Four Anions of a Diimine Ligand

Four-Step Reduction of dpp-bian with Sodium Metal: Crystal Structures of the Sodium Salts of the Mono-, Di-, Tri- and Tetraanions of dpp-bian[**]

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Dedicated to Professor Herbert Schumann
on the occasion of his 68th birthday.

In the beginning of the 1990 s Elsevier, van Asselt and co-workers introduced the bis(*N*-arylimino)acenaphthene ligand (Ar-bian) into coordination chemistry.[1] Over the past decade transition-metal complexes of this ligand have been studied extensively because of a wide range of possible applications in catalysis, for example, in the hydrogenation of alkynes,[2a] in C–C[2b] and C–Sn[2c] bond formation, and especially in olefin polymerization.[3] The Ar-bian ligands combine both the α,α'-diimine and the naphthalene π systems in a single π system. As complexes of the dianions of α,α'-diimines[4] as well as naphthalene[5] were reported, we suggested that Ar-bian ligands might form stable mono- and di-, and possibly even tri- and tetraanions by electron transfer to their mixed 14-electron imine–naphthalene π system. Despite the extensive current interest in hydrocarbons with high negative charge only a few examples of well-defined tetraanions are reported in the literature. Among them are large conjugated systems, for example, rubrene ($C_{42}H_{28}$),[6a] decacyclene ($C_{36}H_{12}$),[6b] corannulene ($C_{20}H_{15}$),[6c,d] indenocorannulene ($C_{26}H_{19}$),[6e] [5] radialene ($C_{29}H_{62}Si_8$),[6f,g] and fullerene (C_{60}).[6h] One common feature of the aromatic hydrocarbon anions is that they often disproportionate to species oxidized and reduced by one electron, thus not allowing the isolation of some intermediate anions. The disproportionation process is dependent on the nature of both anion and cation. For instance, attempts of the exchange reaction between lithium naphthalenide, $Li^+(C_{10}H_8)^-$ and lanthanide halides in THF lead to the disproportionation of the radical anions of $(C_{10}H_8)^-$ to the dianion $(C_{10}H_8)^{2-}$ and neutral naphthalene, affording solely lanthanide complexes with the naphthalene dianion.[5b–e] Recently, Gambarotta, Budzelaar and co-workers reported the formation and crystal structure of a trianion formed by reduction of α,α'-diiminopyridine with lithium.[7] Again, regardless of the stoichiometric ratio, the reduction afforded only the trianionic species. Herein we report the reduction of Ar-bian with alkali metals to $[\text{Ar-bian}]^{n-}$ ($n = 1$–4). For this study we chose the most commonly used Ar-bian ligand—bis[*N*-(2,6-diisopropylphenyl)imino]acenaphthene, $(2,6\text{-}i\text{Pr}_2\text{PhNC})_2(C_{12}H_6)$.

The reduction of $(2,6\text{-}i\text{Pr}_2\text{PhNC})_2(C_{12}H_6)$ with sodium in diethyl ether occurred stepwise (Scheme 1) with the consecutive formation of the sodium complexes of the mono-, di-, tri- and tetraanions of the ligand, $[\{\text{Na}(2,6\text{-}i\text{Pr}_2\text{PhNC})_2(C_{12}H_6)\}_2]$ (**1**), $[\text{Na}_2(\text{Et}_2\text{O})_3(2,6\text{-}i\text{Pr}_2\text{PhNC})_2(C_{12}H_6)]$ (**2**), $[\{\text{Na}_3(\text{Et}_2\text{O})_2(2,6\text{-}i\text{Pr}_2\text{PhNC})_2(C_{12}H_6)\}_2]$ (**3**) and $[\{\text{Na}_4(\text{thf})_4(2,6\text{-}i\text{Pr}_2\text{PhNC})_2(C_{12}H_6)\}_2]$ (**4**). The formation of **1** and **2** can be easily detected by the color change of the reaction solution. During the reduction the color changes in the following sequence: orange (free ligand), red (radical anion) and deep green (dianion). The complexes **3** and **4** precipitate from the reaction solution as brown and brick-red microcrystalline solids, respectively (Scheme 1). Therefore, it is difficult to separately recognize their formation. Complete conversion of the ligand to the tetraanion is achieved reproducibly by stirring vigorously the ligand and sodium for 5 h. The intermediate complexes **1**, **2** and **3** were obtained by the addition of 3, 2 or 0.66 equivalents, respectively, of the free ligand to complex **4**.

Complexes **1**–**4** are thermally quite stable: no changes were observed when crystalline samples of **1**–**4** were heated up to 246 °C in sealed and evacuated capillaries. Compounds **1** and **3** are paramagnetic. Their magnetic moments at room temperature (**1**, 1.95; **3**, 1.68 BM) correspond to one unpaired electron per ligand in both cases. As anticipated, complexes **2** and **4** are diamagnetic. The isopropyl methyl groups appear as two doublets centerd at 1.41 and 1.33 ppm (^3J(H,H) = 8.0 Hz for both doublets) in the ^{1}H NMR spectrum of **2** in C_6D_6 due to the hindered rotation about the aryl carbon-to-nitrogen bond. The signal for the four H-C(CH$_3$)$_2$ protons appears as a septet at 3.85 ppm (^3J(H,H) = 8.0 Hz). The twelve aromatic protons are found in a relatively narrow region (7.32–

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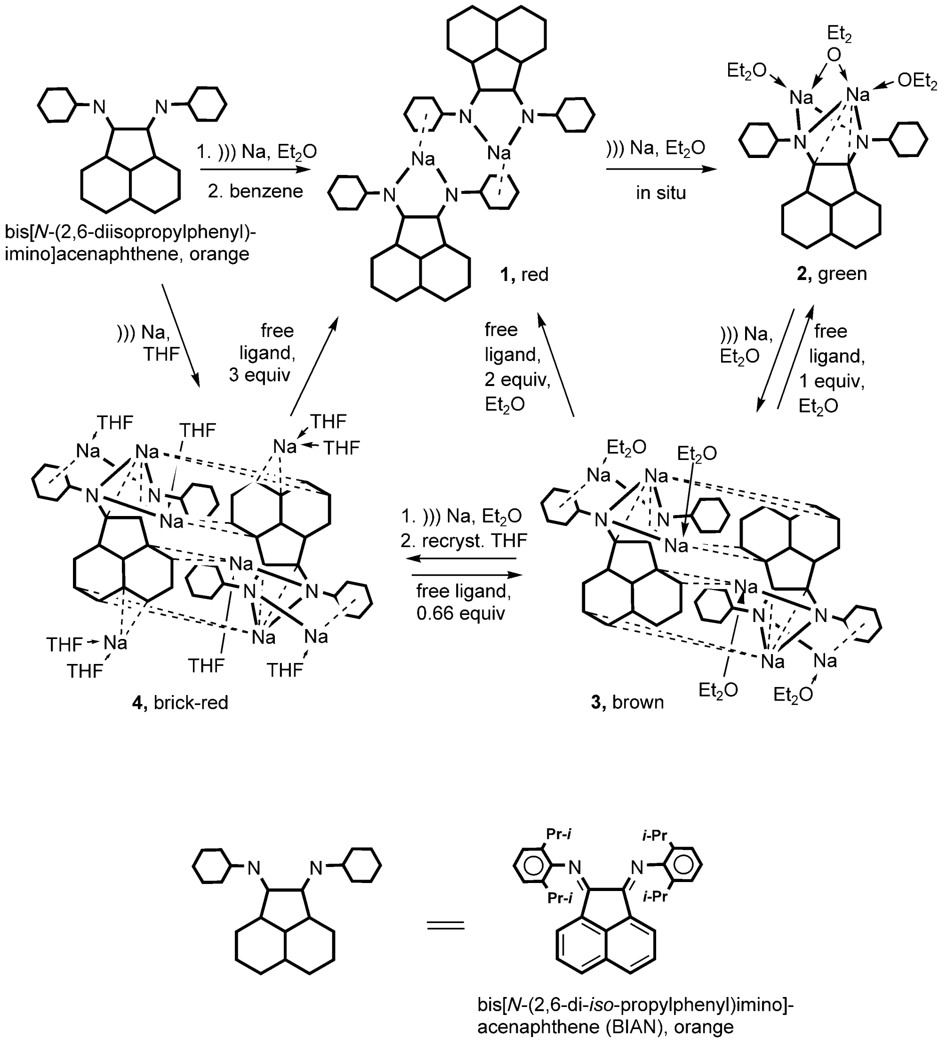

Scheme 1. Synthesis of complexes **1**–**4**.

6.51 ppm). Despite of the extreme sensitivity of complex **4** towards air and moisture attempts to obtain its ^{1}H NMR spectrum were undertaken. The spectrum obtained in [D_8]-THF revealed the presence of some impurities amounting to about 10%. These narrow signals are attributable to those observed for compound **2** in C_6D_6. The dominant signals in the spectrum are noticeably broadened and high-field shifted and probably are from the aromatic protons of the tetraanion ($\delta = 6.56$, 6.45, 5.83, 4.64, 3.93, 2.83 ppm). The signal corresponding to H-$C(CH_3)_2$ protons appears to be partly overlap the THF signal at 3.60 ppm. The isopropyl methyl groups are observed as a broad single signal at 0.91 ppm.

The molecular structures of **1**, **2**, **3** and **4** were determined by single crystal X-ray diffraction. The crystals of **2** and **3** were grown from diethyl ether. The crystals of **1** and **4** were obtained from benzene and THF, respectively. The aggregation of **1** (Figure 1) to the centrosymmetric dimer with arene coordination of the sodium in the solid state is probably a result of the loss of coordinated Et_2O molecules during the crystallization from benzene. The sodium atom deviates from the plane formed with N(1)C(1)C(2)N(2) fragment by only 6.7°. Although there is a significant difference in the sodium to nitrogen bond distances (2.2837(13) and 2.3511(14) Å) in **1**, the similar C(1)-N(1) (1.3239(18) Å) and C(2)-N(2) (1.3326(19) Å) distances indicate a rather symmetrical diimine moiety N=C–C=N. These bonds are elongated compared with those in the neutral ligand in [$CuCl_2(2,6\text{-}i\mathrm{Pr}_2PhNC)_2(C_{12}H_6)(AcOH)$][9] (av 1.287 Å), thus reflecting population of the LUMO which has a high contribution of nitrogen orbitals. In contrast, the C(1)–C(2) bond in **1** is shortened to 1.446 Å compare to that in the copper(II) complex [$CuCl_2(2,6\text{-}i\mathrm{Pr}_2PhNC)_2(C_{12}H_6)(AcOH)$] (1.500 Å).[9] The sodium-to-arene distances in **1** range from 2.7330(19) to 2.972(2) Å (av 2.8571 Å).

The reduction of the radical anion to the dianion causes further elongation of the C–N bonds (1.387(4) and 1.386(4) Å) and shortening of the C(1)-C(2) bond (1.402(4) Å) in the ligand (Figure 2). The second sodium atom in the dianion is situated over the center of the plane formed by the metallacycle -Na(1)N(1)C(1)C(2)N(2). The dihedral angles between planes N(1)Na(1)N(2) and N(1)Na(2)N(2) and the plane formed with enediamido N(1)C(1)C(2)N(2) moiety are 23.9 and 77.0°, respectively. The different positions of the sodium atoms relative to the

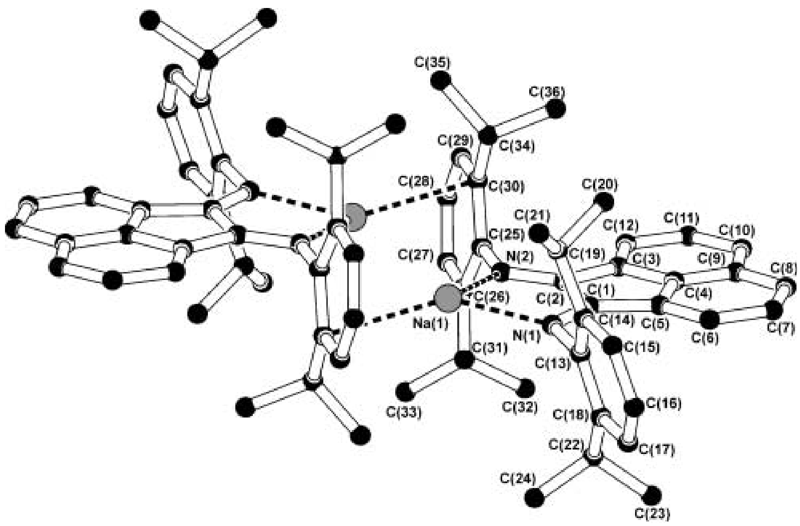

Figure 1. PLATON[8] presentation of the molecular structure of **1**. Selected bond lengths [Å] and angles [°]: Na(1)-N(1) 2.2837(13), Na(1)-N(2) 2.3511(14), Na(1)-C(1) 3.0180(15), Na(1)-C(2) 3.0496(15), Na(1)-C(25) 2.7903(16), Na(1)-C(26) 2.8573(19), Na(1)-C(27) 2.949(2), Na(1)-C(28) 2.972(2), Na(1)-C(29) 2.841(2), Na(1)-C(30) 2.7330(19), N(1)-C(1) 1.3239(18), N(2)-C(2) 1.3326(19), N(1)-C(13) 1.4113(19), N(2)-C(25) 1.406(2), C(1)-C(2) 1.446(2), C(1)-C(5) 1.477(2), C(2)-C(3) 1.475(2), C(3)-C(4) 1.413(2), C(4)-C(5) 1.414(2), C(5)-C(6) 1.376(2), C(3)-C(12) 1.377(2), C(4)-C(9) 1.396(2); C(1)-N(1)-C(13) 118.94(12), C(2)-N(2)-C(25) 117.14(12), N(1)-Na(1)-N(2) 76.04(5), C(1)-Na(1)-C(2) 27.57(4).

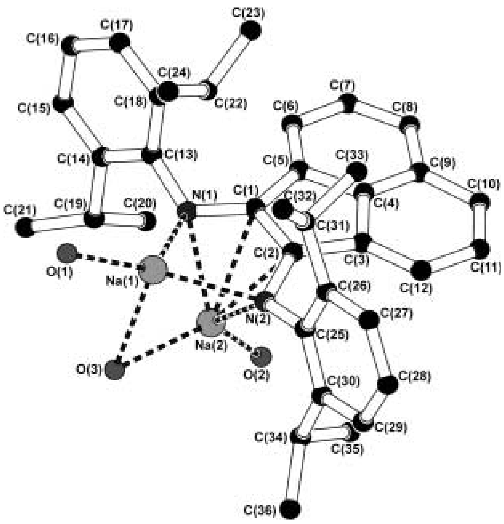

Figure 2. PLATON[8] presentation of the molecular structure of **2**. The carbon atoms of the solvent molecules are omitted. Selected bond lengths [Å] and angles [°]: Na(1)-N(1) 2.343(3), Na(1)-N(2) 2.398(3), Na(1)-O(1) 2.311(3), Na(2)-O(2) 2.289(3), Na(1)-O(3) 2.588(3), Na(2)-O(3) 2.456(3), Na(1)-C(1) 3.053(3), Na(1)-C(2) 3.077(3), Na(2)-N(1) 2.418(3), Na(2)-N(2) 2.465(3), Na(2)-C(1) 2.596(3), Na(2)-C(2) 2.614(3), N(1)-C(1) 1.387(4), N(2)-C(2) 1.386(4), N(1)-C(13) 1.400(4), N(2)-C(25) 1.407(4), C(1)-C(2) 1.402(4), Na(1)-Na(2) 2.9559(18); N(1)-Na(1)-N(2) 75.26(9), C(1)-Na(1)-C(2) 26.45(8), N(1)-Na(2)-N(2) 72.71(9), C(1)-Na(2)-C(2) 31.22(9).

diimine dianion may be explained by different types of bonding of the metal atoms to the −:N:−C=C−:N:− system. The short Na(1)−N(1) (2.343(3) Å) and Na(1)−N(2) (2.398(3) Å) distances may be attributed to σ sodium-to-nitrogen bonding while the longer bonds N(2)−N(1) (2.418(3) Å) and Na(1)−N(2) (2.465(3) Å) may reflect π bonding between Na (2) and enediamido moiety. Each sodium atom in **2** is coordinated by a terminal Et_2O molecule; a third Et_2O molecule bridges the two sodium atoms.

The coordination mode of the metal atoms to the ligand changes significantly on going from **2** to **3** (Figure 3). In the crystal, two $[Na]^+[\{Na(Et_2O)\}^+]_2[(2,6\text{-}i\text{Pr}_2\text{PhNC})_2(C_{12}H_6)]^{-3}$ moieties aggregate to form a centrosymmetric dimer of two coplanar acenaphthylene π systems in a head-to-tail arrangement. Four sodium atoms are placed between the two acenaphtylene planes. A similar structure with four lithium cations between the two layers of the dimeric [corannulene]$^{4-}$ superstructure was deduced from ^{7}Li NMR spectroscopy.[10] Two lithium cations placed between two aromatic systems were recently established by X-ray crystallography for the complex with acenaphthylene dianion, $[Li(Et_2O)_2]_2[@Li]_2[C_{12}H_8]_2$.[11] In **3**, the sodium atom Na(1), which is in a similar position to the Na(1) atoms in molecules **1** and **2**, is coordinated to only one nitrogen atom, N(2). The bonding of Na(2) with the ligand in **3** is similar to that of Na(2) in **2**. An electron pair of N(1), analogous to

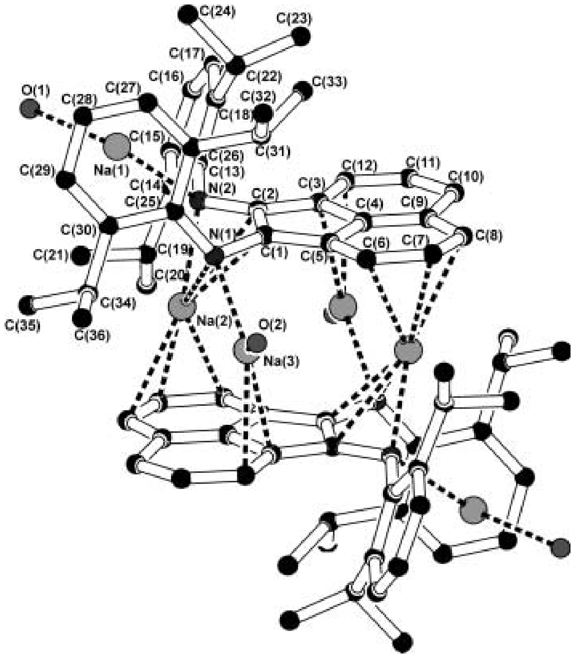

Figure 3. PLATON[8] presentation of the molecular structure of **3**. The carbon atoms of the solvent molecules are omitted. Selected bond lengths [Å] and angles [°]: Na(1)-O(1) 2.329(3), Na(1)-N(2) 2.367(3), Na(1)-C(13) 2.859(4), Na(1)-Na(2) 3.7071(18), Na(2)-N(1) 2.411(3), Na(2)-N(2) 2.402(3), Na(2)-C(1) 2.616(3), Na(2)-C(2) 2.617(3), Na(2)-C(4) 2.963(3), Na(2)-C(5) 2.897(3), Na(2)-C(6) 2.732(3), Na(2)-C(7) 2.656(3), Na(2)-C(8) 2.731(3), Na(2)-C(9) 2.927(3), Na(3)-O(2) 2.347(3), Na(3)-N(1) 2.361(3), Na(3)-C(1) 3.099(3), Na(3)-C(3) 2.714(3), Na(3)-C(4) 3.081(3), Na(3)-C(11) 3.086(4), Na(3)-C(12) 2.688(3), N(1)-C(1) 1.438(4), N(2)-C(2) 1.397(4), C(1)-C(2) 1.424(4), Na(3)-Na(2)′ 4.061(2), Na(2)-Na(3) 3.4814(19); Na(1)-Na(2)-Na(3) 107.65(4), Na(2)-Na(3)-Na(2′) 82.49(4).

that of N(1) bonded to Na(1) in complex **2** , forms a bond with a third sodium atom Na(3). This atom has two short contacts to two carbon atoms of the naphthalene system of its symmetry equivalent subunit. Furthermore, Na(2) also has short contacts with carbon atoms of one benzene ring of the symmetry equivalent naphthalene subunit. This indicates that the negative charge in $\{(2,6\text{-}i\mathrm{Pr}_2\mathrm{PhNC})_2(\mathrm{C}_{12}\mathrm{H}_6)\}^{-3}$ is delocalised over the whole diimine–naphthalene π system. As in **2**, Na(1) is coordinated in η^6 fashion by the phenyl ring attached to N (1). These Na(1)–C(phenyl) bond distances fall in a narrower (2.788(3)-2.905(2) Å, av 2.846 Å) range compared to those in **1**.

The structural motif of complex **4** (Figure 4) is very similar to that of complex **3**. The additional sodium cations Na(7) and Na(8) are situated over each naphthalene system due to the additional negative charge on the naphthalene part of the ligand. It is interesting to note that the coordination sphere of Na(7) and Na(8) is completed by two thf ligands as well as two *i*Pr groups indicating a kind of agostic interaction between H atoms of the *i*Pr groups and sodium atoms Na(7) and Na(8) with distances as small as 2.0545 Å (Na(8)···H(21C)).

In conclusion, we have established that recently commonly used ligand, dpp-bian, may be easily reduced in diethyl ether by sodium metal to mono-, di-, tri- and tetranions. For the first time four anionic forms of a single ligand have been isolated on a preparative scale and unambiguously characterized by single crystal X-ray structure analysis. The structures indicate that the first two electrons are placed at the diimine subsystem and the other two electrons at the naphthalene part. It would be interesting to investigate whether the electronic isomers of the ligand dianion may exist with both negative charges localized either on the diimine, or on the naphthalene moieties. As seen from the crystal data of **1**–**4**, the four reduced forms of the ligand display a variety of the coordination modes. We plan to carry out exchange reactions of the sodium derivatives **3** and **4** with the halides of tri- and tetravalent metals. This may result in the discovery of new complexes, which may serve as reducing agents in organic substrate transformations.

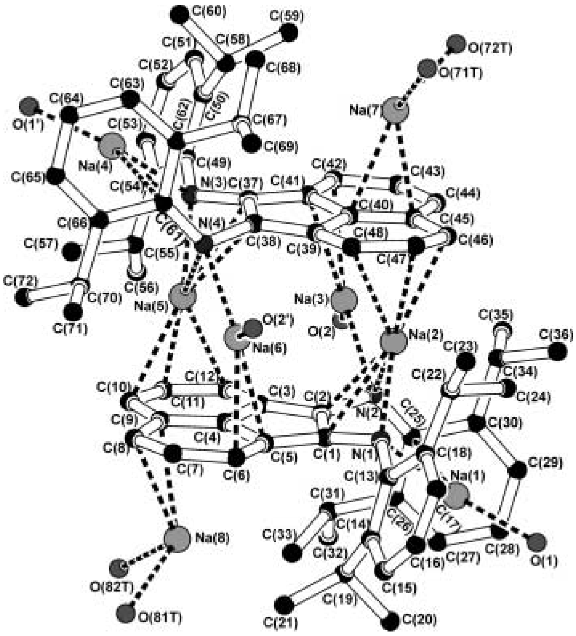

Figure 4. PLATON[8] presentation of the molecular structure of **4**. The carbon atoms of the solvent molecules are omitted. Selected bond lengths [Å] and angles [°]: Na(1)-O(1) 2.248(3), Na(1)-N(1) 2.381(3), Na(2)-N(1) 2.329(4), Na(2)-N(2) 2.398(3), Na(2)-C(1) 2.598(4), Na(2)-C(2) 2.589(3), Na(2)-C(45) 2.927(6), Na(2)-C(46) 2.610(6), Na(2)-C(47) 2.548(5), Na(2)-C(48) 2.733(5), Na(3)-C(40) 2.833(5), Na(3)-C(41) 2.692(5), Na(3)-C(42) 2.684(6), Na(3)-C(43) 2.826(6), Na(8)-O(81T) 2.326(4), Na(8)-O(82T) 2.334(3), Na(8)-C(4) 2.812(4), Na(8)-C(5) 2.923(4), Na(8)-C(6) 2.922(4), Na(8)-C(7) 2.758(4), Na(8)-C(8) 2.584(4), Na(8)-C(9) 2.665(4), Na(8)-C(21) 3.034(5), N(1)-C(1) 1.422(4), N(2)-C(2) 1.441(5), C(1)-C(2) 1.444(5), Na(1)-Na(2) 3.691(2), Na(3)-Na(5) 3.924(3), Na(2)-Na(3) 3.305(3); Na(1)-Na(2)-Na(2) 105.60(6), Na(2)-Na(3)-Na(5) 85.10(6), Na(4)-Na(5)-Na(6) 107.06(5), Na(2)-Na(6)-Na(5) 86.72(6).

Experimental Section

All manipulations were carried out under reduced pressure using Schlenk ampoules. Diethyl ether, THF and benzene were condensed into reaction ampoules from sodium/benzophenon prior to use. The ligand dpp-bian was prepared according to a literature procedure.[9] The ^{1}H NMR spectra were recorded on a Bruker DPX-200 NMR spectrometer. Magnetic moments for **1** and **3** were determined by the Faraday method.

1: A suspension of dpp-bian (0.5 g, 1.0 mmol) in $\mathrm{Et_2O}$ (30 mL) was added to an ampoule containing a single piece of sodium (1.15 g, 50 mmol). The mixture was stirred for 4 h, during which the precipitation of a brick-red solid occurred. The suspension of **4** was decanted from the metal and treated in situ with free ligand (1.45 g, 2.9 mmol); the solids dissolved instantly and the mixture turned red. Evaporation of the solvent in vacuo and crystallization from benzene (60 mL) afforded 1.1 g (55 %) of **1** as red crystals. m.p. > 246 °C; Elemental analysis calcd (%) for $\mathrm{C_{72}H_{80}N_4Na_2}$ (1047.4): C 82.56, H 7.70; found: C 82.34, H 7.93; $\mu_{\mathrm{eff}} = 1.95$ BM. Crystal data for **1**: $\mathrm{C_{72}H_{80}N_4Na_2}$, $M_r = 1047.4$, monoclinic, space group P(2)1/n, $a = 12.7883(7)$, $b = 13.1620(7)$, $c = 18.9586(10)$ Å; $\beta = 106.6330(10)°$, $V = 3057.6(3)$ Å^3, $Z = 4$, $T = 183(2)$ K, $F_{000} = 1124$, $\mu = 0.078$ mm^{-1}, $\theta = 1.91$–$23.29°$, reflection collected 20140, independent reflections 4399 [$R_{\mathrm{int}} = 0.0385$], $GOF = 1.005$, $R = 0.0425$, $wR^2 = 0.1033$, largest diff. peak and hole 0.256/-0.212 e Å^{-3}.

2: The dpp-bian ligand (0.5 g, 1.0 mmol) was added to a suspension of **4** (prepared from 0.5 g, 1.0 mmol of dpp-bian prepared in situ as described for **1**). The resulting green solution was concentrated in vacuo (15 mL), and left to stand at 20 °C to give **2** as large dark-red crystals (0.73 g, 48 %). M.p. > 246 °C; elemental anal (%) calcd for $\mathrm{C_{48}H_{70}N_2Na_2O_3}$ (769.04): C 74.96, H 9.17; found: C 75.02, H 9.30; ^{1}H NMR (200 MHz, $\mathrm{C_6D_6}$, 20 °C, TMS): $\delta = 7.32$–6.51 (12 H, aromatic), 3.85 (sept, 4 H, $CH(\mathrm{Me})_2$), 3.18 (q, 12 H, $\mathrm{CH_2}$), 1.41 (d, 12 H, $\mathrm{CH(C}H_3)_2$, $^3J(\mathrm{H,H}) = 8.0$ Hz), 1.33 (d, 12 H, $\mathrm{CH(C}H_3)_2$, $^3J = 8.0$ Hz), 1.02 ppm (t, 18 H, $\mathrm{CH_3}$). Crystal data for **2**: $\mathrm{C_{48}H_{70}N_2Na_2O_3}$, $M_r = 769.04$, monoclinic, space group P(2)1/n, $a = 12.3158(9)$, $b = 19.3819(14)$, $c = 18.8024(13)$ Å, $\beta = 92.9540(10)°$, $V = 4482.2(6)$ Å^3, $Z = 4$, $T = 100(2)$ K, $F_{000} = 1672$, $\mu = 0.086$ mm^{-1}, $\theta = 1.51$–$22.00°$, reflection collected 24405, independent reflections 5481 [$R_{\mathrm{int}} = 0.0246$], $GOF = 1.090$, $R = 0.0670$, $wR^2 = 0.1903$, largest diff. peak and hole 0.767/−0.330 e Å^{-3}.

3: The ligand dpp-bian (0.17 g, 0.34 mmol) was added to a suspension of **4** (from 0.5 g, 1.0 mmol of the ligand, 20 mL of $\mathrm{Et_2O}$, prepared as described above). The brick-red solid of **4** dissolved partially and the solution became darker. The mixture was centrifuged and the solution was decanted affording 0.11 g (21 %) of compound **3** after drying in vacuo at 20 °C within 2 min. m.p. > 246 °C; $\mu_{\mathrm{eff}} = 1.68$ BM. The extreme air-sensitive nature of compounds **3** and **4** prevented any meaningful analytical data being obtained. Crystals of

3 suitable for X-ray analysis were obtained within two weeks in a flask that was left undisturbed containing sodium metal, dpp-bian, and Et_2O. Crystal data for **3**: $C_{88}H_{120}N_4Na_6O_4{\cdot}C_4H_{10}O$, $M_r = 1510.01$, triclinic, space group P1, $a = 12.792(2)$, $b = 13.034(2)$, $c = 14.323(2)$ Å, $\alpha = 68.204(3)$, $\beta = 85.292(3)$, $\gamma = 79.442(3)°$, $V = 2179.6(6)$ Å^3, $Z = 1$, $T = 183(2)$ K, $F_{000} = 800$, $\mu = 0.094$ mm^{-1}, $\theta = 1.71$–23.35°, reflection collected 12975, independent reflections 6273 [$R_{int} = 0.0362$], GOF = 1.015, $R = 0.$ 0794, $wR^2 = 0.2182$, largest diff. peak and hole 0.786/−0.459 e Å^{-3}.

4: A suspension of **4** (prepared from 0.5 g, 1.0 mmol of dpp-bian prepared as described above) was decanted from the metal and centrifuged. Decantation of the solution left a brick-red solid which was dried at 20 °C in vacuum for 2 min. Yield 0.52 g (57 %). m.p. > 246 °C. As no acceptable elemental analysis on **4** could be obtained we proved the formation of **4** by the oxidation of the complex with iodine. A solution of iodine (0.51 g, 2.0 mmol) in Et_2O (40 mL) was added dropwise to a suspension of **4**, which was obtained from 0.5 g (1.0 mmol) of the ligand. After addition of 50 % of the I_2 solution the mixture turned green and after 75 % the solution became red. The addition of the remaining iodine caused almost complete discoloration of the mixture. Suitable crystals of compound **4** for X-ray analysis were obtained from THF. Crystal data for **4**: $C_{104}H_{144}N_4Na_8O_8{\cdot}C_4H_8O$, $M_r = 1834.25$, monoclinic, space group P(2)1/n, $a = 26.3483(14)$, $b = 16.4269(9)$, $c = 26.9621(14)$ Å, $\beta = 118.9560(10)°$, $V = 10210.9(9)$ Å^3, $Z = 4$, $T = 150(2)$ K, $F_{000} = 3920$, $\mu = 0.103$ mm^{-1}, $\theta = 0.89$–22.00°, reflection collected 59234, independent reflections 12526 [$R_{int} = 0.0554$], $GOF = 1.173$, $R = 0.0968$, $wR^2 = 0.2682$, largest diff. peak and hole 0.674/−0.634 e Å^{-3}. CCDC-205954 (**1**) CCDC-205955 (**2**) CCDC-205956 (**3**) and CCDC-205957 (**4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44–1223/336–033; E-mail: deposit@ccdc.cam.ac.uk].

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