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Alkali metal reduction of 1,3,2-diazaborol and 1,3,2-diazagermol derivatives based on 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene†

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The reduction of [(dpp-bian)BBr] (**1**, dpp-bian = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) with dilithium naphthalenide in Et_2O gives $[\{(\text{dpp-bian})BBr\}Li_2(Et_2O)_2]_2$ (**3**). The treatment of [(dpp-bian)BONa] (**5**) and [(dpp-bian)Ge:] (**7**) with sodium is accompanied by protonation of the acenaphthylene fragment and affords $[\{(\text{H-dpp-bian})BONa(dme)_2\}Na(dme)_3]$ (**6**) and $[(\text{H-dpp-bian})Ge:][Na(dme)_3]$ (**8**), respectively. Compounds **3**, **6** and **8** have been characterized by ^1H NMR and IR spectroscopy. The molecular structures of **3**, [(dpp-bian)BOK] (**4**) and **8** have been established by single crystal X-ray analysis.

Introduction

Hydrocarbons with extended π-electron conjugated systems have attracted considerable attention owing to their unique structures and electronic properties. For example, sp^2-hybridized carbon networks, such as graphite[1,2] and nanotubes,[3,4] serve as key anode components in rechargeable Li-ion batteries. Meanwhile, the electronic saturation of such systems allows fine-tuning their redox potentials and changing their chemical and physical properties. For instance, tetra-reduced nanotubes are more soluble than common nanotubes.[5] However, to date only a few examples of poly-anionic organic systems, in which a high negative charge is delocalized over many atoms, are known. Mainly these are alkali metal salts of the tri-, tetra- or hexa-anions of carbocyclic or heterocyclic hydrocarbons. Among the carbocyclic poly-anions are derivatives of corannulene (Chart 1a), octalene, cycloheptaacenaphthylene, pyracyclene, anthracene, rubrene, fullerene C_{60} and nanotubes.[6–10] Representatives of heterocyclic poly-anions are the tetra-anions of carboranes (Chart 1b), silacyclopentadiene, phthalocyanines and octasilyltrimethylenecyclopentene (Chart 1c).[11–13]

Metal complexes based on redox-active ligands have attracted increasing attention in the last few years. Transition metal complexes with redox-active ligands are promising catalysts for organic synthesis.[14–16] Also, main group metal derivatives reveal specific reactivities due to the presence of the redox-active ligand.[17–21] Among the poly-anionic metal complexes there are only a few compounds containing tri- or tetra-anion of the redox-active ligand. Thus, in 2002 Gambarotta and Budzelaar reported the lithium salt of the tri-anion of the redox-active diiminopyridine (Chart 1d).[22]

In 2015 Bart and co-workers obtained the uranium complex $[(^{Mes}PDI^{Me})UI_3(thf)]$ containing the radical-anion of the pyridinediimine ligand. A subsequent reduction of the prepared complex with potassium graphite led to structurally characterized derivatives with the di-, tri- and tetra-anionic $^{Mes}PDI^{Me}$ ligands.[23] The abovementioned supercharged anions were characterized spectroscopically, and only a few of them were isolated in an individual state and characterized structurally.

In 2003 the formation of four anionic ligands derived from 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-bian) has been documented through isolation and structural characterization of their sodium salts, $[(\text{dpp-bian})^{n-}Na^+_nL_m]$ (n = 1, 2,

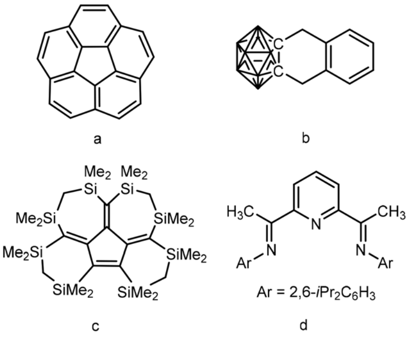

Chart 1 Organic molecules for which poly-anions are known.

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† Electronic supplementary information (ESI) available: Crystallographic data and ^1H, ^{13}C, ^7Li and ^{11}B NMR spectra. See DOI: 10.1039/C9DT04652F

3 or 4; L = diethyl ether or tetrahydrofuran).[24] Stabilization of (dpp-bian)$^{n-}$ with di- and trivalent cations, *e.g.* group II metals and the lanthanides have been demonstrated just recently.[25,26] In this paper we report on the alkali metal reduction of 1,3,2-diazaborol and 1,3,2-diazagermol derivatives derived from 1,2-bis[(2,6-diisopropylphenyl)imino]-acenaphthene.

Results and discussion

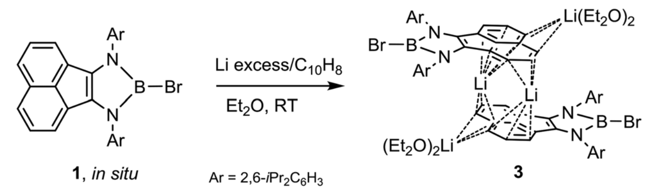
Synthesis and spectroscopic characterization of alkali metal salts of 1,3,2-diazaborol and 1,3,2-diazagermol derivatives derived from dpp-bian

1,3,2-diazaborols [(dpp-bian)BX] (X = Br, **1**; and Cl, **2**) have been prepared by the exchange reaction of [(dpp-bian)Na_2] with BX_3 (1 : 1 molar ratio).[27] The treatment of a suspension of **1** in Et_2O with an excess of lithium in the presence of one molar equivalent of naphthalene resulted in a brown solution. The complex [{(dpp-bian)BBr}$Li_2(Et_2O)_2$]$_2$ (**3**, 54%) has been isolated from the concentrated solution as green crystals (Scheme 1).

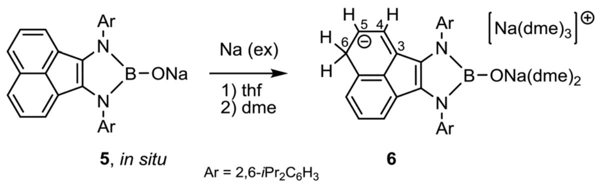
Complex **3** has been characterized by ^1H NMR and IR spectroscopy. The reduction of **1** with lithium results in a formal negative charge of −2 for the acenaphthylene fragment of the dpp-bian ligands in **3**. As a consequence the signals of the acenaphthylene protons in the ^1H NMR spectrum of **3** (Fig. 1) are high-field shifted (δ 4.51, pst, 2H; 3.93, d, 2H; and 2.88, d, 2H) ppm, while those signals of the starting complex **1** are positioned in the range of 7.55–6.50 ppm.[27] The ^{11}B and ^7Li NMR spectra of compound **3** exhibit the ^{11}B and ^7Li signals at δ = 16.5 and 1.0 ppm respectively. The crystal structure of compound **3** has been determined by single crystal X-ray analysis.

The reaction of 1,3,2-diazaborol **2** with KOH afforded the potassium salt of 1,3,2-diazaboronic acid [(dpp-bian)BOK][27] (**4**). The reduction of compound **4** with potassium in thf resulted in a highly soluble product that could not be isolated. Like compound **4**, complex [(dpp-bian)BONa] (**5**) can be prepared by reacting **2** with an excess of NaOH in thf. The reduction of complex **5** with an excess of sodium caused a change in color from blue to red-brown. The replacement of thf with 1,2-dimethoxyethane (dme) and a concentration of the dme solution afforded red-brown crystals of [{(H-dpp-bian)BONa(dme)$_2$}Na(dme)$_3$] (**6**, 86%) (Scheme 2). As for compound **3** the ^1H NMR spectrum of complex **6** (Fig. 2) proves the reduction of the acenaphthylene part of the dpp-bian ligand in complex **5**. However, from the spectrum of **6** it turns out that, in contrast to **3**, the negative charge in **6** is not delocalized over six-membered rings but is located at the C-5 atom (Scheme 2).

The ^1H NMR spectrum of **6** also indicates hydrogenation of the atom C-6. The protons of the non-hydrogenated ring give rise to three signals at δ 5.76 (t, 1H), 5.59 (d, 1H), and 5.27 (d, 1H) ppm. The protons H_2C-6 appear as a slightly broadened signal at δ 3.75 (br s, 2H) ppm, while the HC-4 proton results in a signal at δ 5.45 (d, 1H) ppm. Due to the negative charge the HC-5 signal of the naphthalene fragment is high-field



Scheme 1 Synthesis of compound **3**.



Scheme 2 Synthesis of compound **6**.

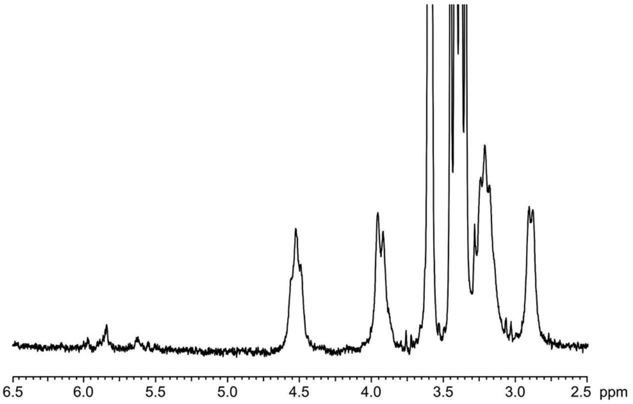


Fig. 1 A section of the ^1H NMR spectrum of **3** (200 MHz, 300 K, thf-d_8). The signals ranging from δ 3.70 to 3.35 ppm correspond to thf and diethyl ether. For a full spectrum see the ESI.†

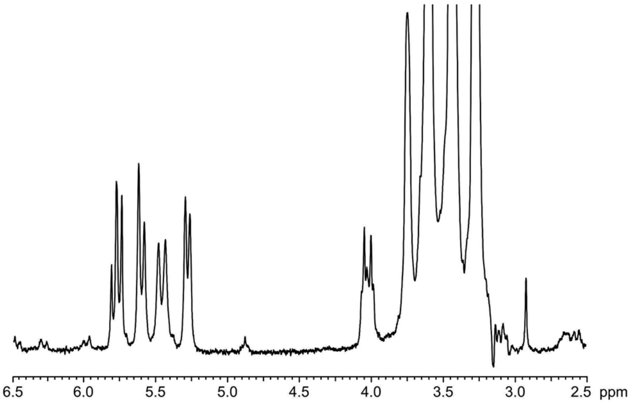


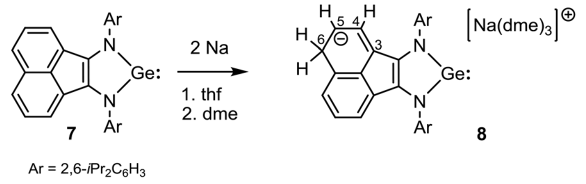
Fig. 2 A section of the ^1H NMR spectrum of **6** (200 MHz, 298 K, thf-d_8). The signals ranging from δ 3.70 to 3.20 ppm correspond to thf and dme. For a full spectrum see the ESI.†

shifted, δ 4.03 (dt, 1H) in comparison with all the other signals of the naphthalene part. The signals of the methyl protons of isopropyl substituents lie in the range of 1.28–0.90 ppm. Thus, the reduction of complex **5** with sodium in thf proceeds with a transfer of two electrons and one proton to dpp-bian. One can suggest that the initially formed dianionic 1,3,2-diazaborol $[(\text{dpp-bian})\text{BO}]^{2-}$ cleaves the C–H bond in the solvent to form complex **6** as the final product.

Upon the reduction of germylene [(dpp-bian)Ge:] (**7**) (*in situ* from GeCl_4 and $[(\text{dpp-bian})\text{Na}_4]$)[28] with two equivalents of sodium in thf, the color of the reaction mixture changed from red-brown to green, and finally to brown. The replacement of thf with dme and concentration of the dme solution afforded brown crystals of complex $[\text{H}(\text{dpp-bian})\text{Ge:}][\text{Na}(\text{dme})_3]$ (**8**, 47%) (Scheme 3).

In contrast to the starting complex **7** product **8** does not possess a mirror plane which bisects the N–Ge–N angle. Therefore, the methine protons of the isopropyl groups become non-equivalent in pairs. In the ^{1}H NMR spectrum of **8** (Fig. 3) these protons afford two septets at δ 3.58 and 3.53 ppm. Four overlapping doublets of methyl protons range from δ 1.42 to 1.21 ppm. The protons of the acenaphthylene moiety in complex **8** produce the NMR signal set (δ = 6.29 (d, 1H), 6.19 (pst, 1H), 6.01 (d, 1H), 5.97 (d, 1H), 4.57 (dt, 1H), and 4.07 (br s, 2H) ppm), which is very similar to that in the spectrum of compound **6**. This leads to the conclusion that the ligand structures of **6** and **8** are identical.

Thus, protonation of dpp-bian under alkali metal reduction of its metal complexes has been observed for [(dpp-bian)BONa] (**5**) and [(dpp-bian)Ge:] (**7**), but not for [(dpp-bian)BBr] (**1**), $[(\text{dpp-bian})\text{Ca}(\text{thf})_4]$,[25] and $[(\text{dpp-bian})\text{LaI}(\text{thf})_2]_2$.[26] This regularity is not well understood. One can suggest that in the intermediates formed in the course of the reduction of **5** and **7** the negative charge is not well delocalized over two six-membered rings but concentrated at the C-6 atom thus making it nucleophilic enough to split the C–H bond of ethereal solvents.



Scheme 3 Synthesis of compound **8**.

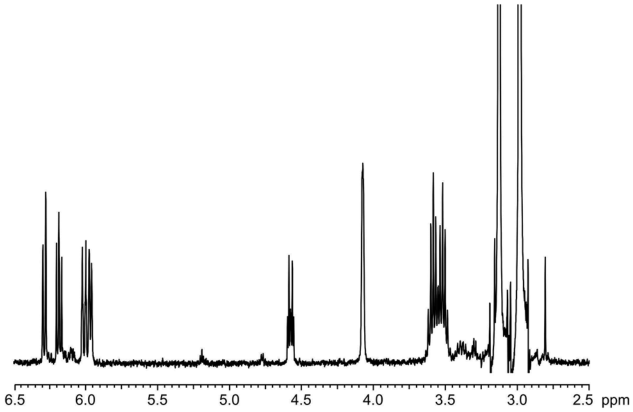


Fig. 3 A section of the ^{1}H NMR spectrum of **8** (400 MHz, 296 K, C_6D_6). The signals at δ 3.12 and 2.98 ppm correspond to dme. For the full spectrum see the ESI.†

The molecular structures of compounds 3, 4 and 8

The molecular structures of compounds **3**, **4** and **8** have been determined by single crystal X-ray analysis and are shown in Fig. 4, 5 and 6, respectively. X-ray quality crystals of **3**, **4** and **8** have been obtained from diethyl ether, toluene and dme, respectively. For the crystal data and structure refinement details see the ESI.†

The unit cell of compound **3** consists of two crystallographically independent molecules whose geometrical parameters are very close. Each of them represents the centrosymmetric

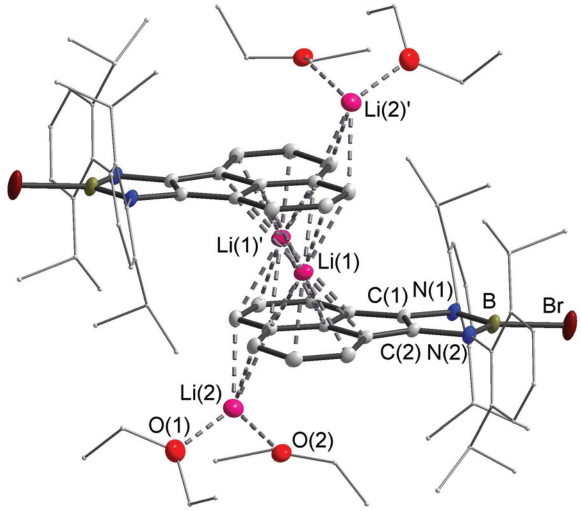


Fig. 4 The molecular structure of **3**. Thermal ellipsoids are of 30% probability. Hydrogen atoms are omitted.

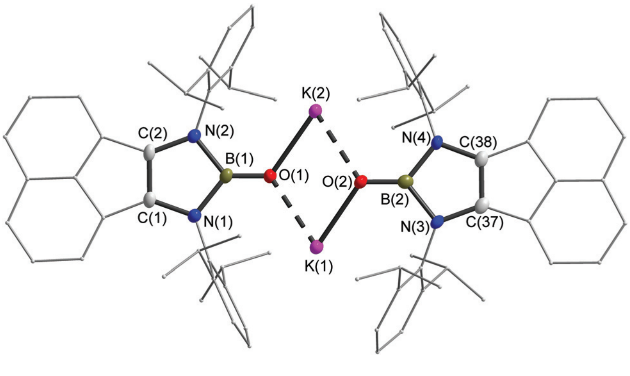


Fig. 5 The molecular structure of **4**. Thermal ellipsoids are of 30% probability. Hydrogen atoms are omitted.

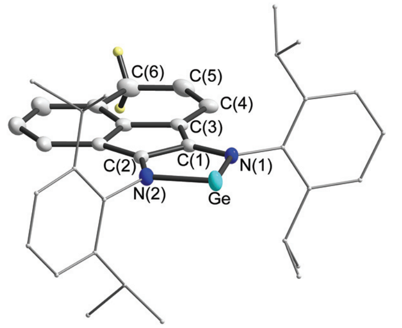


Fig. 6 The molecular structure of anion **8**. Thermal ellipsoids are of 30% probability. Hydrogen atoms are omitted except H(6) and H(6′).

dimer. The inversion center is located in the middle between two dpp-bian ligands that are disposed in parallel planes and connected by two lithium atoms, resulting in a sandwich-like structure. The structural motif of **3** is similar to those in the lithium salt of the acenaphthylene di-anion $[Li(Et_2O)_2]_2\{\mu^2:\eta^3[Li(\eta^3:\eta^3\text{-}C_{12}H_8)]_2\}$[29] and the sodium salt of the dpp-bian tetra-anion $[\{(\text{dpp-bian})Na_4(\text{thf})_4\}_2]$.[24] Further, the structure of **3** can be compared with the sandwich-like structure of the lithium salt of the corannulene tetra-anion $C_{20}H_{10}{}^{4-}$.[7,8] The coordination of lithium cations to six-membered rings in **3** confirms the two-electron reduction of the naphthalene part in complex **3**. The sandwiched lithium atoms do not coordinate solvent molecules, while both the outer sphere lithium cations coordinate two diethyl ether molecules. The distance between the planes of the ligands in **3** is 3.88 Å. The distances from the internal lithium atoms to the normal planes defined by the naphthalene fragments are 1.913 and 1.963 Å. The N(1)–C(1), N(2)–C(2) and C(1)–C(2) bond lengths in compound **3** are close to those in boron complexes of the dpp-bian di-anion, as for instance in [(dpp-bian)BBr][30] (**1**) (N(1)–C(1) 1.395(2), N(2)–C(2) 1.399(2) and C(1)–C(2) 1.364(2) Å); [(dpp-bian)BCl][27] (**2**) (N(1)–C(1) 1.385(3), N(2)–C(2) 1.395(3) and C(1)–C(2) 1.362(4) Å); [(dpp-bian)BH][27] (N(1)–C(1) 1.398(2), N(2)–C(2) 1.391(2) and C(1)–C(2) 1.357(3) Å); and germylene **8** (N(1)–C(1) 1.390(5), N(2)–C(2) 1.392(5) and C(1)–C(2) 1.417(6) Å).

Complex **4** crystallizes in the tetragonal space group $I\bar{4}$ with eight dimeric molecules in the unit cell. The dimers are built from two chemically equivalent fragments (dpp-bian) BOK that are connected through bridging potassium atoms. The latter interacts with the π systems of the Ar substituents of the neighboring fragment. The central K_2O_2 core is nearly flat with the K–O distances lying in the range of 2.533(4)–2.619(4) Å. Interestingly, the B–N bond lengths in complexes **2** and **4** are notably different (**2**: av. 1.435 Å; and **4**: av. 1.490 Å).

Complex **8** crystallizes in the orthorhombic space group $P2_12_12_1$. The chemical entity is composed of the germylene anion (Fig. 6) protonated at the C(6) atom and the solvent separated cation $[Na(\text{dme})_3]$. The metallacycle GeN_2C_2 is flat and well coplanar with two six-membered rings. The planes of the aryl substituents at the nitrogen atoms of the diimine fragment are normal to this plane. Dearomatization of one of the six-membered rings does not lead to the alteration of the N–Ge and N–C bonds within the diazagermole cycle (Ge–N(1) 1.880(3), Ge–N(2) 1.889(3), C(1)–C(2) 1.417(6), N(1)–C(1) 1.390(5), and N(2)–C(2) 1.392(5) Å). Moreover these bond lengths almost coincide with the bond lengths in the starting complex **7** (Ge–N(1) 1.896(3), Ge–N(2) 1.885(3), C(1)–C(2) 1.381(5), N(1)–C(1) 1.374(4), and N(2)–C(2) 1.370(4) Å).[28]

Conclusions

We have shown that compound **1**, in which 1,3,2-diazaborole is fused with the naphthalene system, undergoes two-electron reduction with lithium to afford di-anionic 1,3,2-diazaborole derivative **3**. The reduction of complex **5** with sodium in thf proceeds with a transfer of two electrons and one proton to the di-anionic dpp-bian ligand and results in diamagnetic mono-anionic sodium 1,3,2-diazaborolate **6**. The difference in the structures of **3** and **6** could also be related to the stronger Lewis acidity of Li^+ *vs.* Na^+. Dearomatization of one of the six-membered rings also takes place when germylene **7** is reduced with sodium to afford product **8**. Compounds **6** and **8** represent a new class of metal complexes derived from non-innocent 1,2-bis(arylimino)acenaphthenes. The study of their reactivity towards organic substrates is in progress and will be published elsewhere.

Experimental

General remarks

Compounds **3**, **6** and **8** as well as some of their precursors are sensitive towards oxygen and moisture. Therefore, all manipulations were carried out under vacuum using Schlenk ampoules. Toluene, diethyl ether, 1,2-dimethoxyethane and thf as well as thf-d_8 and C_6D_6 were dried over sodium/benzophenone and condensed under vacuum in a reaction vessel or an NMR tube just prior to use. IR spectra were recorded on an FSM-1201 spectrometer in Nujol and ^1H NMR spectra on Bruker DPX-200 (200 MHz) and Bruker Avance III (400 MHz) NMR spectrometers. The melting points were measured in sealed capillaries. The dpp-bian was prepared by the condensation of acenaphthenequinone with 2,6-diisopropylaniline in acetonitrile under reflux.[31] The yields of the products were calculated from the amount of the dpp-bian used (0.5 g, 1.0 mmol) in the syntheses. Boron halides (1 M solutions in hexane) and germanium chloride(IV) were purchased from Aldrich and used as received.

$[\{(\text{dpp-bian})BBr\}Li_2(Et_2O)_2]_2$ (3)

To a solution of $[(\text{dpp-bian})Na_2]$ [*in situ* from dpp-bian (0.50 g, 1.0 mmol) and sodium (0.10 g, 4.34 mmol)] in toluene (30 mL), 1 M solution of BBr_3 in hexane (1 mL, 1.0 mmol) was added. The color of the solution changed from green to red indicating the formation of [(dpp-bian)BBr]. After the separation of precipitated sodium bromide the solvent was removed under vacuum and diethyl ether (30 mL) was added. The resulting suspension was added to the mixture of lithium metal (0.05 g, 7.14 mmol) and naphthalene (1.28 g, 1.0 mmol). After vigorous stirring for 4 h the initial precipitate was dissolved to form a brown solution, which was decanted from the metal. After concentration of the ether solution (15 mL) the green crystals of compound **3** (0.44 g, 54%) were isolated. M.p. > 240 °C (decomp.). Anal. calcd for $C_{96.75}H_{127}B_2Br_2Li_4N_4O_4$ (1619.22): C, 74.58; H, 7.47. Found: C, 74.27; H, 7.24. ^1H NMR spectrum (200 MHz, thf-d_8, 300 K): δ = 7.27–6.95 (m, 6H, C_6*H_3*^{i}Pr_2), 4.51 (pst, 2H, *J* = 7.7 Hz, CH naphthalene part), 3.93 (d, 2H, *J* = 7.9 Hz, CH naphthalene part), 3.40 (q, 24H, *J* = 7.0 Hz, Et_2O), 3.30–3.10 (m, 4H, C*H*$(CH_3)_2$), 2.88 (d, 2H, *J* = 6.2 Hz, CH naphthalene part), 1.25–1.05 (m, 48H, Et_2O + CH(C*H_3*$)_2$). ^{11}B NMR spectrum (64.21 MHz, thf-d_8, 300 K): δ = 16.5 (s, 1B). ^7Li NMR spectrum (77.78 MHz, thf-d_8, 300 K): δ = 1.0 (s, 2Li). IR (Nujol) ν/cm^{-1}: 1587 s, 1540 s, 1253 m, 1175 m, 1153 w, 1104 w, 1057 m, 1043 w, 1001 w, 977 w, 935 m, 807 s, 764 m, 750 m, 695 w, 678 w, 654 m, 615 w, 579 w, 560 w, 527 w.

[{(H-dpp-bian)BONa(dme)$_2$}Na(dme)$_3$] (6)

To a solution of **2**[27] (1.0 mmol) in thf (30 mL) NaOH (0.20 g, 5 mmol) was added. The reaction mixture was sonicated at 90 °C for 24 h. The color of the solution changed from red to blue. Precipitated NaCl was separated by filtration. The resulting solution of [(dpp-bian)BONa] was poured to an excess of sodium metal (1 g, 4.3 mmol). After stirring for 8 h at ambient temperature the color of the solution changed from blue to red-brown. After evaporation of the solvent under vacuum 1,2-dimethoxyethane (20 mL) was added. Concentration of the resulting solution (10 mL) led to the formation of **7** as red-brown crystals (0.85 g, 83%). M.p. 136 °C (decomp.). Anal. calcd for $C_{56}H_{91}BNa_2N_2O_{11}$ (1023.98): C, 65.63; H, 8.97. Found: C, 65.23; H, 8.44. ^1H NMR (200 MHz, thf-d_8, 298 K): δ = 7.09 (d, 6H, *J* = 3.9 Hz, C_6*H_3*^{i}Pr_2), 5.76 (t, 1H, *J* = 7.3 Hz, CH naphthalene part), 5.59 (d, 1H, *J* = 7.7 Hz, CH naphthalene part), 5.45 (d, 1H, *J* = 9.5 Hz, CH naphthalene part), 5.27 (d, 1H, *J* = 6.3 Hz, CH naphthalene part), 4.03 (dt, 1H, *J* = 9.4, *J* = 3.4 Hz, CH naphthalene part), 3.75 (br s, 2H, CH_2 naphthalene part), 3.68–3.54 (m, 12H, C*H*$(CH_3)_2$ + THF), 3.43 (s, 20H, DME), 3.28 (s, 30H, DME), 1.74 (br s, THF), 1.28–0.90 (m, 24H, CH(C*H_3*$)_2$). ^{13}C NMR (100 MHz, thf-d_8, 295 K): δ = 147.7, 147.1, 126.8, 126.3, 126.2, 124.6, 122.1, 111.4, 109.1, 105.7, 104.9, 104.5, 103.9, 87.3, 82.0, 67.2, 41.5, 38.2, 31.7, 30.1, 28.1, 27.7, 23.08, 22.8, 22.6, 22.5. IR (Nujol) ν/cm^{-1}: 2725 w, 1642 w, 1606 w, 1584 m, 1537 m, 1305 w, 1250 m, 1192 m, 1115 m, 1087 m, 1059 w, 1032 w, 974 m, 935 w, 894 w, 858 m, 819 w, 802 s, 747 s, 736 s, 703 w, 670 m, 615 w, 562 w, 504 w, 474 w.

[(H-dpp-bian)Ge:][Na(dme)$_3$] (8)

To a solution of [(dpp-bian)Na_4] [*in situ* from dpp-bian (1.0 g, 2.0 mmol) and excess of sodium metal (0.2 g, 8.7 mmol) with stirring for 24 h] in thf (30 mL) germanium tetrachloride (0.43 g, 2.0 mmol) was added by condensation under vacuum. The reaction mixture was stirred at ambient temperature for 2 h. After the separation of sodium chloride from the red-brown solution of [(dpp-bian)Ge:] sodium metal (0.09 g, 4.0 mmol) was added. After stirring for 6 h at room temperature the color of the solution changed from red-brown to green and finally to brown. The solvent was removed under vacuum and the residue was dissolved in dme (15 mL). The solution formed was filtered off. Concentration of the solution under vacuum caused the precipitation of brown crystals of complex **8** (0.81 g, 47%). M.p. 168 °C. Anal. calcd for $C_{48}H_{71}GeN_2NaO_6$ (867.64): C, 66.45; H, 8.24. Found: C, 65.87; H, 8.03. ^1H NMR (400 MHz, C_6D_6, 296 K): δ = 7.38 (m, 6H, C_6*H_3*$(Pr^i)_2$), 6.29 (d, 1H, *J* = 7.5 Hz, CH naphthalene part), 6.19 (pst, 1H, *J* = 6.8 Hz, CH naphthalene part), 6.01 (d, 1H, *J* = 9.5 Hz, CH naphthalene part), 5.97 (d, 1H, *J* = 6.5 Hz, CH naphthalene part), 4.57 (dt, 1H, *J* = 9.5, *J* = 3.8 Hz, CH naphthalene part), 4.07 (br s, 2H, *J* = 1.3 Hz, CH_2 naphthalene part), 3.58 (sept, 2H, *J* = 7.0 Hz, C*H*$(CH_3)_2$), 3.53 (sept, 2H, *J* = 7.0 Hz, C*H*$(CH_3)_2$), 3.12 (s, 12H, DME), 2.98 (s, 18H, DME), 1.42 (pst, 18H, *J* = 7.0 Hz, CH(C*H_3*$)_2$), 1.21 (d, 6H, *J* = 7.0 Hz, CH(C*H_3*$)_2$). ^{13}C NMR (100 MHz, C_6D_6, 296 K): δ = 146.2, 145.9, 145.5, 141.9, 141.5, 140.8, 133.3, 126.0, 125.9, 124.9, 124.8, 122.9, 122.8, 111.8, 31.7, 28.1, 27.9, 27.2, 26.3, 24.0, 23.5. IR (Nujol) ν/cm^{-1}: 1932 w, 1860 w, 1811 w, 1670 w, 1645 m, 1612 w, 1587 m, 1562 s, 1540 s, 1517 w, 1405 w, 1363 w, 1349 w, 1325 m, 1298 m, 1253 m, 1192 m, 1167 m, 1112 s, 1084 s, 1029 m, 1010 w, 982 w, 957 w, 938 m, 902 m, 855 s, 803 s, 792 m, 775 w, 761 s, 695 m, 673 w, 665 m, 651 w, 618 w, 596 w, 582 w, 568 w, 543 w, 532 m, 516 w, 493 w, 460 m.

Conflicts of interest

There are no conflicts to declare.

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