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Coordination of benzene to a sodium cation*

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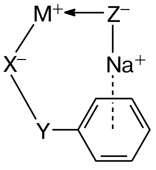
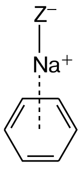
The complexes Na(Et_2O)(dpp-BIAN)$AlEt_2$ (**5**) and Na(η^6-C_6H_6)(dpp-BIAN)$AlEt_2$ (**6**) were synthesized by reactions of the disodium salts of dpp-BIAN (dpp-BIAN is 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) with 1 equiv. of Et_2AlCl in diethyl ether and benzene, respectively. The structures of both complexes were established by X-ray diffraction. In molecules **5** and **6**, diethylaluminum is chelated by the dianionic dpp-BIAN ligand. The sodium cations in molecules **5** and **6** are located above the plane of the diimine fragments and coordinate the Et_2O or benzene molecule, respectively.

Key words: *N*-chelating ligands, main-group metals, arene coordination.

The coordination of unsaturated hydrocarbons by metal complexes and the reactivities of organic molecules bound to metal atoms are among fundamental problems of coordination and organometallic chemistry. A great diversity of organic reactions catalyzed by transition metal compounds is based on the ability of these metals to coordinate unsaturated substrates, such as olefins or arenes. Main-group metals do not form stable π complexes because they have no electrons for the back donation to the antibonding orbitals of π ligands, which strengthens metal—π-ligand interactions. Nevertheless, the coordination of arenes to alkali metal cations was documented. All structurally characterized complexes, in which arenes are coordinated to alkali metal cations, can be divided into two classes. One class (**A**) includes complexes, in which the arene fragment (substituted or unsubstituted Ph ring) is involved in an anionic ligand coordinated to any other metal. Numerous examples of this "forced" coordination of arenes to alkali metal cations were published in the literature.[1]



A



B

Another class (**B**) includes complexes, in which a neutral free arene ligand is coordinated exclusively to an alkali metal cation. The K[$Al_7O_6Me_{16}$](η^6-C_6H_6) complex is the first structurally characterized compound of this class.[2]

In recent years, several analogous Na and K compounds were synthesized and characterized by X-ray diffraction.[3] The nature of interactions between alkali metal cations and arenes was investigated by quantum-chemical methods in several studies.[4] The coordination of arenes to Group I metal cations is described as the attraction between the metal cation and the dipole of the arene π system. Complexes of Group I metal cations with arenes do not exist in donor solvents. As a rule, these complexes can be prepared by crystallization of organic derivatives of alkali metals from arenes. The dissolution of these complexes in donor solvents, for example, in Et_2O, leads to the replacement of arene by a solvent molecule. In spite of the fact that the reactions of arenes with alkali metal cations can play an important role in the development of such a fundamental concept of chemistry as the chemical bond, the X-ray diffraction analysis is the only experimental method used for investigation of these interactions. Moreover, data on the reactivities of arenes coordinated to alkali metal atoms are lacking. It should be noted that first alkene derivatives of alkaline-earth metals were synthesized and structurally characterized in 2004.[5] The coordination of alkenes to metal atoms in these compounds was confirmed not only by X-ray diffraction data but also by ^{1}H NMR spectra.

Recently,[6] we have synthesized several aluminum complexes with the radical-anion and dianionic diimine

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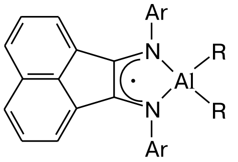
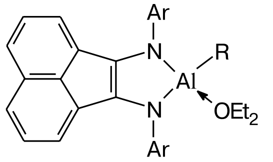
ligand dpp-BIAN (dpp-BIAN is 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) and characterized these complexes by EPR and NMR spectroscopy and X-ray diffraction. The reduction of dpp-BIAN with aluminum in the presence of its halides afforded (dpp-BIAN)$AlCl_2$, (dpp-BIAN)AlI(Et_2O), and (dpp-BIAN)AlCl(Et_2O). The alkylaluminum derivatives (dpp-BIAN)AlR_2 (**1**) and (dpp-BIAN)AlR(Et_2O) (**2**) were synthesized by the exchange reaction of (dpp-BIAN)Na with one equivalent of R_2AlX (R = Me, Et, or Bu^i; X = Cl or Br)[7] or the exchange reaction of (dpp-BIAN)Na_2 with two equivalents of R_2AlX (R = Me, Et, or Bu^i; X = Cl).[8] In the latter case, the initially formed dialuminum derivatives undergo disproportionation to give R_3Al and compounds **2**.

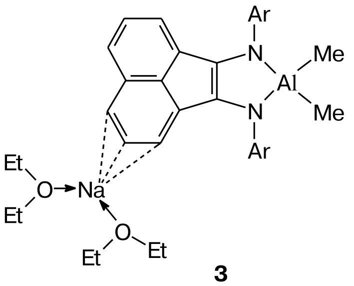


1

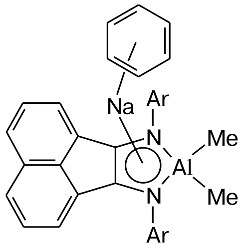


2

The reaction of (dpp-BIAN)Na_2 with one equivalent of Me_2AlCl in diethyl ether[9] produced the mixed sodium aluminum complex $Na(Et_2O)_2$(dpp-BIAN)$AlMe_2$ (**3**). According to the X-ray diffraction study, the dpp-BIAN dianion is coordinated to the Me_2Al fragment through the nitrogen atoms, and the Na cation is coordinated by one of the six-membered rings of the naphthalene moiety of the ligand. This reaction performed in benzene instead of diethyl ether or the recrystallization of $Na(Et_2O)_2$(dpp-BIAN)$AlMe_2$ (**3**) from benzene affords a complex, in which the sodium atom migrates from the naphthalene moiety of the molecule to the diimine fragment and coordinates neutral benzene (**4**).



3



4

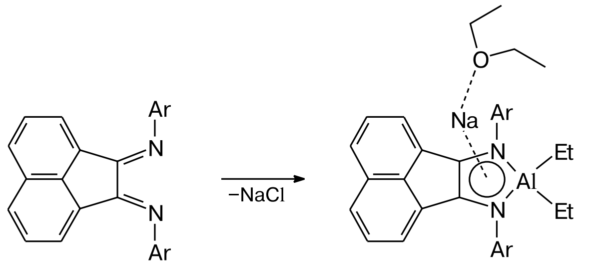
In both types of compounds (**3** and **4**), there is an additional coordination of one CH_3 group of the Me_2Al fragment to the sodium cation. In compound **3**, this coordination belongs to intermolecular agostic interactions; in compound **4**, to intramolecular interactions.

We suggested that the position of the sodium cation with respect to the dianionic diimine ligand dpp-BIAN in mixed Na—Al derivatives and the ability to coordinate arenes are determined by a combination of several interactions, including interactions between the sodium cation and alkyl groups at the aluminum atom. Hence, is seemed reasonable to perform the experimental study of the influence of the alkyl groups at the aluminum atom on both the position of the sodium cation with respect to the dpp-BIAN dianion and the coordination of arene by the sodium cation. In the present study, we synthesized the ethyl derivatives $Na(Et_2O)$(dpp-BIAN)$AlEt_2$ (**5**) and $Na(C_6H_6)$(dpp-BIAN)$AlEt_2$ (**6**) and characterized them by X-ray diffraction.

Results and Discussion

Synthesis of complexes 5 and 6. The $Na(Et_2O)$(dpp-BIAN)$AlEt_2$ compound (**5**) was synthesized by the reaction of the disodium derivative of dpp-BIAN (prepared *in situ* from dpp-BIAN and 2 equiv. of Na) with diethylaluminum chloride in diethyl ether (Scheme 1) and isolated by crystallization from diethyl ether as dark-green crystals in 37% yield.

Scheme 1



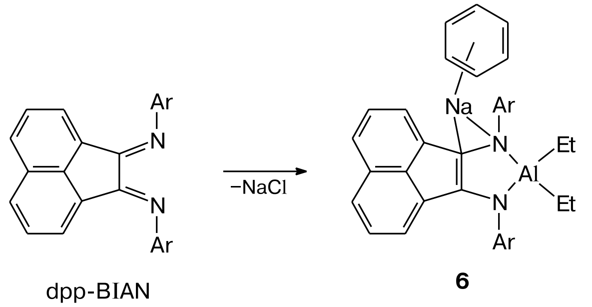
dpp-BIAN **5**

Reagents and conditions: 1) 2 equiv. of Na, Et_2O, 2) Et_2AlCl.

The X-ray diffraction study showed that, unlike compound **3**, which crystallizes from an Et_2O—benzene mixture (1 : 1) with two diethyl ether molecules, complex **5** crystallizes from diethyl ether with one Et_2O molecule coordinated to sodium. The position of the sodium cation with respect to the dpp-BIAN ligand in compound **3** radically differs from that in compound **5**.

The use of benzene as the solvent in the reaction of Na_2(dpp-BIAN) with Et_2AlCl led to the formation of $Na(\eta^6\text{-}C_6H_6)$(dpp-BIAN)$AlMe_2$ (**6**) (Scheme 2), in which the sodium cation is coordinated by a benzene molecule instead of a diethyl ether molecule. Compound **6** was isolated from benzene in 65% yield as dark-green crystals.

Scheme 2



Reagents and conditions: 1) 2 equiv. of Na, C_6H_6, 2) Et_2AlCl

Molecular structures of compounds 5 and 6. The molecular structures of compounds **5** and **6** are presented in Figs 1 and 2, respectively. For comparison, Fig. 3 shows the molecular structure of compound **4**, which has been determined by X-ray diffraction in the very recent past.[9] The crystallographic data and the X-ray diffraction data collection and refinement statistics for compounds **5** and **6** are given in Table 1. Selected bond lengths and bond angles are listed in Table 2. For comparison, this table gives also the corresponding parameters for the derivative $Na(\eta^6-C_6H_6)(dpp-BIAN)AlMe_2$ (**4**). Before comparing the geometric parameters of molecules **4**, **5**, and **6** and revealing the possible influence of the nature of alkyl groups at the Al atom on the position of the sodium cation and its coordination by the benzene molecule, common features of molecules **4**, **5**, and **6** should be mentioned.

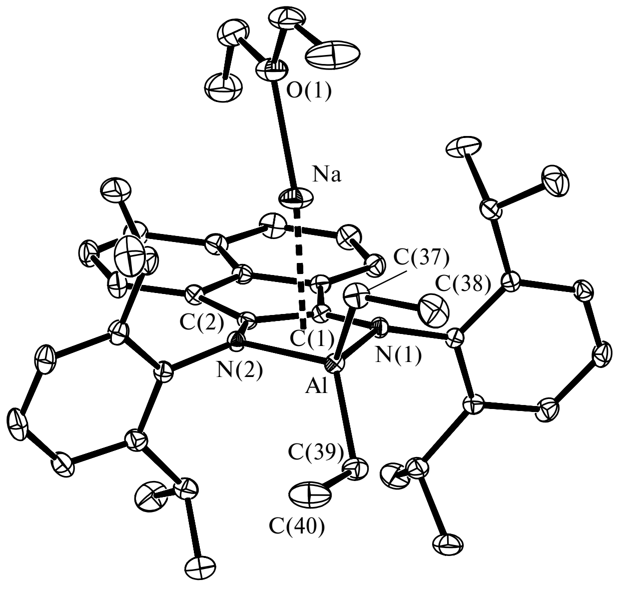


Fig. 1. Molecular structure of compound **5**. Displacement ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted.

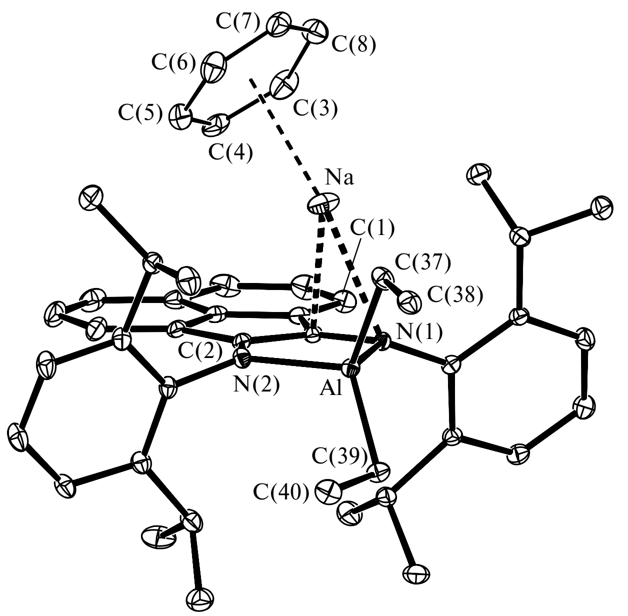


Fig. 2. Molecular structure of compound **6**. Displacement ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted.

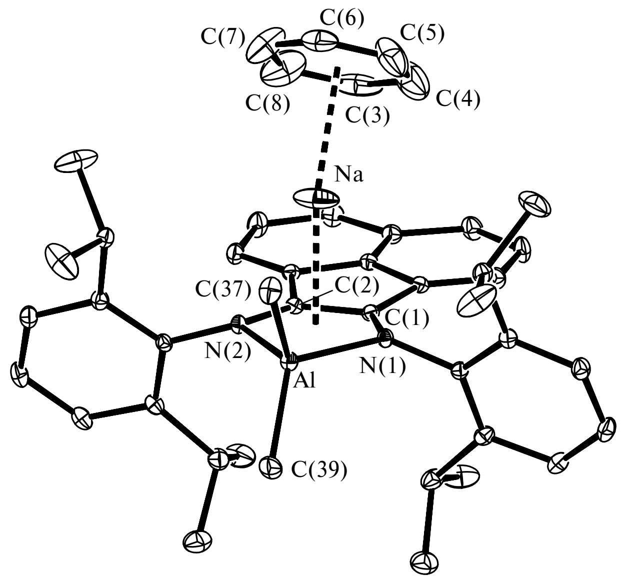


Fig. 3. Molecular structure of compound **4**. Displacement ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted.

1. In complexes **4**, **5**, and **6**, the dpp-BIAN dianion acts as the conformationally rigid chelating ligand with respect to the R_2Al groups. In compounds **4**, **5**, and **6**, the Al—N distances have similar values and vary in a rather narrow range (1.913—1.947 Å).

Table 1. Crystallographic parameters and the X-ray diffraction data collection and refinement statistics for compounds **5** and **6**

Parameter	**5**	**6**
Molecular formula	$C_{44}H_{60}AlN_2NaO$	$C_{46}H_{56}AlN_2Na$
Molecular weight	1365.82	686.90
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a/Å	10.6656(2)	9.9186(5)
b/Å	34.6986(2)	10.9538(6)
c/Å	22.8093(3)	17.8635(10)
α/deg	90	90.456(2)
β/deg	99.4070(10)	90.997(2)
γ/deg	90	96.031(2)
V/Å^3	8327.8(2)	1929.68(18)
Z	4	2
d_{calc}/g cm^{-3}	1.089	1.182
μ/mm^{-1}	0.092	0.098
F(000)	2960	740
Crystal dimensions/mm	0.66×0.35×0.28	0.52×0.45×0.34
Scan range, θ/deg	1.08/27.50	1.87/25.00
Indices of measured reflections	$-13 \le h \le 13$ $-45 \le k \le 45$ $-29 \le l \le 18$	$-11 \le h \le 11$ $-13 \le k \le 12$ $-16 \le l \le 21$
Number of measured reflections	60226	12206
Number of independent reflections	19020	6741
Number of independent reflections with $I > 2\sigma(I)$	8842	4882
R_{int}	0.1119	0.0714
Goodness-of-fit on F^2	1.007	1.055
R_1/wR_2 ($I > 2\sigma(I)$)	0.0853/0.2075	0.0658/0.2032
R_1/wR_2 (based on all reflections)	0.1854/0.2588	0.0969/0.2197
Residual electron density, ρ_{max}/ρ_{min}, e Å^{-3}	0.582/−0.410	0.451/−0.393

2. Dianionic character of the dpp-BIAN ligand is confirmed by the bond lengths in the diimine fragment. Thus, the C(1)—N(1) and C(2)—N(2) distances are elongated, whereas the C(1)—C(2) distance (see Table 2) is, on the contrary, shortened compared to the corresponding parameters in free dpp-BIAN (both C—N distances are 1.282(4) Å; C(1)—C(2), 1.534(6) Å).[10]

3. In complexes **4**, **5**, and **6**, the Al—alkyl bond lengths are slightly different. In our opinion, an elongation of the C(37)—Al bonds (**4**, 2.004(4) Å; **5**, 1.994(4)/2.003(4) Å; **6**, 2.020(3) Å) compared to the C(39)—Al bonds (**4**, 1.962(4) Å; **5**, 1.953(4)/1.966(4) Å; **6**, 1.972(3) Å) is attributed to a weak intermolecular agostic interaction between the sodium cation and the methylene group (or the methyl group in compound **4**) (C(37) atom, see Figs 1—3).

The position of the sodium cation in molecule **4** (see Fig. 3) is virtually identical to that in **5** (see Fig. 1). The cation is located above the center of the —N(1)—C(1)—C(2)—N(2)—Al— metallocycle. Molecule **4** has a crystallographic mirror plane passing through the Al and Na atoms and the N—Al—N angle bisector. As opposed to the analogous benzene derivative **4**, the sodium cation in compound **6** is shifted to the C(1) and N(1) atoms, as evidenced by the corresponding bond lengths in complexes **4** and **6** (in **4**, Na—C(1) and Na—C(2), 2.634(3) Å; Na—N(1) and Na—N(2), 2.729(2) Å; in **6**, Na—C(1), 2.641(3) Å; Na—C(2), 2.824(3) Å, Na—N(1), 2.629(3) Å; Na—N(2), 3.013(3) Å).

The most important difference in the structures of complexes **4** and **6** is associated with the coordination of a benzene molecule to the sodium cation. The average Na—C(benzene) distance in molecule **4** (2.82 Å) is substantially shorter than the corresponding distance in molecule **6** (3.02 Å). In addition, the Na—C(benzene) bond lengths in **4** vary in a substantially narrower range compared to those in **6** (**4**, 2.79—2.85 Å; **6**, 2.90—3.15 Å). A weakening of the sodium—arene interaction in **6** compared to that in **4** is, apparently, associated with both a strengthening of the Na—N(1) interaction in **6** compared to this interaction in **4** (**4**, 2.729(2) Å; **6**, 2.629(3) Å) and a slight strengthening of the Na—C(37) agostic interaction in ethyl derivative **6** (**4**, 2.887(4) Å; **6**, 2.863(4) Å).

In addition to the crystallographic parameters for molecules containing benzene coordinated to sodium, the spectroscopic (for example ^{1}H NMR) data could pro-

Table 2. Selected bond lengths (*d*) and bond angles (ω) in $Na(\eta^6-C_6H_6)$(dpp-BIAN)$AlMe_2$ (**4**), $Na(Et_2O)$(dpp-BIAN)$AlEt_2$ (**5**), and $Na(\eta^6-C_6H_6)$(dpp-BIAN)$AlEt_2$ (**6**)

Parameter	4	5*	6
Bond		*d*/Å	
Al—C(37)	2.000(4)	1.994(4)/2.003(4)	2.020(3)
Al—C(39)	1.962(4)	1.953(4)/1.966(4)	1.972(3)
Al—N(1)	1.9205(18)	1.915(3)/1.913(3)	1.947(3)
Al—N(2)	1.9205(18)	1.926(3)/1.916(3)	1.929(3)
C(1)—N(1)	1.404(3)	1.397(4)/1.403(4)	1.409(4)
C(2)—N(2)	1.404(3)	1.406(4)/1.406(4)	1.396(4)
C(1)—C(2)	1.392(4)	1.373(4)/1.386(5)	1.370(4)
Na—O(1)		2.288(3)/2.304(4)	—
Na—C(1)	2.634(3)	2.662(3)/2.719(4)	2.641(3)
Na—C(2)	2.634(3)	2.622(3)/2.646(4)	2.824(3)
Na—C(3)	2.813(5)	—	3.005(19)
Na—C(4)	2.793(5)	—	2.942(17)
Na—C(5)	2.832(5)	—	2.90(3)
Na—C(6)	2.847(5)	—	2.98(3)
Na—C(7)	2.832(5)	—	3.13(3)
Na—C(8)	2.793(5)	—	3.15(3)
Na—C(37)	2.887(4)	2.953(3)/3.155(3)	2.863(4)
Na—N(1)	2.729(2)	2.794(3)/2.854(3)	2.629(3)
Na—N(2)	2.729(2)	2.711(3)/2.703(3)	3.013(3)
Angle		ω/deg	
N(1)—Al—N(2)	88.78(11)	87.36(12)/88.16(13)	88.62(11)
C(37)—Al—C(39)	110.74(19)	108.33(17)/107.4(2)	112.34(14)

* The data are given for two crystallographically independent molecules.

vide additional information on the character of the arene—alkali metal action interaction. Unfortunately, the ^1H NMR spectra of compounds **4** and **6** recorded in C_6D_6 showed broadened signals, which did not allow us to assign these signals to particular groups of protons. Apparently, this is due both to the slow migration (on the NMR time scale) of the cation over the π system of the diimine ligand and the exchange of the coordinated benzene with deuterobenzene. In THF-d_8, compounds **4** and **6** are characterized by the well-resolved ^1H NMR spectra (see the Experimental section), which show signals of free benzene.

Therefore, we demonstrated that, in the absence of donor solvents, the sodium cation readily coordinates a benzene molecule. The strength of the interaction between the cation and the arene is determined by a combination of all other bonded and nonbonded interactions of the cation. A weakening of these interactions leads to a strengthening of the interaction between the cation and arene.

Experimental

Since compounds **5** and **6** are sensitive to atmospheric oxygen and moisture, all operations associated with the synthesis, isolation, and identification of the reaction products were carried out *in vacuo* using the Schlenk technique to preclude contact with atmospheric oxygen and moisture. Diimine dpp-BIAN was prepared by the condensation of acenaphthenequinone with 2,6-diisopropylaniline (Aldrich) in acetonitrile. Diethyl ether and benzene were dried and stored over sodium benzophenone and were withdrawn by vacuum condensation immediately before use. The melting points were determined in sealed evacuated tubes. The ^1H NMR spectra were recorded on a Bruker ARX 400 spectrometer; the chemical shifts are given in ppm. Solutions of Na_2(dpp-BIAN) were prepared *in situ* from dpp-BIAN and 2 equivalents of sodium in diethyl ether or benzene with vigorous stirring at room temperature. The solutions thus prepared were used in the reactions with diethylaluminum chloride after the complete dissolution of sodium. The reaction giving Na_2(dpp-BIAN) was completed in ~12 and 48 h in diethyl ether and benzene, respectively.

1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthenediethylaluminum sodium diethyl etherate, $Na(Et_2O)$(dpp-BIAN)$AlEt_2$ (5). A solution of $(C_2H_5)_2AlCl$ (1.0 mol L^{-1}) in hexane (1.0 mL) was added to a solution of Na_2(dpp-BIAN), which was prepared from dpp-BIAN (0.5 g, 1.0 mmol) in Et_2O (30 mL). The reaction mixture was stirred at room temperature for 1 h and then filtered off from the sodium chloride precipitate. The solution was concentrated by removing the solvent *in vacuo*. Compound **5** was isolated from the concentrated solution as dark-green crystals in a yield of 0.25 g (37%), m.p. 266 °C. Found (%): C, 77.12; H, 8.66. Calculated (%): C, 77.39; H, 8.86. ^1H NMR (400 MHz, THF-d_8, 294 K), δ: 6.98—6.89 (m, 6 H, $C_6\underline{H}_3Pr^i{}_2$); 6.48 (d, 2 H, arom., *J* = 8.1 Hz); 6.43 (dd, 2 H, arom., *J* = 8.1, *J* = 6.6 Hz);

5.96 (d, 2 H, arom., *J* = 6.6 Hz); 4.11 (sept, 4 H, $C\underline{H}(CH_3)_2$, *J* = 6.9 Hz); 3.39 (q, 4 H, Et_2O, *J* = 7.1 Hz); 1.19 (d, 12 H, $CH(C\underline{H}_3)(CH_3)$, *J* = 6.9 Hz); 1.12 (t, 6 H, Et_2O, *J* = 7.1 Hz); 1.02 (d, 12 H, $CH(CH_3)(C\underline{H}_3)$, *J* = 6.9 Hz); 0.94 (t, 6 H, $Al—CH_2C\underline{H}_3$, *J* = 7.9 Hz); −0.13 (q, 4 H, $Al—C\underline{H}_2CH_3$, *J* = 7.9 Hz).

1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthenediethylaluminum sodium benzene, Na(η^6-C_6H_6)(dpp-BIAN)AlEt$_2$ (6). A solution of $(C_2H_5)_2AlCl$ (1.0 mol L^{-1}) in hexane (1.0 mL) was added to a solution of Na$_2$(dpp-BIAN), which was prepared from dpp-BIAN (0.5 g, 1.0 mmol) in benzene (30 mL). The reaction mixture was stirred for 1 h, and the solution was filtered off from the NaCl precipitate. The solution was concentrated by removing the solvent *in vacuo*. After 24 h, compound **6** was isolated from the solution as dark-green crystals in a yield of 0.48 g (65%). Found (%): C, 80.60; H, 8.21. Calculated (%): C, 80.43; H 8.22. ^{1}H NMR (400 MHz, THF-d$_8$, 294 K), δ: 7.31 (s, 6 H, C_6H_6); 6.98—6.89 (m, 6 H, $C_6\underline{H}_3Pr^i{}_2$); 6.48 (d, 2 H, arom., *J* = 8.1 Hz); 6.43 (dd, 2 H, arom., *J* = 8.1 Hz, *J* = 6.6 Hz); 5.96 (d, 2 H, arom., *J* = 6.6 Hz); 4.11 (sept, 4 H, $C\underline{H}(CH_3)_2$, *J* = 6.9 Hz); 1.19 (d, 12 H, $CH(C\underline{H}_3)(CH_3)$, *J* = 6.9 Hz); 1.02 (d, 12 H, $CH(CH_3)(C\underline{H}_3)$, *J* = 6.9 Hz); 0.94 (t, 6 H, $Al—CH_2C\underline{H}_3$, *J* = 7.9 Hz); −0.13 (q, 4 H, $Al—C\underline{H}_2CH_3$, *J* = 7.9 Hz).

X-ray diffraction study of compounds 5 and 6. The 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. Absorption corrections were applied using the SADABS program.[11] The structures were solved by direct methods with the use of the SHELXS97 program package[12] and refined by the full-matrix least-squares method based on F^2 with the use of the SHELXL97 program package.[13] All nonhydrogen atoms were refined anisotropically. The hydrogen atoms were placed in idealized positions (U_{iso} = 0.08 Å^3).

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