned ketones to an ethereal solution of complex **1**, the color of the solution rapidly changes from blue to red-brown. In the case of benzophenone and 4,4′-bis(methoxy)benzophenone, the initially formed crystalline reaction products were not isolated in individual state, whereas precipitation of the reaction product of **1** with fluoren-9-one starts already in the course of the synthesis. The compounds produced in the reactions of complex **1** with benzophenone and 4,4′-bis(methoxy)benzophenone were identified by ESR spectroscopy and based on analysis of their hydrolysis products by ^{1}H NMR spectroscopy. The results provide evidence that the reactions of **1** with the above-mentioned aromatic ketones proceed with the formation of pinacolates [(dpp-BIAN)AlI]$_2$[μ-$O_2C_2Ph_4$] (**2**) and [(dpp-BIAN)AlI]$_2$[μ-$O_2C_2(C_6H_4OMe)_4$] (**3**) (Scheme 1).

The ESR spectra of the solutions formed immediately after mixing of complex **1** with benzophenone or 4,4′-bis(methoxy)benzophenone show a signal of the radical anion of dpp-BIAN, which is indicative of the one-electron transfer from the dianion of dpp-BIAN to the corresponding ketone. After hydrolysis of these solutions, the presence of the corresponding benzpinacols in the reaction mixtures was established by ^{1}H NMR spectroscopy. However, the [(dpp-BIAN)AlI]$_2$O compound (**4**) was isolated from these solutions after storage at room temperature for several hours. Compound **4** is one of the pinacolone rearrangement products of complexes **2** and **3** (see Scheme 1). Compound **4** was characterized by elemental analysis and X-ray diffraction. The reaction of the magnesium derivative (dpp-BIAN)Mg$(THF)_3$ with benzophenone produced a stable dimeric radical-anionic pinacolate complex.[18]

We failed to isolate the pinacolone rearrangement products, *viz.*, ketones **5** and **6**, in individual state, but their formation was proved by NMR spectroscopy. Within 10 days after mixing of complex **1** and 4,4′-bis(methoxy)benzophenone, the precipitate of compound **4** that formed was filtered off, and the ethereal mother liquor was subjected to hydrolysis and oxidation with atmospheric oxygen. The resulting neutral dpp-BIAN was separated by decantation. According to the results of ^{1}H NMR and ^{1}H—^{1}H COSY spectroscopy, the ethereal solution obtained after hydrolysis and oxidation contained compound **6**,* pinacol 1,1,2,2-tetrakis(4-methoxyphe-

* ^{1}H NMR ($CDCl_3$, δ) of compound **6**: 7.69 and 6.65 (both d, 2 H each, O=C—$C_6\underline{H}_4$—OMe, J = 9.0 Hz); 7.19 and 6.78 (both d, 6 H each, —C($C_6\underline{H}_4$—OMe)$_3$, J = 8.8 Hz); 3.76 (s, 3 H, O=C—C_6H_4—O<u>Me</u>); 3.75 (s, 9 H, —C(C_6H_4—O<u>Me</u>)$_3$).

Scheme 2



nyl)ethane-1,2-diol,* and the starting ketone.** The ratio of these three compounds in the hydrolysis products varies depending on the time of storage of complex **3** in an ethereal solution. Within 10 and 30 days after storage of complex **3** in an ethereal solution, ketone **6** (35 and 66%, respectively), pinacol 1,1,2,2-tetrakis(4-methoxyphenyl)ethane-1,2-diol (30 and 9%), and the starting 4,4′-bis(methoxy)benzophenone (35 and 25%) were found in the hydrolysis products.

Since pinacol, which can be generated by dimerization of the radical anions of fluoren-9-one, cannot undergo the pinacolone rearrangement, the reaction of complex **1** with this ketone affords stable pinacolate (dpp-BIAN)Al[μ-$O_2(C_{13}H_8)_2$] (**7**) (Scheme 2). Apparently, complex **7** is formed *via* disproportionation of the initially formed ketyl derivative (see Scheme 2). The (dpp-BIAN)AlI_2 compound (**8**) was also isolated as the product of the reaction of **1** with fluoren-9-one, which is evidence that the initially formed ketyl derivative undergoes disproportionation. Within 30 min after mixing of the reagents, compound **7** was isolated from the reaction mixture as crystals in 94% yield, whereas compound **8** remained in solution. After separation of compound **7**, the mother liquor was concentrated to give compound **8** as green crystals. Compounds **7** and **8** were identified by ESR spectroscopy and elemental analysis. The molecular structure of complex **7** was established by X-ray diffraction.

Complex **8** was also prepared by the reaction of dpp-BIAN with aluminum metal in the presence of aluminum triiodide in toluene according to a procedure, which has been used earlier for the synthesis of the chloride analog (dpp-BIAN)$AlCl_2$.[13]

We failed to detect the formation of the ketyl intermediate in the reaction of **1** with fluoren-9-one by the ESR method. This can be attributed to both a short lifetime of this intermediate and the fact that the spectrum of the reaction mixture gives two signals of disproportionation products of the intermediate, which hinder the appearance of the signal of the ketyl derivative.

Molecular structures of compounds 4 and 7. The structures of compounds **4** and **7** were established by X-ray diffraction (Figs 1 and 2). 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 are listed in Table 2.

Table 3 gives a comparison of the bond lengths in the diimine fragment and the N—Al—N bond angles and the Al—N bond lengths in compounds **4** and **7** with the corresponding data for (dpp-BIAN)$AlCl_2$.[13] It can be seen that the C—N bonds in compounds **4** and **7** are shorter, whereas the C(1)—C(2) bond is longer than the corre-

* ^{1}H NMR ($CDCl_3$, δ) of pinacol 1,1,2,2-tetrakis(4-methoxyphenyl)ethane-1,2-diol: 7.19 and 6.70 (both d, 8 H each, —$C_6\underline{H}_4$—OMe, J = 8.9 Hz); 5.79 (s, 2 H, —OH); 3.75 (s, 12 H, —OMe)]

** ^{1}H NMR ($CDCl_3$, δ) of the starting ketone: 7.79 and 6.96 (both d, 4 H each, —$C_6\underline{H}_4$—OMe, J = 8.8 Hz); 3.88 (s, 6 H, —OMe).

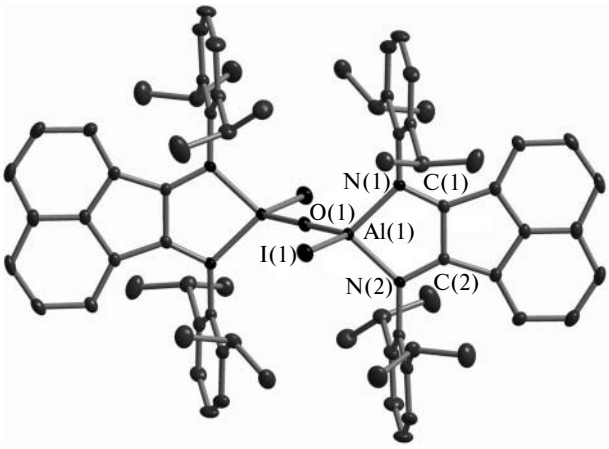


Fig. 1. Molecular structure of compound **4**. The hydrogen atoms are omitted. The atoms are represented by anisotropic displacement ellipsoids drawn at the 30% probability level.

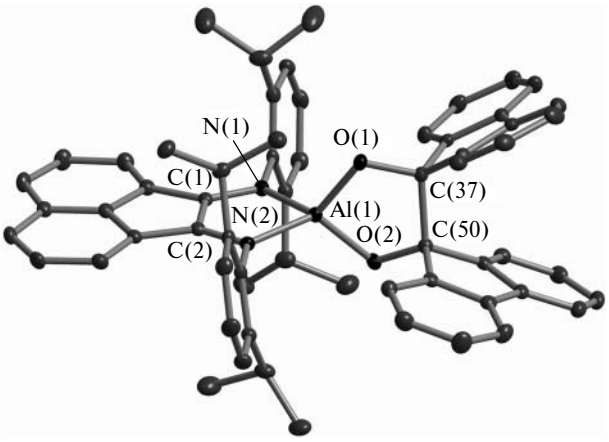


Fig. 2. Molecular structure of compound **7**. The hydrogen atoms are omitted. The atoms are represented by anisotropic displacement ellipsoids drawn at the 30% probability level.

Table 1. Crystallographic parameters, details of X-ray diffraction data collection, and characteristics of the structure refinement of compounds **4** and **7**

Parameter	**4**	**7**
Molecular formula	$C_{76}H_{91}Al_2I_2N_4O_2$	$C_{66}H_{66}AlN_2O_3$
Molecular weight	1400.29	962.19
T/K	173(2)	100(2)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a/Å	13.2076(4)	12.2193(17)
b/Å	16.7653(4)	30.107(4)
c/Å	18.6406(6)	14.997(2)
α/deg	70.2790(10)	90
β/deg	87.8700(10)	101.719(3)
γ/deg	68.8200(10)	90
V/Å^3	3606.09(18)	5402.2(13)
Z	2	4
d_{calc}/g cm^{-3}	1.290	1.183
μ/mm^{-1}	0.942	0.086
F(000)	1446	2052
Crystal dimensions/mm	0.50×0.36×0.16	0.15×0.10×0.08
Scan range, θ/deg	1.39—27.50	1.83—25.00
Indices of measured reflections	$-16 \le h \le 17$ $-15 \le k \le 21$ $-20 \le l \le 24$	$-14 \le h \le 14$ $-35 \le k \le 35$ $-17 \le l \le 17$
Number of observed reflections	28065	29625
Number of independent reflections	16552	9526
R_{int}	0.0554	0.0517
Goodness-of-fit on F^2	1.042	0.956
R_1/wR_2 ($I > 2\sigma(I)$)	0.0463/0.1016	0.0476/0.1006
R_1/wR_2 (based on all reflections)	0.0769/0.1185	0.0855/0.1107
Residual electron density/e Å^{-3}, ρ_{max}/ρ_{min}	1.342/−0.823	0.667/−0.202

sponding bonds in **1**. This indicates that the dianion of dpp-BIAN is oxidized to give the monoanion upon the formation of complexes **4** and **7** from **1**.

The aluminum atoms in complexes **4** and **7** have a tetrahedral coordination. In both compounds, the radical anion of dpp-BIAN chelates the metal atom. In dinuclear complex **4**, the aluminum atoms are linked to each other by the bridging oxygen atom lying on an inversion center. The central Al—O—Al fragment is linear (Al(1)—O(1) and Al(1#)—O(1), 1.677(1) Å; Al(1)—O—Al(1#), 180°). An analogous linear Al—O—Al fragment was found in the structure of an vinamidine complex.[21] Complex **7** lies on a twofold rotation axis passing through the Al atom, the midpoint of the C(1)—C(2) bond of the radical-anionic dpp-BIAN ligand, and the midpoint of the C(37)—C(50) bond of the pinacolate dianion. The C(37)—C(50) distance (1.631 Å) is substantially larger than the C—C single bond length (1.54 Å) but is comparable with the length of the corresponding bond in dinuclear pinacolate [(dpp-BIAN)Mg]$_2$[μ-O$_2$C$_2$Ph$_4$],[18] which was prepared by the reaction of the magnesium complex (dpp-BIAN)Mg(THF)$_3$ with benzophenone.

Study of compounds 2—4, 7, and 8 by the ESR method. Compounds **2**, **3**, **7**, and **8** are paramagnetic. In solution, these compounds give ESR spectra characteristic of aluminum compounds with the radical-anionic dpp-BIAN ligand (Table 4). The ESR spectra of compounds **2**, **3**, and **7** have similar parameters and are similar in shape to the ESR signal of the (dpp-BIAN)AlMe$_2$ compound.[14a] The ESR spectrum of complex **7** (Fig. 3) shows splitting of the unpaired electron on ^{27}Al (100%, I = 5/2), ^{14}N (99.64%, I = 1), and ^{1}H (99.99%, I =1/2).

A comparison of the ESR spectroscopic data for compounds **2**, **3**, **7**, and (dpp-BIAN)AlMe$_2$ demonstrated that

Table 2. Selected bond lengths (*d*) and bond angles (ω) in compounds **4** and **7**

Parameter	**4**	**7**
Bond	*d*/Å	
Al(1)—N(1)	1.914(4)	1.906(1)
Al(1)—N(2)	1.909(3)	1.917(1)
Al(1)—O(1)	1.677(1)	1.744(2)
Al(1)—O(2)	—	1.748(2)
Al(1)—I(1)	2.521(2)	—
N(1)—C(1)	1.336(4)	1.339(1)
N(2)—C(2)	1.346(5)	1.342(1)
C(1)—C(2)	1.437(5)	1.429(1)
C(37)—C(50)	—	1.631(0)
O(1)—C(37)	—	1.419(1)
O(1)—C(50)	—	1.412(2)
Angle	ω/deg	
O(1)—Al(1)—O(2)	—	95.03(1)
N(1)—Al(1)—N(2)	88.02(13)	87.30(1)
O(1)—Al(1)—I(1)	108.32(5)	—

Table 3. Comparison of the bond lengths and bond angles in the diimine fragment in compounds **1**, **4**, **7**, and (dpp-BIAN)$AlCl_2$ (see Ref. 13) (**A**)

Parameter	**1**	**4**	**7**	**A**
Bond		*d*/Å		
N—C	1.394(8)	1.336(4)	1.339(1)	1.346(3)
	1.418(9)	1.346(5)	1.342(1)	1.341(3)
C(1)—C(2)	1.390(11)	1.437(5)	1.429(1)	1.431(3)
Al—N	1.833(6)	1.914(4)	1.906(1)	1.890(2)
	1.839(5)	1.909(3)	1.917(1)	1.888(2)
Angle		ω/deg		
N(1)—Al—N(2)	95.49(25)	88.02(13)	87.30(1)	89.19(9)

the replacement of the alkyl groups at the aluminum atom with the pinacolone groups containing strongly electron-withdrawing oxygen atoms leads to a redistribution of the

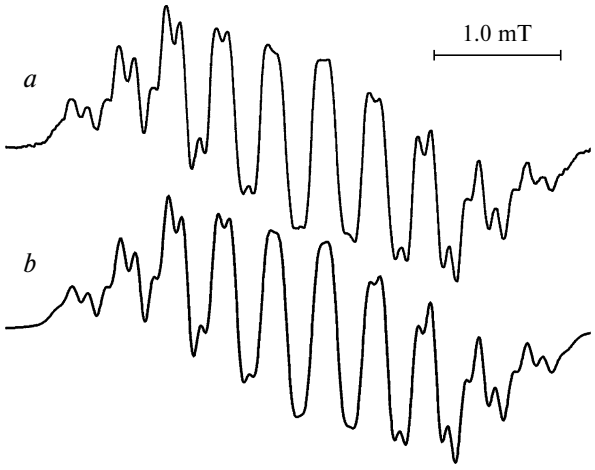


Fig. 3. (*a*) ESR spectrum of compound **7** ($g = 2.0031$) in toluene (298 K) and (*b*) the calculated spectrum of **7** (parameters are given in Table 4).

electron density throughout the molecule and its decrease on the ligand and the aluminum atom. This is evidenced by a decrease in the hyperfine coupling constants of the unpaired electron on the aluminum and nitrogen atoms in compounds **2**, **3**, and **7**. This, in turn, leads to a decrease in the total extension of the spectra of **2**, **3**, and **7** ($\Delta H = 4.3$ mT) compared to that of (dpp-BIAN)$AlMe_2$ ($\Delta H = 5.6$ mT).

The ESR spectrum of compound **8** (Fig. 4) reveals splitting of the unpaired electron on ^{27}Al (100%, $I = 5/2$), ^{14}N (99.64%, $I = 1$), ^{127}I (100%, $I = 5/2$), and ^{1}H (99.99%, $I = 1/2$). A comparison of the hyperfine coupling constants in the spectra of complex **8**, (dpp-BIAN)$AlCl_2$,[13] and (dpp-BIAN)$AlMe_2$ (see Ref. 14a) demonstrated that the spin density on the metal atom in the halide derivatives is lower than that in (dpp-BIAN)$AlMe_2$. In going from the Me derivative to **8** and (dpp-BIAN)$AlCl_2$, the hyperfine coupling constants with the nitrogen nuclei in

Table 4. Isotropic *g* factors and hyperfine splitting constants for compounds **2—4**, **7**, **8**, (dpp-BIAN)$AlCl_2$ (see Ref. 13), and (dpp-BIAN)$AlMe_2$ (see Ref. 14a)

Compound	g_i	Al	^{14}N	$^{1}H^a$	$^{1}H^a$	Hal[b]	ΔH/mT
2	2.0030	0.395	0.35	0.12	0.11		0.18
3	2.0030	0.405	0.355	0.12	0.11		0.13
4	2.0032						0.12
7	2.0031	0.40	0.36	0.12	0.11		
8	2.0032	0.28	0.49	0.10	0.10	0.05 (^{127}I)	0.10
(dpp-BIAN)$AlCl_2$	2.0026	0.515	0.38	0.13	0.10	0.125 (^{35}Cl) 0.104 (^{37}Cl)	
(dpp-BIAN)$AlMe_2$	2.0031	0.60	0.46	0.14	0.10		

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

[b] The signal of Hal belongs to the nuclei of the corresponding halogens (^{35}Cl and ^{37}Cl or ^{127}I) in the following compounds: **8**, for two equivalent iodine atoms; (dpp-BIAN)$AlCl_2$, for two equivalent chlorine atoms.

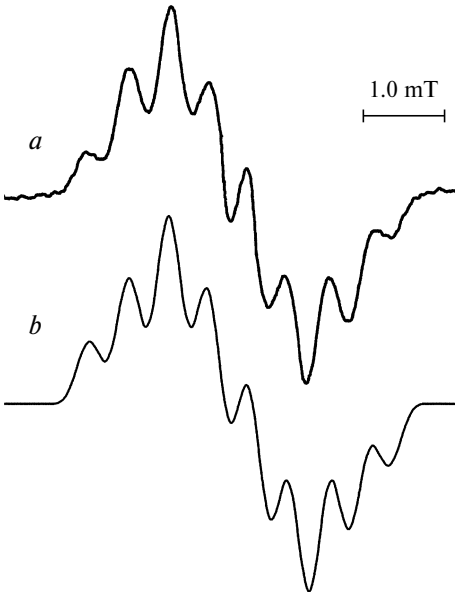


Fig. 4. (*a*) ESR spectrum of compound **8** (g = 2.0032) in toluene (298 K) and (*b*) the calculated spectrum of **8** (parameters are given in Table 4).

dpp-BIAN change in the opposite directions. In the chlorine-containing complex, this constant decreases, whereas it increases in the iodine-containing complex.

Since compound **4** is poorly soluble in organic solvents, the resolved spectrum of this compound was not obtained. In the crystalline state, compound **4** has an ESR signal with the g factor of 2.0032.

Experimental

All operations associated with the synthesis, isolation, and identification of the reaction products were carried out *in vacuo* using the Schlenk technique. Diimine dpp-BIAN was prepared by condensation of acenaphthenequinone with 2,6-diisopropylaniline (Aldrich) in acetonitrile. Commercial bis(4-methoxyphenyl)methanone and fluoren-9-one (Aldrich) were used. Complex **1** was synthesized according to a known procedure.[13] Diethyl ether and toluene were dried and stored over sodium benzophenone ketyl and were distilled off *in vacuo* immediately before use. The yields of the reaction products were calculated based on dpp-BIAN consumed (0.5 g, 1.0 mmol). The IR spectra were recorded on a Magne System 750 spectrometer (Nujol mulls). The ^{1}H NMR spectra of the pinacolone rearrangement products were measured on a Bruker DPX 200 spectrometer; the chemical shifts are given with respect to the chemical shifts of the residual protons of $CDCl_3$. The ESR signals of compounds **2—4**, **7**, and **8** were recorded on a Bruker ER 200D-SRC spectrometer relative to the signal of diphenylpicrylhydrazyl (DPPH, g = 2.0037).

Bis[1,2-bis{(2,6-diisopropylphenyl)imino}acenaphthenealuminum iodide] 1,1,2,2-tetraphenylethane-1,2-bis(olate) (2). Benzophenone (0.18 g, 1.00 mmol) was added to a solution of complex **1**, which was prepared from dpp-BIAN (0.5 g, 1.0 mmol) and I_2 (0.13 g, 0.5 mmol) in Et_2O. The color of the solution rapidly changed from blue to red-brown. The resulting solution was used for recording the ESR spectrum. ESR (298 K, Et_2O): g = 2.0030, a_{Al}(1 Al) = 0.395, a_N(2 N)= 0.35, a_H(2 H) = 0.12, a_H(2 H) = 0.11 mT.

Bis[1,2-bis{(2,6-diisopropylphenyl)imino}acenaphthenealuminum iodide] 1,1,2,2-tetrakis(4-methoxyphenyl)ethane-1,2-bis(olate) (3). Bis(4-methoxyphenyl)methanone (0.24 g, 1.0 mmol) was added to a solution of complex **1**, which was prepared from dpp-BIAN (0.5 g, 1.0 mmol) and I_2 (0.13 g, 0.5 mmol) in Et_2O. The color of the solution rapidly changed from blue to red-brown. The resulting solution was used for recording the ESR spectrum. ESR (298 K, Et_2O): g = 2.0030, a_{Al}(1 Al) = 0.405, a_N(2 N)= 0.355, a_H(2 H) = 0.12, a_H(2 H) = 0.11 mT.

Bis[1,2-bis{(2,6-diisopropylphenyl)imino}acenaphthenealuminum iodide] oxide (4). Red-brown crystals of compound **4** (43%) were obtained upon storage of an ethereal solution of compound **3** at room temperature for 10 days. T.decomp. 382 °C. Found (%): C, 65.17; H, 6.52. $C_{76}H_{91}Al_2I_2N_4O_2$ (1400.29 g mol^{-1}). Calculated (%): C, 65.19; H, 6.55. IR (Nujol mulls), ν/cm^{-1}: 2724 w, 1933 w, 1819 w, 1671 w, 1590 m, 1532 s, 1321 m, 1254 m, 1213 w, 1188 m, 1116 m, 1099 w, 1040 s, 950 w, 934 w, 895 m, 822 s, 802 s, 786 w, 763 s, 723 w, 669 m, 648 m, 620 w, 594 s, 548 w, 521 m, 488 w, 466 s, 451 w, 431 s. ESR (298 K, toluene): g = 2.0032.

1,2-Bis{(2,6-diisopropylphenyl)imino}acenaphthenealuminum 9,9´-bis(9*H*-fluorene)-9,9´-bis(olate) (7). Fluoren-9-one (0.18 g, 1.0 mmol) was added to a solution of complex **1**, which was prepared from dpp-BIAN (0.5 g, 1.0 mmol) and I_2 (0.13 g, 0.5 mmol) in Et_2O. The color of the solution rapidly changed from blue to red-brown. Brown crystals of complex **7** precipitated from the solution during 5 min (0.45 g, 94%). M.p. 266—267 °C. Found (%): C, 82.31; H, 6.91. $C_{62}H_{56}AlN_2O_2 \cdot C_4H_{10}O$ (962.19 g mol^{-1}). Calculated (%): C, 82.39; H, 6.86. IR (Nujol mulls), ν/cm^{-1}: 3064 w, 2726 w, 1940 w, 1724 s, 1670 w, 1608 w, 1588 m, 1539 m, 1320 w, 1190 w, 1152 m, 1123 m, 1023 m, 953 w, 898 m, 803 m, 771 m, 737 s, 724 s, 671 w, 620 m, 594 w, 568 m, 548 w, 524 m, 487 m. ESR (298 K, toluene): g = 2.0031, a_{Al}(1 Al)= 0.40, a_N(2 N) = 0.36, a_H(2 H) = 0.12, a_H(2 H) = 0.11 mT. After separation of the crystals of complex **7**, the removal of the solvent *in vacuo* led to crystallization of the (dpp-BIAN)AlI_2 compound (**8**). Complex **8** was obtained as green crystals in a yield of 0.13 g (33%). Found (%): C, 55.19; H, 5.13; I, 32.11. $C_{36}H_{40}N_2I_2Al$ (781.61 g mol^{-1}). Calculated (%): C, 55.32; H, 5.16; I, 32.50. ESR (298 K, toluene): g = 2.0032, a_{Al}(1 Al) = 0.28, a_N(2 N) = 0.49, a_I(2 I) = 0.05, a_H(2 H) = 0.10, a_H(2 H) = 0.10 mT.

1,2-Bis{(2,6-diisopropylphenyl)imino}acenaphthenealuminum iodide (8) from AlI_3, dppBIAN, and aluminum metal. A solution containing AlI_3 (0.27 g, 0.7 mmol) and dpp-BIAN (0.5 g, 1 mmol) in toluene was poured 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 excess aluminum by decantation. Compound **8** was isolated from the resulting solution as green crystals in a yield of 0.49 g (83%).

X-ray diffraction study of compounds 4 and 7. X-ray diffraction data for compound **4** were collected on a Siemens SMART CCD diffractometer (graphite monochromator, λ(Mo-Kα) = 0.71073 Å, 173 K, ω-scanning technique). X-ray diffraction

data for compound **7** were collected on a Bruker SMART APEX diffractometer (graphite monochromator, λ(Mo-Kα) = 0.71073 Å, 100 K, ω-scanning technique). The crystallographic data and details of the structure refinement for compounds **4** and **7** are given in Table 1. Absorption corrections were applied using the SADABS program.[22] The structures were solved by direct methods using the SHELXS97 program package[23] and refined by the full-matrix least-squares method against F^2 with the use of the SHELXL97 program package.[24] All nonhydrogen atoms were refined anisotropically. The hydrogen atoms were placed in idealized positions (U_{iso} = 0.08 Å^3). The geometric characteristics were analyzed using the DIAMOND program.[25]

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

This study was financially supported by the Russian Foundation for Basic Research (Project No. 05-03-32643) and the German Research Society (die Deutsche Forschungsgemeinschaft, Graduiertenkolleg, DFG).

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. J. Kiesewetter and W. Kaminsky, *Chem. Eur. J.* 2003, **9**, 1750.
8. D. Takeuchi, A. Yasuda, and K. Osakada, *Dalton Trans.*, 2003, 2029.
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. I. L. Fedushkin, A. A. Skatova, V. A. Chudakova, and G. K. Fukin, *Angew. Chem., Int. Ed.*, 2003, **42**, 3294.
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, 409 [*Russ. Chem. Bull., Int. Ed.*, 2006, **55**, 422].
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**, 1471.
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**, 74].
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. N. Kuhn, S. Fuchs, E. Niquet, M. Richter, and M. Steimann, *Z. Anorg. Allg. Chem.*, 2002, **628**, 717.
22. G. M. Sheldrick, *SADABS Program for Empirical Absorption Correction of Area Detector Data*, Universität Göttingen, Göttingen (Germany), 1996.
23. G. M. Sheldrick, *SHELXS-97 Program for the Solution of Crystal Structures*, Universität Göttingen, Göttingen (Germany), 1990.
24. G. M. Sheldrick, *SHELXL-97 Program for the Refinement of Crystal Structures*, Universität Göttingen, Göttingen (Germany), 1997.
25. K. Brandenburg, *Diamond Version 2.1c*, Institut für Anorganische Chemie Universität Kiel, 1999.

Received February 22, 2006;
in revised form May 15, 2006