

# Monomeric Alkylaluminum Complexes (dpp-BIAN)AlR<sub>2</sub> (R = Me, Et, <sup>i</sup>Bu) Supported by the Rigid Chelating Radical-Anionic 1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthene Ligand (dpp-BIAN)

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Me<sub>2</sub>AlCl, Et<sub>2</sub>AlBr, and <sup>i</sup>Bu<sub>2</sub>AlCl react with (dpp-BIAN)Na (dpp-BIAN = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) in Et<sub>2</sub>O to give the dialkylaluminum complexes (dpp-BIAN)AlR<sub>2</sub> (R = Me (**1**), Et (**2**), <sup>i</sup>Bu (**3**)). Compounds **1–3** have been characterized by elemental analysis, IR and ESR spectroscopy, and X-ray crystal structure analysis. In the molecules of **1–3** the Al atoms are tetrahedrally coordinated by two alkyl groups and the two N atoms of the dpp-BIAN ligand. The ESR spectra of the complexes prove the radical character of the dpp-BIAN ligand and show a hyperfine structure due to the coupling of the unpaired electron with the <sup>14</sup>N, <sup>27</sup>Al, and <sup>1</sup>H nuclei.

## Introduction

Besides alkyl lithium and Grignard compounds, aluminum alkyls are the most widely used alkylating reagents in organic synthesis.<sup>1</sup> In the past decade the authors representing the Berlin group prepared a number of intramolecularly O- and N-donor-stabilized alkyl aluminum compounds which serve well as reagents for the transfer of alkyl groups to organic molecules<sup>2</sup> and as cocatalysts in the Ziegler–Natta olefin polymerization.<sup>3</sup> In general, aluminum alkyls tend to form dimers. However, monomeric aluminum dialkyls can be prepared using either intramolecularly coordinating alkyl ligands<sup>3</sup> or monoanionic, rigid chelating ligands bearing bulky substituents such as amidinates,<sup>4</sup> amino-amides,<sup>5</sup> ketiminates,<sup>6</sup> and tropoiminates.<sup>7</sup>

While Ar-BIAN transition metal complexes have already been recognized as versatile catalysts in a number of important organic reactions,<sup>8</sup> main group metal complexes containing this ligand were unknown until quite recently. Therefore, we focused our interest on the preparation and characterization of such Ar-BIAN, especially of dpp-BIAN-stabilized main group metal complexes (dpp-BIAN = 1,2-bis[(2,6-diisopropyl-

phenyl)imino]acenaphthene). We established that metals of groups 1, 2, and 14 can form complexes with different anionic types of the dpp-BIAN ligand and that this ligand once being bound to the metal can receive

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and release electrons and protons, thus giving rise to a quite specific reactivity of such complexes toward inorganic and organic substrates as demonstrated by the following examples. The reduction of the ligand with Li or Na in ether leads to the consequent formation of mono-, di-, tri-, and tetra-anions of dpp-BIAN, yielding salts of the type  $(\text{dpp-BIAN})\text{M}(\text{Et}_2\text{O})_n$  ( $\text{M} = \text{Li, Na}; n = 1 \text{ to } 4$ ).<sup>9</sup> Metallic Mg and Ca react with dpp-BIAN in THF to form the monomeric complexes  $(\text{dpp-BIAN})\text{M}(\text{THF})_n$  ( $\text{M} = \text{Mg, Ca}$ ) containing the ligand as dianion.<sup>10</sup> The oxidation of the magnesium complex  $(\text{dpp-BIAN})\text{-Mg}(\text{THF})_3$  with different halogen-containing substances, such as  $\text{CuCl}$ ,  $\text{Ph}_3\text{SnCl}$ ,  $\text{Ph}_2\text{CHCHBr}_2$ , or  $\text{I}_2$ , result in the formation of  $(\text{dpp-BIAN})\text{MgX}(\text{L})_n$  ( $\text{X} = \text{Cl, Br, I}; \text{L} = \text{THF, DME}$ ),<sup>11</sup> and the metal exchange reaction of this magnesium complex with  $\text{GeCl}_2$  affords the solvent-free two- and three-coordinate germanium(II) compounds  $(\text{dpp-BIAN})\text{Ge}$  and  $(\text{dpp-BIAN})\text{GeCl}$ , containing the dianion and the radical-anion of the ligand, respectively.<sup>12</sup>  $(\text{dpp-BIAN})\text{Mg}(\text{THF})_3$  also reveals an exceptional reactivity toward organic substrates, such as aro-

matic<sup>13</sup> and aliphatic<sup>14</sup> ketones and terminal alkynes.<sup>15</sup> Just recently we observed the unprecedented reductive elimination of isopropyl radicals from  $(\text{dpp-BIAN})\text{Mg}(\text{Et}_2\text{O})_2$ , yielding  $(\text{dpp-BIAN})\text{Mg}(\text{Et}_2\text{O})_2$ , a process that is connected with the reduction of the  $(\text{dpp-BIAN})$  radical-anions to dianions and oxidation of the isopropyl carbanions to isopropyl radicals.<sup>16</sup>

In this paper we report on the synthesis, crystal structure, and ESR spectra of the monomeric dialkyl aluminum complexes  $(\text{dpp-BIAN})\text{AlR}_2$  ( $\text{R} = \text{Me, Et, } ^i\text{Bu}$ ), which are, as far as we know, the first examples of structurally characterized alkyl aluminum derivatives with a paramagnetic radical-anionic ligand.

## Results and Discussion

**Synthesis of  $(\text{dpp-BIAN})\text{AlMe}_2$  (1),  $(\text{dpp-BIAN})\text{-AlEt}_2$  (2), and  $(\text{dpp-BIAN})\text{Al}^i\text{Bu}_2$  (3).** The compounds **1**, **2**, and **3** were prepared by the metathetical reactions of  $(\text{dpp-BIAN})\text{Na}$ , prepared from dpp-BIAN and metallic sodium, with the respective dialkylaluminum halide in  $\text{Et}_2\text{O}$  at ambient temperature (Scheme 1). Crystallization of the crude products from hexane affords **1**, **2**, and **3** in yields of 70–80% as deep red, air- and moisture-sensitive crystals that melt in the temperature range 190–198 °C. At room temperature, the methyl and ethyl derivatives are stable in solution for several weeks, whereas the isobutyl derivative decomposes slowly. **3** decomposes in solution at temperatures above 60 °C within a few hours to give free  $(\text{dpp-BIAN})$  and unidentified aluminum-containing products.

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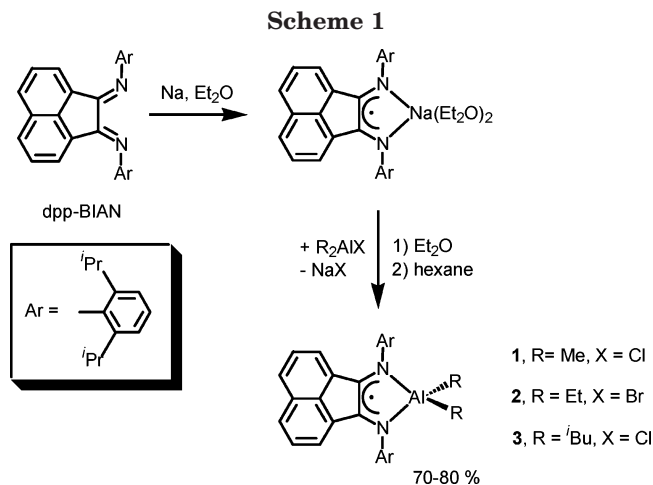
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The IR and ESR data of **1**, **2**, and **3** are consistent with the presence of  $(\text{dpp-BIAN})$  radical-anions, which, on the other hand, prevents meaningful NMR spectroscopic results. In the IR spectrum of free dpp-BIAN, the

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Table 1. Crystal Data and Structure Refinement Details for 1, 2, and 3

	1	2	3
formula	C <sub>38</sub> H <sub>46</sub> AlN <sub>2</sub>	C <sub>40</sub> H <sub>50</sub> AlN <sub>2</sub>	C <sub>44</sub> H <sub>58</sub> AlN <sub>2</sub>
fw	557.75	585.80	641.90
cryst syst	monoclinic	triclinic	monoclinic
space group	<i>P2<sub>1</sub>/c</i>	<i>P1</i>	<i>P2<sub>1</sub>/n</i>
unit cell dimens Å, deg	<i>a</i> = 10.5377(1) <i>b</i> = 20.3034(2) <i>c</i> = 16.0634(1) <i>β</i> = 104.554(1)	<i>a</i> = 13.4475(2) <i>b</i> = 15.6574(2) <i>c</i> = 18.3550(3) <i>α</i> = 104.543(1) <i>β</i> = 110.323(1) <i>γ</i> = 91.070(1)	<i>a</i> = 15.2396(2) <i>b</i> = 16.4503(1) <i>c</i> = 15.8537(2) <i>β</i> = 101.282(1)
volume, Å <sup>3</sup>	3326.50(5)	3483.94(9)	3897.66(7)
<i>Z</i>	4	4	4
density(calc), mg m <sup>-3</sup>	1.114	1.117	1.094
abs coeff, mm <sup>-1</sup>	0.088	0.087	0.083
<i>F</i> (000)	1204	1268	1396
cryst size, mm <sup>3</sup>	0.45 × 0.28 × 0.20	0.36 × 0.32 × 0.28	0.40 × 0.38 × 0.18
<i>θ</i> range for data collection, deg	1.65 to 25.50	1.35 to 25.50	1.70 to 26.00
index ranges	-12 ≤ <i>h</i> ≤ 12 -19 ≤ <i>k</i> ≤ 24 -19 ≤ <i>l</i> ≤ 19	-15 ≤ <i>h</i> ≤ 16 -18 ≤ <i>k</i> ≤ 16 -21 ≤ <i>l</i> ≤ 22	-18 ≤ <i>h</i> ≤ 18 -20 ≤ <i>k</i> ≤ 18 -19 ≤ <i>l</i> ≤ 19
no. of reflns collected	22 377	22 088	25 605
no. of indep reflns	6181 [ <i>R</i> (int) = 0.0850]	12 735 [ <i>R</i> (int) = 0.0859]	7648 [ <i>R</i> (int) = 0.1046]
max. and min. transmn	0.980076 and 0.719916	0.971948 and 0.661609	0.967345 and 0.537371
no. of data/restraints/params	6181/0/380	12 735/0/795	7648/2/466
goodness-of-fit on <i>F</i> <sup>2</sup>	1.024	0.938	1.014
final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> 1 = 0.0619 w <i>R</i> 2 = 0.1283	<i>R</i> 1 = 0.0683 w <i>R</i> 2 = 0.1176	<i>R</i> 1 = 0.0707 w <i>R</i> 2 = 0.1558
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1187 w <i>R</i> 2 = 0.1509	<i>R</i> 1 = 0.1848 w <i>R</i> 2 = 0.1499	<i>R</i> 1 = 0.1377 w <i>R</i> 2 = 0.1889
largest diff peak and hole, e Å <sup>-3</sup>	0.289 and -0.316	0.405 and -0.353	0.614 and -0.342

Table 2. Selected Bond Lengths and Angles in 1, 2, 3, [<sup>*i*</sup>BuC(N-Ph-2,6-<sup>*i*</sup>Pr)<sub>2</sub>]AlMe<sub>2</sub> (A), [HCMe<sub>2</sub>C<sub>2</sub>(N-Ph-2,6-<sup>*i*</sup>Pr)<sub>2</sub>]AlMe<sub>2</sub> (B), and [C<sub>7</sub>H<sub>5</sub>(N-<sup>*i*</sup>Pr)<sub>2</sub>]AlMe<sub>2</sub> (C)

	1	2	3	A	B	C
			Bond Length, Å			
Al-C	1.972(3)	1.958(4)	1.968(3)	1.952(3)	1.958(3)	1.969(2)
	1.965(3)	1.967(4)	1.965(4)	1.955(3)	1.970(3)	1.969(2)
Al-N	1.949(2)	1.945(3)	1.956(2)	1.940(2)	1.922(2)	1.915(1)
	1.950(2)	1.968(3)	1.974(2)	1.936(2)	1.935(2)	1.915(1)
N-C <sup>a</sup>	1.330(3)	1.339(4)	1.340(3)	1.356(3)	1.337(2)	1.337(2)
	1.331(3)	1.323(4)	1.345(3)	1.339(3)	1.337(2)	1.337(2)
C(1)-C(2)	1.441(3)	1.439(4)	1.424(4)			1.496(3)
			Bond Angles, deg			
N-Al-N	86.25(8)	85.31(12)	85.46(9)	68.15(7)	96.18(9)	83.3(1)
C-Al-C	117.07(13)	110.21(18)	119.48(16)	115.8(1)	115.4(2)	114.6(1)

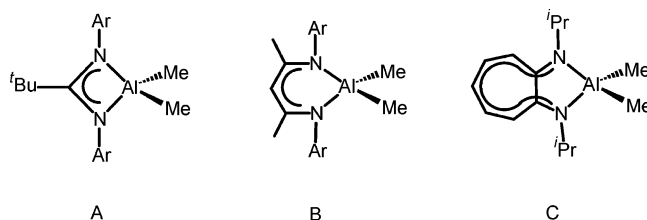
<sup>a</sup> C atoms within the metallacycle.

$\nu(\text{C}=\text{N})$  vibrations cause the strongest absorptions and appear in the range 1600–1700 cm<sup>-1</sup>.<sup>17,18</sup> The corresponding vibrations of the complex [(dpp-BIAN)-CuBr]<sub>2</sub>,<sup>18</sup> in which dpp-BIAN acts as a neutral ligand, are shifted only little to lower wavenumbers compared to those of the free ligand. However, on going from the free (dpp-BIAN) ligand to the radical-anionic ligand in **1**, **2**, and **3**, the  $\nu(\text{C}=\text{N})$  vibrations get shifted by ca. 100 cm<sup>-1</sup> to lower wavenumbers and appear at 1520 cm<sup>-1</sup>.

#### Molecular Structures of Compounds 1, 2, and 3.

The crystal and structure refinement data of the compounds **1**, **2**, and **3** are listed in Table 1, their molecular structures are depicted in Figures 1, 2, and 3, and Table 2 summarizes selected bond lengths and angles together with comparable parameters of related four-coordinate dialkylaluminum compounds stabilized by other biden-

Chart 1



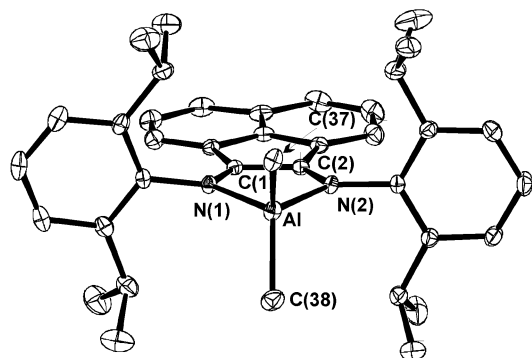
Ar = 2,6-<sup>*i*</sup>Pr<sub>2</sub>-phenyl

tate nitrogen ligands such as amidinate (A),<sup>4b</sup> ketimininate (B),<sup>6b</sup> or tropoimininate (C)<sup>7a</sup> ligands (Chart 1).

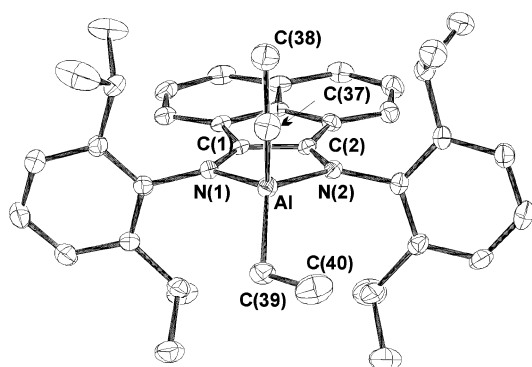
Compounds **1** and **3** crystallize in the monoclinic space groups *P2<sub>1</sub>/c* and *P2<sub>1</sub>/n*, respectively, each with four molecules in the unit cell. Compound **2** crystallizes in the triclinic space group *P1* with two independent molecules in the unit cell. Since the molecular parameters of the two molecules of **2** are very much alike and differ only little with respect to the C<sub>Et</sub>-Al-C<sub>Et</sub> angle (110.21° and 115.39°), the molecular structure and the appropriate data of only one of the two molecules are

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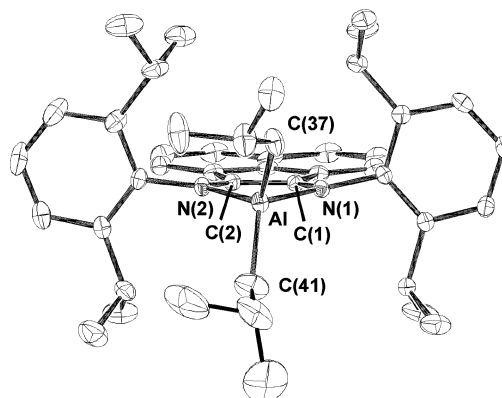
**Figure 1.** ORTEP presentation of the molecular structure of **1**. Thermal ellipsoids are drawn at 30% probability. The hydrogen atoms are omitted.



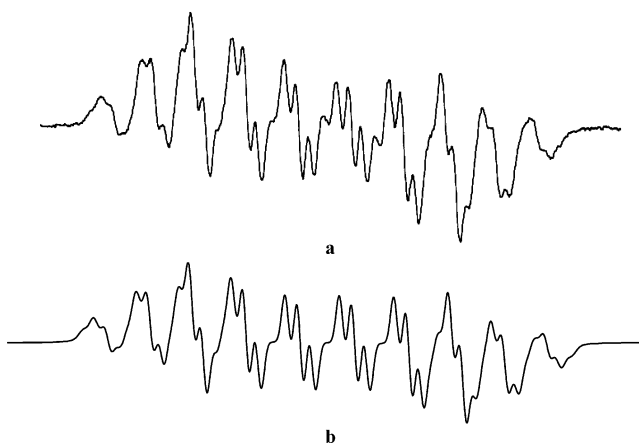
**Figure 2.** ORTEP presentation of the molecular structure of **2**. Thermal ellipsoids are drawn at 30% probability. The hydrogen atoms are omitted.

presented. In the molecules of all three complexes the Al atom is tetrahedrally coordinated by the respective two alkyl groups and the two N atoms of the dpp-BIAN ligand. With regard to a comparison of the structural data of compounds **1**, **2**, and **3** with those of the related compounds shown in Chart 1 or between each other, two aspects appear to be of special interest: (1) the influence of the bite angle N(1)–Al–N(2) of the respective 2-fold coordinating ligand on the geometry of the AlMe<sub>2</sub> unit going from **1** to **A**, **B**, and **C** and (2) the influence of the kind of alkyl group bonded to aluminum in the complexes **1**, **2**, and **3** on the geometry of the –Al–N–C–C–N– metallacycle.

The bite angles N–Al–N become larger on going from the four-membered metallacycle in **A** to the five-membered metallacycles in **1**, **2**, **3**, and **C** and further on to the six-membered metallacycle in **B**. Within the five-membered metallacycles in **1**, **2**, and **3** the bite angles N–Al–N are fairly the same and close to that in **C**. It is remarkable that the significant differences of the bite angles within the series **1** (86.3 Å), **A** (68.2 Å), **B** (96.2 Å), and **C** (83.3 Å) hardly influence the angles and distances in the AlMe<sub>2</sub> unit. Likewise, the increasing bulkiness of the alkyl groups going from **1** to **2** and **3** does not considerably influence the bond lengths within the –Al–N–C–C–N– metallacycle. The Al–C(Et) distances in **2** [1.958(4) and 1.967(4) Å] can be compared with those in the four-coordinate aluminum complex [3-Et-2-(N-C<sub>6</sub>H<sub>3</sub>-2,6-<sup>i</sup>Pr<sub>2</sub>)-1-{N(H)-C<sub>6</sub>H<sub>3</sub>-2,6-<sup>i</sup>Pr<sub>2</sub>}C<sub>6</sub>H<sub>3</sub>]AlEt<sub>2</sub><sup>5c</sup> [1.958(6) and 1.974(6) Å]. Besides the ESR data, also the bond lengths within the diimine fragment of the dpp-BIAN ligand in **1**, **2**, and **3** confirm



**Figure 3.** ORTEP presentation of the molecular structure of **3**. Thermal ellipsoids are drawn at 30% probability. The hydrogen atoms are omitted.



**Figure 4.** (a) ESR spectrum of **1** ( $g = 2.0031$ ) in toluene at 293 K. (b) Calculated spectrum [ $A_N = 0.46$  (2 N),  $A_{Al} = 0.60$ ,  $A_H = 0.14$  (2 H),  $A_H = 0.10$  (2 H) mT,  $\Delta H = 0.12$  mT].

its radical-anionic character. The values of the lengths of the two N–C bonds (ranging from 1.323 to 1.345 Å) and of the C–C bond (ranging from 1.424 to 1.441 Å) are intermediate between those in free dpp-BIAN (N–C: both 1.282(4) Å; C–C 1.534(4) Å)<sup>17</sup> and those in (dpp-BIAN)Mg(THF)<sub>3</sub> containing the dianionic dpp-BIAN ligand (N–C 1.378(7) and 1.389(7) Å; C–C 1.401(6) Å).<sup>10a</sup> These facts are in accordance with the LUMO symmetry, which predicts that with increasing population of this orbital the N–C bonds get longer and the C–C bond gets shorter. The N–C and C–C bond distances in **1**, **2**, and **3** compare well with those in the germanium(II) complex (dpp-BIAN)GeCl [N–C 1.326(3) and 1.329(3) Å; C–C 1.421(3) Å]<sup>12b</sup> also containing the radical anionic dpp-BIAN ligand.

**ESR Spectra of 1, 2, and 3.** The radical-anionic character of the dpp-BIAN ligand in **1**, **2**, and **3** is confirmed by their ESR spectra recorded in toluene. The signals are moderately resolved at 293 K and show a hyperfine structure due to the coupling of the unpaired electron with the <sup>14</sup>N ( $I = 1$ , 99.6% natural abundance), <sup>73</sup>Al ( $I = 5/2$ , 100% natural abundance), and <sup>1</sup>H ( $I = 1/2$ , 99.99% natural abundance) nuclei. The ESR spectrum of **1** and the corresponding computer-simulated spectrum are shown in Figure 4. The isotropic  $g$  factors and hyperfine coupling (hfc) constants of the ESR signals of **1**, **2**, and **3**, as well as of (dpp-BIAN)MgI(DME) and (dpp-BIAN)GeCl, also containing the radical-anionic

**Table 3. Isotropic  $g$  and hfc Constants (mT) for **1**, **2**, **3**, (dpp-BIAN)MgI(DME),<sup>11</sup> (dpp-BIAN)GeCl,<sup>12b</sup> and [C<sub>2</sub>H<sub>2</sub>(N-Ph-2,6-*i*Pr)<sub>2</sub>AlI<sub>2</sub>]<sup>19</sup>**

	$g_{\text{iso}}$	M <sup>a</sup>	<sup>14</sup> N <sup>b</sup>	<sup>1</sup> H <sup>c</sup>	<sup>1</sup> H <sup>d</sup>	Hal <sup>e</sup>	$\Delta H$ (mT)
<b>1</b>	2.0031	0.60	0.46	0.14	0.10		0.12
<b>2</b>	2.0033	0.62	0.46	0.14	0.10		0.16
<b>3</b>	2.0032	0.61	0.46	0.14	0.10		0.14
(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 ( <sup>35</sup> Cl) 0.65 ( <sup>37</sup> Cl)	
[C <sub>2</sub> H <sub>2</sub> (N-Ph-2,6- <i>i</i> Pr) <sub>2</sub> AlI <sub>2</sub> ]	2.0038	0.285	0.67	0.59		0.04 <sup>f</sup>	

<sup>a</sup> M refers to Al (**1–3**), Mg, or Ge. <sup>b</sup> <sup>14</sup>N refers to two equivalent nitrogen nuclei. <sup>c</sup> <sup>1</sup>H refers to two equivalent protons in *ortho* positions of the naphthalene system (relative to the diimine fragment). <sup>d</sup> <sup>1</sup>H refers to two equivalent protons in *para* positions of the naphthalene system (relative to the diimine fragment). <sup>e</sup> Hal refers to <sup>127</sup>I and <sup>35</sup>Cl and <sup>37</sup>Cl nuclei simulated in (dpp-BIAN)MgI(DME), [C<sub>2</sub>H<sub>2</sub>(N-Ph-2,6-*i*Pr)<sub>2</sub>AlI<sub>2</sub>], and (dpp-BIAN)GeCl, respectively. <sup>f</sup> Refers to two <sup>127</sup>I nuclei.

dpp-BIAN ligand, and of [C<sub>2</sub>H<sub>2</sub>(N-C<sub>6</sub>H<sub>3</sub>-2,6-*i*Pr)<sub>2</sub>AlI<sub>2</sub>], containing a diimine radical anion, are presented in Table 3.

The values of the constants of the hfc with <sup>14</sup>N in **1**, **2**, and **3** (0.46 mT for all three compounds) are in the range of the respective values recorded for (dpp-BIAN)-MgI(DME) (0.44 mT)<sup>11</sup> and (dpp-BIAN)GeCl (0.48 mT),<sup>12b</sup> which also contain the dpp-BIAN radical anion, but are smaller than that of [C<sub>2</sub>H<sub>2</sub>(N-Ph-2,6-*i*Pr)<sub>2</sub>AlI<sub>2</sub>] (0.67 mT).<sup>19</sup> This is due to a significant delocalization of the unpaired electron over the naphthalene part of the dpp-BIAN ligand, a fact that is confirmed by the observed hfc with the two equivalent *ortho* and *para* protons of the naphthalene unit (Table 3). On the other hand, the values of the constants of the hfc with <sup>27</sup>Al in **1**, **2**, and **3** (0.60, 0.62, and 0.61 mT, respectively) are more than twice as high as the value recorded for [C<sub>2</sub>H<sub>2</sub>(N-Ph-2,6-*i*Pr)<sub>2</sub>AlI<sub>2</sub>] (<sup>27</sup>Al = 0.285 mT).<sup>19</sup> This fact can be explained by a swinging of the spin density from aluminum to the two electronegative iodine atoms (<sup>127</sup>I = 0.04 mT).

### Conclusion

We have prepared three new monomeric, four-coordinate dialkylaluminum compounds of the type (dpp-BIAN)AlR<sub>2</sub> (R = Me (**1**), Et (**2**), *i*Bu (**3**)) containing the rigid chelating radical-anion of 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-BIAN) as a ligand. The compounds were characterized by their molecular structure and their ESR spectra. The comparative structural analysis of compounds **1**, **2**, and **3** with other dialkylaluminum compounds bearing chelating N-based ligands demonstrates that the type of chelating ligand influences only little the bond lengths and bond angles of the AlR<sub>2</sub> unit, and, conversely, the kind of alkyl groups R does not markedly influence the N–Al–N bite angle. The ESR spectroscopic data indicate that in **1**, **2**, and **3** the unpaired electron is mainly delocalized over the dpp-BIAN ligand, although a spin density is also detected at the Al atom.

### Experimental Section

**General Remarks.** All manipulations were carried out under vacuum using Schlenk techniques. The solvents diethyl ether, hexane, and toluene were dried by distillation from sodium-benzophenone. The starting aluminum compounds Me<sub>2</sub>AlCl, Et<sub>2</sub>AlBr, and *i*Bu<sub>2</sub>AlCl were purchased from ABCR. 1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthene was prepared according to the published procedure.<sup>18a</sup> The melting

points were measured in sealed capillaries. The IR spectra were recorded on a Specord M80 spectrometer. The ESR spectra were obtained using a Bruker ER 200D-SRC spectrometer, and the signals were referred to the signal of diphenylpicrylhydrazyl (DPPH,  $g = 2.0037$ ).

**(dpp-BIAN)Na.** Solutions of (dpp-BIAN)Na were prepared by stirring dpp-BIAN (0.5 g, 1.0 mmol) and sodium metal (0.023 g, 1.0 mmol) in Et<sub>2</sub>O (35 mL) at room temperature. After complete reaction of sodium (ca. 4 h), the ethereal solutions containing the (dpp-BIAN)Na formed were directly used for the further reactions with the dialkylaluminum halides.

**Synthesis of (dpp-BIAN)AlMe<sub>2</sub> (**1**).** Me<sub>2</sub>AlCl (0.093 g, 1.0 mmol) was added to the ethereal solution of (dpp-BIAN)Na (1.0 mmol). With precipitation of NaCl, the reaction mixture turned red-brown. The mixture was stirred for 2 h at room temperature. The residue left after evaporation of the solvent in a vacuum was treated with hexane (50 mL). The deep red solution formed was filtered off from NaCl. Concentration of the hexane solution under vacuum caused the precipitation of complex **1** (0.46 g, 83%) as deep red crystals. Mp = 193 °C. IR (Nujol): 3050 w, 1585 w, 1570 w, 1520 m, 1430 s, 1350 m, 1250 m, 1170 m, 810 m, 790 w, 750 m, 700 m, 690 m, 660 m, 640 m cm<sup>-1</sup>. ESR (25 °C, toluene):  $g = 2.0031$ ,  $A_N = 0.46$  (2 N),  $A_{Al} = 0.60$ ,  $A_H = 0.10$  (2H),  $A_H = 0.14$  (2H) mT. Anal. for C<sub>36</sub>H<sub>46</sub>N<sub>2</sub>Al (557.78): calcd C 81.82, H 8.31; found C 80.46, H 8.05.

**Synthesis of (dpp-BIAN)AlEt<sub>2</sub> (**2**).** Similar to the procedure described for the synthesis of **1**, the reaction of Et<sub>2</sub>AlBr (0.165 g, 1.0 mmol) with (dpp-BIAN)Na (1.0 mmol) produced **2** (0.47 g, 80%) as deep red crystals. Mp = 190 °C. IR (Nujol): 3050 w, 1660 w, 1580 w, 1520 m, 1440 w, 1350 m, 1310 m, 1250 m, 1170 m, 810 m, 790 w, 750 m, 710 w, 630 m, 610 w cm<sup>-1</sup>. ESR (25 °C, toluene):  $g = 2.0033$ ,  $A_N = 0.46$  (2 N),  $A_{Al} = 0.62$ ,  $A_H = 0.1$  (2H),  $A_H = 0.14$  (2H) mT. Anal. for C<sub>40</sub>H<sub>50</sub>N<sub>2</sub>Al (585.83): calcd C 82.01, H 8.60; found C 81.42, H 8.75.

**Synthesis of (dpp-BIAN)Al<sup>*i*</sup>Bu<sub>2</sub> (**3**).** Similar to the procedure described for the synthesis of **1**, the reaction of *i*Bu<sub>2</sub>AlCl (0.18 g, 1.0 mmol) with (dpp-BIAN)Na (1.0 mmol) produced **3** (0.48 g, 75%) as dark red crystals. Mp = 198 °C. IR (Nujol): 3050 w, 1640 w, 1580 w, 1520 s, 1445 vs, 1480 s, 1415 s, 1245 s, 1200 w, 1175 m, 1145 m, 1100 w, 1050 m, 1000 w, 935 w, 925 w, 885 w, 865 w, 810 m, 800 m, 760 vs, 715 w, 660 vs, 580 w, 430 vs cm<sup>-1</sup>. ESR (25 °C, toluene):  $g = 2.0032$ ,  $A_N = 0.46$  (2 N),  $A_{Al} = 0.61$ ,  $A_H = 0.14$ , (2H),  $A_H = 0.095$  (2H) mT. Anal. for C<sub>44</sub>H<sub>58</sub>N<sub>2</sub>Al (641.90): calcd C 82.33, H 9.11; found C 82.01, H 8.98.

**X-ray Crystal Structure Determination of Compounds 1–3.** The data were collected on a SMART CCD diffractometer (graphite-monochromated Mo K $\alpha$  radiation,  $\omega$ - and  $\psi$ -scan technique,  $\lambda = 0.71073$  Å) at 173(2) K. The structures were solved by direct methods using SHELXS-97<sup>20</sup> and were refined

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on  $F^2$  using SHELXL-97.<sup>21</sup> All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed in calculated positions and assigned to an isotropic displacement parameter of 0.08 Å<sup>2</sup>. SADABS<sup>22</sup> was used to perform area-detector scaling and absorption corrections. The geometrical aspects of the structures were analyzed using the PLATON program.<sup>23</sup>

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**Supporting Information Available:** Full details of the X-ray structural analyses of compounds **1–3**, including complete tables of crystal data, atomic coordinates, bond lengths and bond angles, as well as the positional and anisotropic thermal parameters are available free of charge via the Internet at <http://pubs.acs.org>.

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