

## Sodium Cation Migration Above the Diimine $\pi$ -System of Solvent Coordinated dpp-BIAN Sodium Aluminum Complexes (dpp-BIAN = 1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthene)

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**Abstract:** The reactions of the disodium salt of the 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-BIAN) ligand with one equivalent of  $\text{Me}_2\text{AlCl}$  in diethyl ether, toluene, and benzene produced the complexes  $[\text{Na}(\text{Et}_2\text{O})_2(\text{dpp-BIAN})\text{AlMe}_2]$  (**1**),  $[\text{Na}(\eta^6\text{-C}_7\text{H}_8)(\text{dpp-BIAN})\text{AlMe}_2]$  (**2**) and  $[\text{Na}(\eta^6\text{-C}_6\text{H}_6)(\text{dpp-BIAN})\text{AlMe}_2]$  (**3**), respectively. Recrystallization of **1** from

hexane afforded solvent-free  $[\{\text{Na}(\text{dpp-BIAN})\text{AlMe}_2\}_n]$  (**4**) or  $[\text{Na}(\text{Et}_2\text{O})(\text{dpp-BIAN})\text{AlMe}_2]$  (**5**) depending on the temperature of the solvent. The molecular structures of **1–5** have been deter-

mined by single-crystal X-ray diffraction. The sodium cation coordinates either one of the naphthalene rings (**1**) or the diimine part of the dpp-BIAN ligand (**2–5**). In the complexes **2** and **3**, the sodium cation additionally coordinates the toluene (**2**) or benzene molecule (**3**) in an  $\eta^6$ -fashion.

**Keywords:** arenes • main group elements • N ligands • pi interactions • sodium

### Introduction

The coordination of unsaturated organic molecules to a metal center and the reactivity of the coordinated ligands are one of the most fundamental topics in organometallic chemistry. An enormous variety of transition-metal-catalyzed organic reactions is based on the capability of transition metals to coordinate unsaturated organic substrates, such as olefins and arenes. In contrast to transition metals, the main-group metals should not be able to form stable complexes with neutral  $\pi$ -ligands due to the lack of electrons that might strengthen the metal-to- $\pi$ -ligand interaction by back-donation. Nevertheless,  $\pi$ -arene complexes of alkali

metal cations are known and the structurally characterized complexes can be divided into two classes. To the first class belong those complexes in which the metal-coordinated arene group (substituted or non substituted phenyl ring) is part of an anionic ligand backbone. Many examples for such a constrained arene/metal-cation coordination are described in the literature.<sup>[1]</sup> The second class comprises those complexes in which neutral arene ligands are bound to the alkali metal cation. The first structurally characterized complex of this type, the potassium complex  $[\text{K}(\text{Al}_7\text{O}_6\text{Me}_{16})(\eta^6\text{-C}_6\text{H}_6)]$ , was reported by Atwood in 1985.<sup>[2]</sup> Within the next decades, only a few complexes of this type were synthesized and characterized by X-ray crystal structure analysis.<sup>[3]</sup> The nature of the bonding between alkali metal cations and arene  $\pi$ -systems has been the subject of several computational studies.<sup>[4]</sup> It is described in terms of electrostatic attraction between the cation and the cation-induced dipole of the aromatic system. Alkali-metal-cation/arene complexes are accessible by reactions carried out in an arene as the solvent. In general, dissolution of these complexes in coordinating solvents, for example ethers, cause immediate substitution of the arene ligand by the respective solvent donor molecule. Up to now, single-crystal X-ray analysis has been the only experimental method used for the characterization of such complexes. Also no data concerning the reactivity of alkali-metal-cation-coordinated arene ligands are known.

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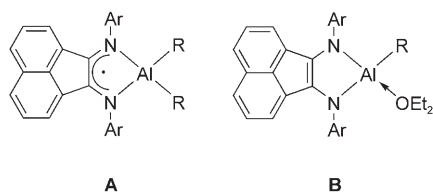
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Recently, the first olefin complexes of alkaline earth metals were synthesized and structurally characterized.<sup>[5]</sup> The coordination of the olefin to the alkaline earth metal center has been confirmed not only crystallographically but also by means of <sup>1</sup>H NMR spectroscopy.

For several years, we have been interested in the preparation and reactivity of 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-BIAN) complexes of main-group metals. This ligand can exist in different oxidation states as demonstrated by its sequential reduction with alkali metals to mono-, di-, tri- and tetra-anions.<sup>[6]</sup> The reduction of dpp-BIAN with alkaline earth metals affords only dianions according to the formation of the complexes [M(dpp-BIAN)(thf)<sub>n</sub>] (M = Mg, Ca; n = 2–4).<sup>[7]</sup> The variability of the oxidation state of the dpp-BIAN ligand is impressively demonstrated by the reductive elimination of *i*Pr radicals from [Mg(dpp-BIAN)(*i*Pr)(Et<sub>2</sub>O)] to give the dianionic product [Mg(dpp-BIAN)(thf)<sub>3</sub>].<sup>[8]</sup> The reverse process—oxidation of the dpp-bian dianion to the radical anion—is to observe in the reactions of [Mg(dpp-BIAN)(thf)<sub>3</sub>] with aromatic ketones<sup>[9]</sup> and stable free radicals like 2,2,6,6-tetramethylpiperidine-*N*-oxide (TEMPO). The course of the reactions of [Mg(dpp-BIAN)(thf)<sub>3</sub>] with ethyl halides further demonstrates the noninnocence of the dpp-BIAN ligand in its metal complexes. They proceed by single-electron transfer from the dianionic dpp-BIAN ligand to EtX yielding ethyl radicals, which in turn attack the ligand, now a radical anion at one of the imino carbon atoms, resulting in the formation of the amido-imino chelating complexes [MgX(dpp-BIAN)(Et)(thf)<sub>n</sub>].<sup>[10]</sup> Acidic substances such as aliphatic ketones, terminal alkynes, and nitriles add to [Mg(dpp-BIAN)(thf)<sub>3</sub>] with protonation of one of the ligand nitrogen atoms producing unsymmetrical amido-imino dpp-BIAN complexes.<sup>[11]</sup>

Depending on the solvent used, the reduction of dpp-BIAN with aluminum in the presence of its halides gives [AlCl<sub>2</sub>(dpp-BIAN)], [Al(dpp-BIAN)(Et<sub>2</sub>O)], and [AlCl(dpp-BIAN)(Et<sub>2</sub>O)].<sup>[12]</sup> Alkylaluminum complexes with dpp-BIAN radical anions and dianions as ligands are obtained by the reaction of Na[dpp-BIAN] with one equivalent of R<sub>2</sub>AlX (R = Me, Et, *i*Bu; X = Cl, Br) (**A**)<sup>[13]</sup> and Na<sub>2</sub>[dpp-BIAN] with two equivalents of R<sub>2</sub>AlX (R = Me, Et, *i*Bu; X = Cl) in Et<sub>2</sub>O (**B**), respectively.<sup>[14]</sup>

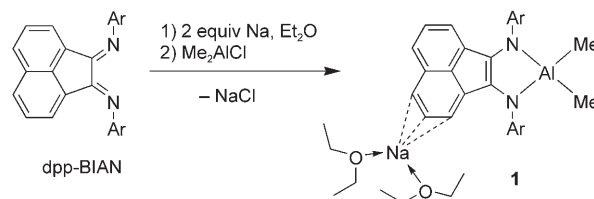
The examples given above demonstrate the manifold redox properties of the dpp-BIAN ligand. To gain more insight into the coordination abilities of the dpp-BIAN ligand, we investigated the reaction of Na<sub>2</sub>[dpp-BIAN] with Me<sub>2</sub>AlCl. It is to be supposed that the elimination of sodium chloride leads to the formation of a heterometallic sodium–aluminum–dpp-BIAN complex in which, depending



on the solvent used, the sodium cation may occupy different coordination sites of the ligand. In this paper we report on the results of these investigations.

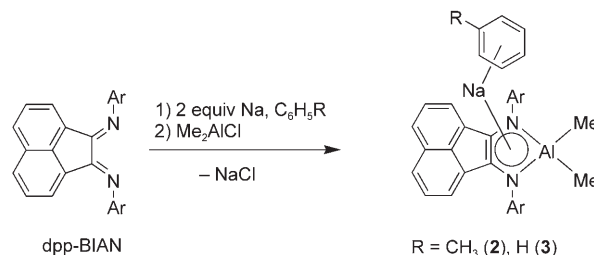
## Results and Discussion

**Syntheses of complexes 1–5:** [Na(Et<sub>2</sub>O)<sub>2</sub>(dpp-BIAN)AlMe<sub>2</sub>] (**1**) was obtained by reacting the disodium salt of dpp-BIAN (prepared in situ from dpp-BIAN and 2 equiv of sodium metal) with Me<sub>2</sub>AlCl in diethyl ether (Scheme 1). Crystallization from Et<sub>2</sub>O/benzene (v/v 1:1) afforded **1** as dark green crystals with 74% yield.



Scheme 1.

The use of toluene or benzene instead of Et<sub>2</sub>O as reaction medium afforded the complexes [Na(η<sup>6</sup>-C<sub>7</sub>H<sub>8</sub>)(dpp-BIAN)AlMe<sub>2</sub>] (**2**) and [Na(η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>)(dpp-BIAN)AlMe<sub>2</sub>] (**3**), respectively (Scheme 2). The compounds **2** and **3** were isolated as dark green crystals in 83 and 89% yield, respectively.



Scheme 2.

Treatment of crude **1** with hot hexane resulted in the elimination of the sodium-coordinated Et<sub>2</sub>O molecules and formation of the polymeric, solvent-free complex [[Na(dpp-BIAN)AlMe<sub>2</sub>]<sub>n</sub>] (**4**).

Dissolving crude **1** in hexane at room temperature resulted in the isolation of the mono etherate [Na(Et<sub>2</sub>O)(dpp-BIAN)AlMe<sub>2</sub>] (**5**). Unfortunately, this reaction was not reproducible. Nevertheless, we discuss the crystal structure of compound **5** in connection with those of complexes **1** to **4**, because it again reveals an unexpected variation of the coordination abilities of the dpp-BIAN dianion.

**Molecular structures of the complexes 1–5:** The crystal collection data and structure refinement data are listed in Table 1, and selected bond lengths and angles are listed in Table 2. The most fascinating feature of the molecular structures of **1** to **5** is the migration of the sodium cation over the whole diimine π-system, depending on the kind and number of solvent molecules connected to the sodium cation. Fur-

Table 1. Crystal data and structure refinement details for 1–5.

	1	2	3	4	5
formula	C <sub>46</sub> H <sub>60</sub> AlN <sub>2</sub> NaO <sub>2</sub>	C <sub>48.5</sub> H <sub>58</sub> AlN <sub>2</sub> Na	C <sub>47</sub> H <sub>55</sub> AlN <sub>2</sub> Na	C <sub>38</sub> H <sub>46</sub> AlN <sub>2</sub> Na	C <sub>42</sub> H <sub>56</sub> AlN <sub>2</sub> NaO
<i>M</i> <sub>r</sub>	768.03	718.94	697.90	580.74	654.86
crystal system	monoclinic	tetragonal	tetragonal	monoclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>I</i> 4 <sub>1</sub> <i>md</i>	<i>I</i> 4 <sub>1</sub> <i>md</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> [Å]	11.1202(1)	28.891(5)	28.7592(6)	11.3609(4)	10.818(5)
<i>b</i> [Å]	22.9304(1)	28.891(5)	28.7592(6)	20.8691(8)	11.274(5)
<i>c</i> [Å]	18.8678(2)	9.946(5)	9.9216(4)	14.5666(5)	31.612(5)
<i>α</i> [°]	90	90	90	90	90
<i>β</i> [°]	98.109(1)	90	90	100.735(1)	94.225(5)
<i>γ</i> [°]	90	90	90	90	90
<i>V</i> [Å <sup>3</sup> ]	4763.01(7)	8302(5)	8206.1(4)	3393.2(2)	3845(3)
<i>Z</i>	4	8	8	4	4
<i>ρ</i> <sub>calcd</sub> [g cm <sup>-3</sup> ]	1.071	1.150	1.130	1.137	1.131
<i>μ</i> [mm <sup>-1</sup> ]	0.089	0.094	0.093	0.100	0.097
<i>F</i> (000)	1668	3096	3000	1248	1416
crystal size [mm <sup>3</sup> ]	0.56 × 0.26 × 0.14	0.30 × 0.28 × 0.25	0.70 × 0.46 × 0.33	0.50 × 0.42 × 0.22	0.62 × 0.45 × 0.32
<i>θ</i> <sub>min</sub> / <i>θ</i> <sub>max</sub>	1.78/25.00	1.99/26.00	2.00/27.00	1.73/25.00	1.89/25.00
index ranges	−13 ≤ <i>h</i> ≤ 13 −27 ≤ <i>k</i> ≤ 26 −19 ≤ <i>l</i> ≤ 22	−35 ≤ <i>h</i> ≤ 20 −35 ≤ <i>k</i> ≤ 35 −12 ≤ <i>l</i> ≤ 12	−36 ≤ <i>h</i> ≤ 35 −36 ≤ <i>k</i> ≤ 33 −10 ≤ <i>l</i> ≤ 12	−13 ≤ <i>h</i> ≤ 13 −19 ≤ <i>k</i> ≤ 24 −17 ≤ <i>l</i> ≤ 17	−12 ≤ <i>h</i> ≤ 12 −12 ≤ <i>k</i> ≤ 13 −23 ≤ <i>l</i> ≤ 37
reflections collected	23 454	27 929	29 919	21 122	23 379
independent reflections	8333	4254	4419	5977	6753
<i>R</i> <sub>int</sub>	0.0951	0.0880	0.0690	0.1312	0.1678
completeness to <i>θ</i> <sub>max</sub> [%]	99.3	99.9	100	99.9	99.7
max/min transmission	0.9877/0.9520	0.9768/0.9723	0.9698/0.9374	0.9766/0.4022	0.9696/0.9422
data/restraints/parameters	8333/69/565	4254/48/336	4419/5/261	5977/4/419	6753/0/436
GOF on <i>F</i> <sup>2</sup>	1.026	1.013	1.038	1.006	1.000
final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]					
<i>R</i> <sub>1</sub>	0.0770	0.0435	0.0479	0.0686	0.0754
<i>wR</i> <sub>2</sub>	0.1767	0.0777	0.1046	0.1326	0.1270
<i>R</i> indices (all data)					
<i>R</i> <sub>1</sub>	0.1585	0.0715	0.0688	0.1324	0.1958
<i>wR</i> <sub>2</sub>	0.2155	0.0880	0.1161	0.1558	0.1656
largest diff. peak/hole [e Å <sup>-3</sup> ]	0.632/−0.334	0.196/−0.172	0.300/−0.300	0.350/−0.297	0.256/−0.243

Table 2. Selected bond lengths [Å] and angles [°] for 1–5.

	1	2	3	4	5
Al(1)–C(37)	1.991(4)	2.004(4)	2.000(4)	1.990(3)	2.010(4)
Al(1)–C(38)	1.977(4)	1.947(4)	1.962(4)	1.951(4)	1.959(4)
Al(1)–N(1)	1.894(3)	1.9257(19)	1.9205(18)	1.920(3)	1.913(3)
Al(1)–N(2)	1.899(3)	1.9257(19)	1.9205(18)	1.900(2)	1.924(3)
C(1)–N(1)	1.386(4)	1.408(3)	1.404(3)	1.417(4)	1.403(4)
C(2)–N(2)	1.392(4)	1.408(3)	1.404(3)	1.381(4)	1.410(4)
C(1)–C(2)	1.387(5)	1.393(4)	1.392(4)	1.381(4)	1.358(5)
Na(1)–C(3)		2.887(12)	2.813(5)		
Na(1)–C(4)		2.914(6)	2.793(5)		
Na(1)–C(5)		2.871(5)	2.832(5)		
Na(1)–C(6)	3.013(4)	2.792(6)	2.847(5)		
Na(1)–C(7)	2.785(4)	2.729(6)	2.832(5)		
Na(1)–C(8)	2.910(4)	2.795(11)	2.793(5)		
Na(1)–C(16)				2.728(4)	
Na(1)–O(1)	2.325(4)				2.230(3)
Na(1)–O(2)	2.308(4)				
Na(1)–C(37)	2.815(4)	2.843(4)	2.887(4)	2.932(4)	2.859(3)
Na(1)–C(1)		2.659(3)	2.634(3)	2.608(3)	2.686(4)
Na(1)–C(2)		2.659(3)	2.634(3)	3.074(3)	2.642(4)
Na(1)–N(1)		2.722(2)	2.729(2)	2.595(3)	2.776(4)
Na(1)–N(2)		2.722(2)	2.729(2)	3.495(4)	2.671(3)
N(1)–Al(1)–N(2)	89.33(12)	88.70(11)	88.78(11)	89.86(11)	87.79(14)
C(38)–Al(1)–C(37)	109.15(18)	110.38(19)	110.74(19)	112.72(18)	107.69(19)

thermore, complexes **2** and **3** are two of the few examples of interactions between alkali metal cations and arene ligands. Before the detailed discussion of the structures of **1** to **5**, some general remarks should be noted:

- 1) In all complexes, the dpp-BIAN dianion acts as a rigid, symmetric chelating ligand towards the Me<sub>2</sub>Al group. The two Al–N bond lengths are of the same order in each complex.
- 2) The dianionic character of the diimine ligand is apparent from the elongation of the C(1)–N(1) and C(2)–N(2) bonds and the shortening of the C(1)–C(2) bond relative to the respective

bonds in free dpp-BIAN (both C–N 1.282(4), C(1)–C(2) 1.534(6) Å).<sup>[15]</sup>

3) In all five complexes different Al–CH<sub>3</sub> distances are observed. We suggest that the elongation of the C(37)–Al bond (**1**: 1.991(4); **2**: 2.004(4); **3**: 2.000(4); **4**: 1.990(3); **5**: 2.010(4) Å) relative to the C(38)–Al bond (**1**: 1.977(4); **2**: 1.947(4); **3**: 1.962(4); **4**: 1.951(4); **5**: 1.959(4) Å) is caused by interaction of the C(37) atoms with sodium cations. In the case of **1** this interaction occurs intermolecularly resulting in a chain structure (Figure 1 b), whereas in **2** to **5** intramolecular interactions take place.

The position of the sodium cation on going from **1** to **2** and **3** changes dramatically. In **1** the sodium atom resides above one of the six-membered rings of the naphthalene part of the dpp-BIAN ligand and is slipped towards the atoms C(6), C(7), and C(8) with distances of 3.013(4), 2.785(4) and 2.910(4) Å, respectively (Figure 1 a). The C–C bond lengths in the naphthalene part are virtually the same as those in free dpp-BIAN and free naphthalene. These facts together with the geometrical parameters of the diimine fragment mentioned above indicate that the negative charge of the dpp-BIAN dianion is distributed over the N(1)–C(1)–C(2)–N(2) fragment. Therefore, the sodium atom in **1** interacts with a more or less neutral arene  $\pi$ -system. The pronounced shift of the sodium atom towards C(8) follows from the symmetry of the HOMO which reveals a larger  $\pi$ -electron density at C(8) with respect to the other carbon atoms. Besides the interaction with the  $\pi$ -system, the sodium atom coordinates two diethyl ether molecules and interacts with the C(37) atom of a neighboring molecule (Figure 1 b).

In the molecules of **2** (Figure 2 a) and **3** (Figure 2 b) the sodium atoms are located above the center of the five-membered metalocycle formed by the –N(1)–C(1)–C(2)–N(2)–Al–atoms. Both molecules possess a crystallographic mirror plane that contains the Al and Na atoms and bisects the N–Al–N angle. The toluene molecule of **2** is disordered with regard to two crystallographically symmetry equivalent positions. For clarity Figure 2 a shows the toluene molecule only in one of the two positions. The distances of the Na atom to the toluene carbon atoms C(3)–C(8) range from 2.729(6) to 2.914(6) Å. The average Na–C(toluene) distance of 2.844 Å compares well with the distance Na–C(37) (2.843 Å). Comparatively, the distances Na–C(1) and Na–C(2) are much shorter (both 2.659(3) Å), thus reflecting the significant ionic character of the interaction of the metal with the negatively charged diimine system. The phenyl rings at both nitrogen atoms are turned away from the coordinated toluene molecule thus minimizing the steric stress between their ortho positioned isopropyl substituents and the toluene molecule.

The most significant difference in the molecular structures of **2** and **3** concerns the arene–sodium coordination. The Na–C(benzene) distances in **3** cover a smaller range from 2.793 to 2.847 Å and the average Na–C(benzene) distance is shorter (2.818 Å) with respect to the average Na–C(toluene)

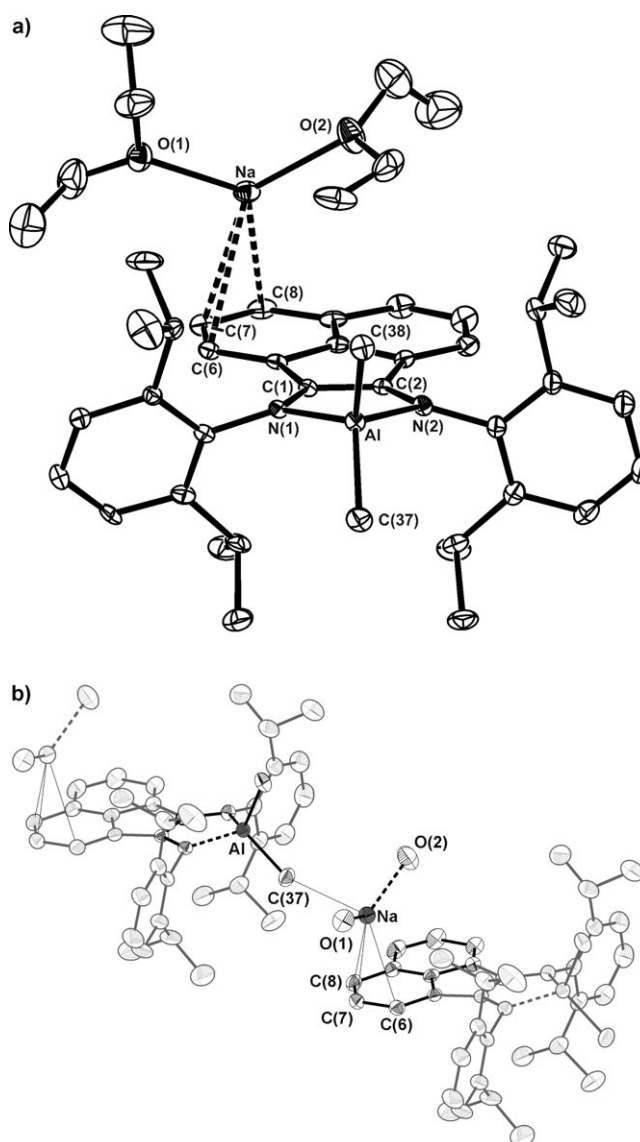


Figure 1. a) ORTEP drawing of complex **1** with thermal ellipsoids drawn at 20% probability. Hydrogen atoms are omitted for clarity. b) ORTEP drawing of the intermolecular chain formation in complex **1**.

distance in **2** (2.844 Å). Toluene is more sterically demanding than benzene on account of its Me group, hence benzene can approach sodium more closely. At the same time this strengthening of the interaction between the Na atom and the benzene molecule in **3** results in a weakening of the Na–C(37) interaction (**3**: 2.887(4); **2**: 2.843 Å).

The loss of the arene ligand on going from **2** and **3** to **4** causes a further change of the position of the sodium atom relative to the dpp-BIAN ligand. In the molecular structure of **4** (Figure 3) the sodium cation is completely shifted to one side of the diimine fragment as can be seen from the Na–C(1) (2.608(3) Å), Na–C(2) (3.074(3) Å), Na–N(1) (2.595(3) Å), and Na–N(2) (3.495(4) Å) distances. To meet its coordinative requirements despite the absence of an arene ligand, the sodium atom not only strengthens its bonding to the diimine system, but also recruits the nitro-

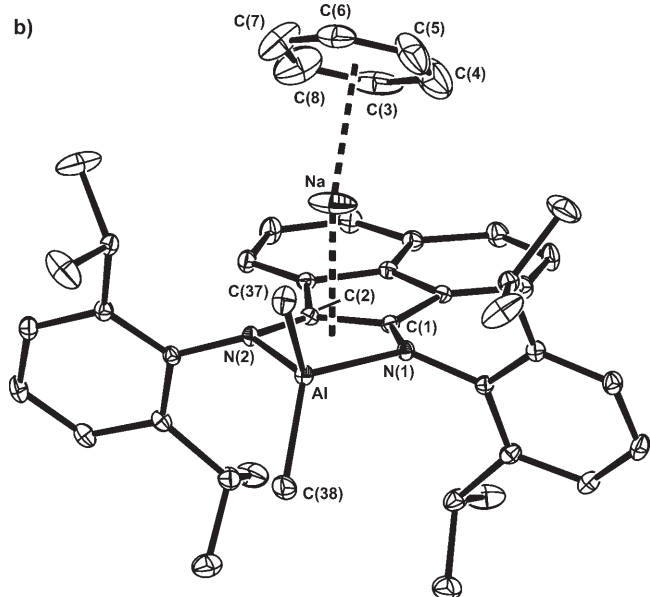
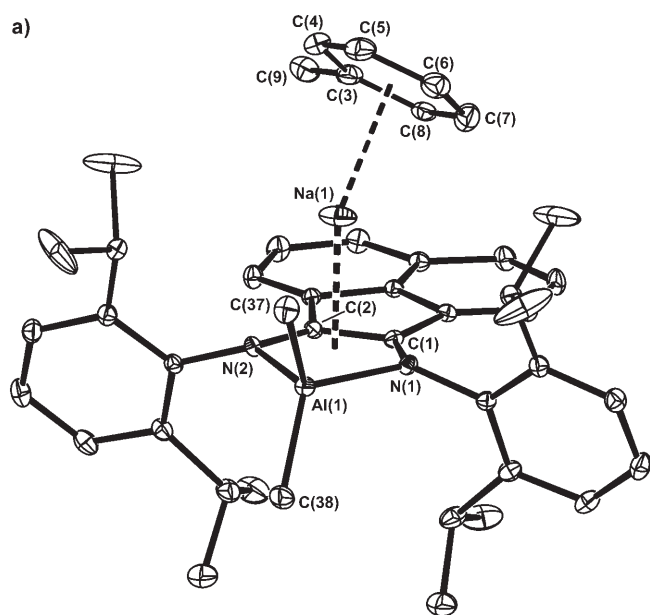


Figure 2. ORTEP drawings of complexes a) **2** and b) **3**; with thermal ellipsoids drawn at 20% probability. Hydrogen atoms are omitted for clarity.

gen-bonded phenyl groups of neighboring molecules for interaction according to the intermolecular short contacts (2.728(4) Å) between Na and C(16).

The molecular structure of **5** (Figure 4) can be used for a rough, non-quantitative estimation of the bond strength between the sodium atom and the arene ligands in **2** and **3**. The position of the sodium cation relative to the dpp-BIAN system in **5** is the same as in **2** and **3**; it resides above the center of the diimine system and coordinates instead of an arene one diethyl ether molecule. One may assume that a strengthening of the interaction between the sodium cation and a solvent molecule (arene in **2** and **3**; Et<sub>2</sub>O in **5**) must

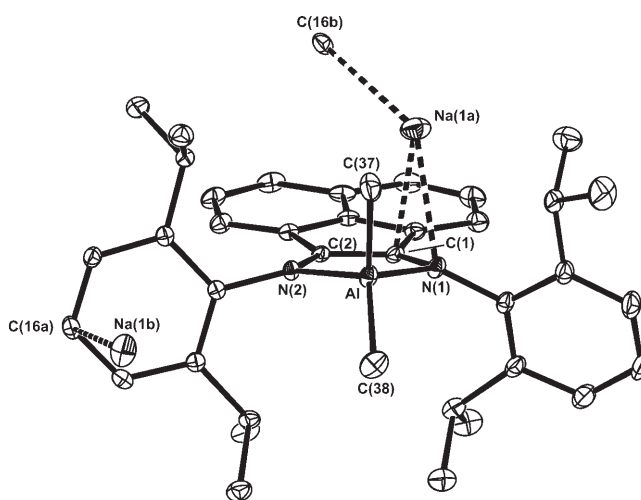


Figure 3. ORTEP drawing of complex **4** with thermal ellipsoids drawn at 20% probability. Hydrogen atoms are omitted for clarity.

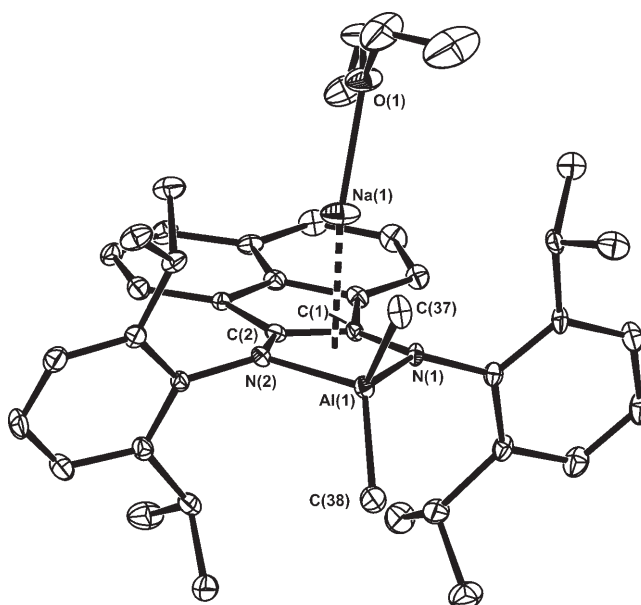


Figure 4. ORTEP drawing of complex **5** with thermal ellipsoids drawn at 20% probability. Hydrogen atoms are omitted for clarity.

result in a weakening of the interaction between the sodium cation and the diimine system. The Na(1)–O(1) bond length in **5** (2.230(3) Å) is much shorter than the Na–O(1,2)(Et<sub>2</sub>O)<sub>2</sub> bond lengths in **1** (2.325(4) and 2.308(4) Å). The bond lengths between Na(1) and the atoms of the diimine moiety (Na(1)–N(1) 2.776(4) Å, Na(1)–N(2) 2.671(3) Å, Na(1)–C(1) 2.686(4) Å, and Na(1)–C(2) 2.642(4) Å) are conversely elongated compared to those in, for example, complex **3** (Na–N(1,2) 2.729(2), Na–C(1,2) 2.634(3) Å). Besides the fact that **1** crystallizes from a mixture of equal parts of benzene and Et<sub>2</sub>O as the diethyl ether complex, the consideration of the bond lengths indicates that the bonding strength of the sodium metal cation to the arene is much

weaker than that of the sodium cation to the electron-donating ether molecule.

Besides the X-ray crystallographic results, the spectroscopic data, for example,  $^1\text{H}$  NMR data would provide more insight in the character of the alkali metal cation interactions. Unfortunately, all signals in the  $^1\text{H}$  NMR spectra of **2** and **3** recorded in deuterated toluene or deuterated benzene, respectively, are very broad, thus preventing a definition of the signals of the coordinated arene. This is probably due to the slow (on the NMR timescale) dynamic process associated with the migration of the cation over the diimine  $\pi$ -system. In contrast, the  $^1\text{H}$  NMR spectra of **2** and **3** recorded in  $[\text{D}_8]\text{THF}$  (see Experimental Section) show the expected well-resolved signals, including those of free toluene and benzene. The signals of free toluene and benzene arise as a result of coordination of  $[\text{D}_8]\text{THF}$  on the sodium cation, which probably leads to a solvent-separated ion-pair system.

## Conclusion

We could demonstrate that the dpp-BIAN ligand provides besides its unique redox properties also a rich coordination chemistry. It offers different sites for the coordination of metal cations, for example, the aromatic naphthalene rings as well as the negatively charged diimine system. In the absence of competitive donor solvents the sodium cation readily coordinates neutral arene molecules. The simultaneous coordination of two different metal cations, aluminum and sodium cations, in and above the dpp-BIAN diimine plane provides intramolecular interactions between the metals through their organic ligands, for instance through the methyl groups at the aluminum atom as it is the case in molecules **2** and **3**.

## Experimental Section

**General remarks:** All manipulations were carried out in vacuum or under nitrogen by using Schlenk glassware. The solvents diethyl ether, benzene, toluene, and hexane were dried by distillation from sodium benzophenone prior to use. The deuterated solvents used for the NMR measurements were dried with sodium benzophenone at ambient temperature and were, just prior to use, condensed under vacuum into the NMR tubes already containing the respective compound. Melting points were measured in sealed capillaries. The IR-spectra were recorded on Magne System 750 and Specord M80 spectrometers, the  $^1\text{H}$  NMR spectra on Bruker ARX 400 and Bruker ARX 200 NMR spectrometers, and the mass spectra on a Varian 311 A/AMD (EI, 70 eV) spectrometer. The solutions of the starting sodium salt  $\text{Na}_2[\text{dpp-BIAN}]$  were prepared in situ from dpp-BIAN and sodium metal (1:2 mole ratio) in diethyl ether, toluene, or benzene at ambient temperature with vigorous stirring. The reaction was defined to be finished when no more unreacted sodium metal was observed in the reaction mixture. In diethyl ether the reaction is completed within about 12 h, in toluene or benzene it takes about 48 h.

**$[\text{Na}(\text{Et}_2\text{O})_2(\text{dpp-BIAN})\text{AlMe}_2]$  (**1**):**  $\text{Me}_2\text{AlCl}$  (1.6 mL, 1.0 M solution in hexane) was added to a solution of  $\text{Na}_2[\text{dpp-BIAN}]$  [obtained in situ from dpp-BIAN (0.8 g, 1.6 mmol) and sodium (0.74 g, 3.2 mmol) in  $\text{Et}_2\text{O}$  (50 mL)] at 25 °C. The mixture was stirred at ambient temperature for

1 h and was then filtered off from the precipitated sodium chloride. The resulting clear green solution was concentrated to a volume of 5 mL by evaporation of the solvent in vacuum at room temperature. Then benzene (5 mL) was added. After standing of the solution for 24 h, dark green crystals of **1** (0.46 g, 74%) were isolated from the mother liquor by decantation. M.p. 349–353 °C (decomp);  $^1\text{H}$  NMR (400 MHz,  $[\text{D}_8]$ toluene, 20 °C):  $\delta = 7.23$  (s, 6H;  $\text{C}_6\text{H}_3\text{Pr}_2$ ), 7.15 (s, 3H;  $\text{C}_6\text{H}_6$ ), 6.85 (d,  $J = 8.0$  Hz, 2H; naphthalene part), 6.66 (dd,  $J = 6.7$ , 8.2 Hz, 2H; naphthalene part), 5.96 (d,  $J = 6.7$  Hz, 2H; naphthalene part), 3.84 (sept,  $J = 6.9$  Hz, 4H;  $\text{CH}(\text{CH}_3)_2$ ), 3.11 (q,  $J = 6.9$  Hz, 8H;  $\text{Et}_2\text{O}$ ), 1.37 (d,  $J = 6.9$  Hz, 12H;  $\text{CH}_3\text{-CH-CH}_3$ ), 1.14 (d,  $J = 6.9$  Hz, 12H;  $\text{CH}_3\text{-CH-CH}_3$ ), 0.94 (t,  $J = 6.9$  Hz, 12H;  $\text{Et}_2\text{O}$ ),  $-0.44$  ppm (s, 6H;  $\text{Al}(\text{CH}_3)_2$ );  $^{13}\text{C}$  NMR (200 MHz,  $[\text{D}_8]$ toluene, 22 °C):  $\delta = 145.9$ , 144.5, 135.6, 134.3, 124.0, 123.7, 117.7, 66.0, 28.6, 25.3, 24.9, 15.3 ppm; IR (Nujol):  $\tilde{\nu} = 2726$  (w), 1586 (m), 1536 (m), 1322 (w), 1182 (s), 1152 (w), 1123 (s), 1078 (w), 1057 (w), 1038 (w), 935 (m), 923 (m), 892 (m), 845 (w), 819 (m), 803 (m), 764 (s), 727 (s), 694 (m), 675  $\text{cm}^{-1}$  (vs); elemental analysis calcd (%) for  $\text{C}_{46}\text{H}_{66}\text{AlN}_2\text{NaO}_2 \cdot 0.5\text{C}_6\text{H}_6$  (768.03): C 76.63, H 9.05; found: C 76.69, H 8.91.

**$[\text{Na}(\eta^6\text{-C}_7\text{H}_8)(\text{dpp-BIAN})\text{AlMe}_2]$  (**2**):**  $\text{Me}_2\text{AlCl}$  (1.3 mL, 1.54 M solution in hexane) was added to a solution of  $\text{Na}_2[\text{dpp-BIAN}]$  [obtained in situ from dpp-BIAN (1.0 g, 2.0 mmol) and sodium (0.92 g, 4.0 mmol) in toluene (50 mL)] at 0 °C. The reaction mixture was stirred at ambient temperature for 1 h and was then filtered off from precipitated sodium chloride. Concentration of the green solution by evaporation of the solvent in vacuum at room temperature resulted in the precipitation of **2** (1.2 g, 83%) as dark green crystals. X-ray quality crystals were obtained by re-crystallization of the crude product from toluene. M.p. 211 °C;  $^1\text{H}$  NMR (200 MHz,  $[\text{D}_8]\text{THF}$ , 20 °C):  $\delta = 7.31$ – $6.87$  (m, 17.5H; arom.), 6.25 (dd,  $J = 6.7$ , 8.2 Hz, 2H; naphthalene part), 4.11 (sept,  $J = 6.7$  Hz, 4H;  $\text{CH}(\text{CH}_3)_2$ ), 2.31 (s, 4.5H;  $\text{C}_6\text{H}_5\text{CH}_3$ ), 1.17 (d,  $J = 6.7$  Hz, 12H;  $\text{CH}_3\text{-CH-CH}_3$ ), 1.03 (d,  $J = 6.7$  Hz, 12H;  $\text{CH}_3\text{-CH-CH}_3$ ),  $-0.92$  ppm (s, 6H;  $\text{Al}(\text{CH}_3)_2$ );  $^{13}\text{C}$  NMR ( $[\text{D}_8]\text{THF}$ , 100 MHz):  $\delta = 146.3$ , 139.4, 138.4, 137.2, 129.6, 128.9, 127.4, 127.0, 126.0, 126.4, 124.9, 124.2, 122.9, 122.6, 119.9, 28.8 ( $\text{CH}(\text{CH}_3)_2$ ), 28.0 ( $\text{CH}(\text{CH}_3)_2$ ), 21.5 ( $\text{C}_6\text{H}_5\text{CH}_3$ ), 1.5 ppm (s, 6H;  $\text{Al}(\text{CH}_3)_2$ );  $^{27}\text{Al}$  NMR (104 MHz,  $[\text{D}_8]\text{THF}$ , 20 °C):  $\delta = 153$  ppm ( $w_{1/2} = 7.3$  kHz); MS (70 eV, 238 °C):  $m/z$  (%): 44 (59)  $[\text{C}_3\text{H}_8]^+$ , 91 (18)  $[\text{C}_2\text{H}_7]^+$ , 162 (32)  $[\text{C}_{12}\text{H}_{18}]^+$ , 176 (11)  $[\text{iPr}_2\text{C}_6\text{H}_3\text{NH}]^+$ , 312 (48)  $[\text{C}_{23}\text{H}_{22}\text{N}]^+$ , 457 (100)  $[\text{BIAN-C}_3\text{H}_7]^+$ , 500 (12)  $[\text{BIAN}]^+$ , 542 (79)  $[(\text{BIAN})\text{AlMe}_2]^+$ , 557 (19)  $[(\text{BIAN})\text{AlMe}_2]^+$ ; elemental analysis calcd (%) for  $\text{C}_{45}\text{H}_{54}\text{AlN}_2\text{Na} \cdot 0.5\text{C}_7\text{H}_8$  (718.97): C 81.01, H 8.13; found: C 80.99, H 8.21.

**$[\text{Na}(\eta^6\text{-C}_6\text{H}_6)(\text{dpp-BIAN})\text{AlMe}_2]$  (**3**):** Compound **3**, the benzene analogue of **2**, was prepared in the same way as described for **2**, but by using dpp-BIAN (1.0 g, 2.0 mmol), sodium (0.92 g, 4.0 mmol),  $\text{Me}_2\text{AlCl}$  (1.3 mL, 1.54 M solution in hexane), and benzene instead of toluene as solvent. Compound **3** was isolated as dark green crystals. Yield 1.25 g (89%). M.p. 201 °C. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **3** in  $[\text{D}_8]\text{THF}$  are identical to those of compound **2** except the signals of benzene ( $\delta = 7.4$  ppm) and toluene ( $\delta = 2.31$  ppm). Elemental analysis calcd (%) for  $\text{C}_{44}\text{H}_{52}\text{AlN}_2\text{Na} \cdot 0.5\text{C}_6\text{H}_6$  (697.94): C 80.88, H 7.94; found: C 80.61, H 7.90.

**$[\text{Na}(\text{dpp-BIAN})\text{AlMe}_2]_n$  (**4**):** For the synthesis of **4**, a solution of **1** in diethyl ether was prepared as described above by using dpp-BIAN (0.3 g, 0.6 mmol), sodium (0.14 g, 0.6 mmol),  $\text{Me}_2\text{AlCl}$  (0.6 mL, 1.0 M solution in hexane) and  $\text{Et}_2\text{O}$  (30 mL). From the filtered ether solution of **1** the volatiles were evaporated in vacuum. The remaining solid was dried in vacuum for 30 min and then treated with hexane (30 mL). The resulting suspension was refluxed for 30 min. After that the solvent was removed under reduced pressure. Hexane (100 mL) was added to the remaining solid and the mixture was refluxed for several minutes. The resulting solution was filtered warm. Cooling to ambient temperature caused crystallization of compound **4** (0.11 g, 32%) as dark green crystals. M.p. 310 °C (decomp);  $^1\text{H}$  NMR (400 MHz,  $[\text{D}_8]\text{THF}$ , 20 °C):  $\delta = 7.01$ – $6.82$  (m, 6H; arom), 6.51– $6.38$  (m, 4H; arom), 5.38 (dd,  $J = 6.1$ , 1.4 Hz, 2H; arom), 4.11 (sept,  $J = 6.7$  Hz, 4H;  $\text{CH}(\text{CH}_3)_2$ ), 1.16 (d,  $J = 6.7$  Hz, 12H;  $\text{CH}_3\text{-CH-CH}_3$ ), 1.02 (d,  $J = 6.7$  Hz, 12H;  $\text{CH}_3\text{-CH-CH}_3$ ),  $J = 6.7$ ),  $-0.93$  ppm (s, 6H;  $\text{Al}(\text{CH}_3)_2$ ); elemental analysis calcd (%) for  $\text{C}_{38}\text{H}_{46}\text{N}_2\text{NaAl}$  (580.74): C 78.59, H 7.98; found: C, 78.48; H, 7.95.



**Na(Et<sub>2</sub>O)(dpp-BIAN)AlMe<sub>2</sub> (5):** This compound was isolated in a yield of 7% from the solution obtained by extraction of oily crude **1** with hexane at ambient temperature. However, all attempts to reproduce compound **5** failed.

**Single-crystal X-ray structure determination of 1–5:** The crystallographic data of **1–5** were collected on a SMART CCD diffractometer (graphite-monochromated MoK $\alpha$  radiation,  $\omega$ - and  $\psi$ -scan technique,  $\lambda = 0.71073$  Å). The structures were solved by direct methods by using SHELXS-97<sup>[16]</sup> and were refined by a full-matrix least-squares method on  $F^2$  by using SHELXL-97.<sup>[17]</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions by using a riding model except those of the CH<sub>3</sub>-Al groups of compounds **2** and **3**, which were found from the electron density map. SADABS<sup>[18]</sup> was used to perform area-detector scaling absorption corrections. The absolute structure of the non-centrosymmetric space groups was determined with SHELXL-97 according to Flack.<sup>[19]</sup> The geometrical aspects of the structures were analyzed by using PLATON.<sup>[20]</sup> CCDC-633298 (**1**), CCDC-633296 (**2**), CCDC-633297 (**3**), CCDC-633295 (**4**), and CCDC-633299 (**5**) contain the respective supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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