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Reduction of Disulfides with Magnesium(II) and Gallium(II) Complexes of a Redox-Active Diimine Ligand

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The reactions of (dpp-bian)Mg(thf)$_3$ (**1**) {dpp-bian = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene} with 0.5 molar equivalents of RS–SR (R = Bz, *s*Bu, C(S)NMe$_2$) occur with a cleavage of the S–S bond to afford monosulfide complexes (dpp-bian)Mg(SBz)(dme) (**2**), (dpp-bian)Mg[S(*s*Bu)](dme) (**3**), and (dpp-bian)Mg[SC(S)NMe$_2$](thf) (**4**). Compounds **2**, **3**, and **4** are paramagnetic due to the presence of dpp-bian radical-anions that are formed in the course of one-electron transfer from the dpp-bian dianion in **1** to the sulfur-containing substrate. Reduction of BzS–SBz with gallane (dpp-bian)Ga–Ga(dpp-bian) (**5**) gives a mononuclear Ga^{III} complex with the dpp-bian radical-anion, (dpp-bian)Ga(SBz)$_2$ (**6**). The reaction of **5** with RS–SR (R = C(S)NMe$_2$) proceeds with a cleavage of the S–S and Ga–Ga bonds and affords (dpp-bian)Ga[SC(S)NMe$_2$] (**7**), in which the dpp-bian ligand retains its dianionic state. Complexes **2**, **3**, **4**, and **6** have been characterized by ESR and IR spectroscopy, and complex **7** has been studied by ^{1}H MNR spectroscopy. The molecular structures of **2**–**4**, **6**, and **7** have been determined by X-ray crystallography.

Introduction

Acenaphthene-1,2-diimine (bian) ligands proved to be versatile in coordination chemistry. For complex formation with transition metals, bian ligands have been first used in the groups of Elsevier, Coates, and Brookhart in the beginning of the 1990s. To date, a number of transition-metal complexes of neutral bian ligands have been reported.[1–7] Many of them serve well as catalysts in organic reactions, especially in the polymerization of α-olefins.[7] In 2003, we disclosed the ability of 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-bian) to act as an "electron sponge". Reduction of dpp-bian with sodium metal resulted in the formation of its mono-, di-, tri-, and tetraanions.[8] Further, redox-activity of dpp-bian has been documented by preparation of a series of group II[9] and XIII[10] metal complexes with radical-anionic and dianionic dpp-bian ligands. The electronic and spatial features of dpp-bian allowed the isolation of molecular species with direct Zn–Zn,[11] Ga–Ga,[12] Zn–Ga,[12] and Li–Ga[13] bonds. Very recently, the development in the field of the coordination chemistry of bian ligands with s- and p-block elements has been reviewed.[14] Complexes of lanthanides with neutral, radical-anionic, and dianionic bian ligands have been reported as well.[15,16] The first redox isomerism phenomenon involving a lanthanide ion in solution[17] has also been observed between the dpp-bian complexes (dpp-bian)$^{1-}$-Yb^{2+}Br and (dpp-bian)$^{2-}$Yb^{3+}Br.

One of our interests concerns the use of metal complexes that combine redox-active ligands with redox-inactive metals, like Mg or Al, in organic synthesis. In such systems the metal is supposed to provide a coordination site for the organic substrate, which may be reduced or oxidized by the ligand bound to the metal.

In this respect, the reactivity of magnesium(II) complexes with mono- and dianions of dpp-bian is studied most intensively. Thus, complex (dpp-bian)$^{2-}$Mg^{2+}(thf)$_3$ (**1**) readily reacts with oxidants (Ox), e.g. CuCl,[18] I$_2$,[18] Ph(Br)CHCH(Br)Ph,[18] TEMPO,[19] or diphenylketone,[9c] to yield complexes with the dpp-bian radical-anion, (dpp-bian)$^{\cdot-}$-MgOx(thf)$_n$ (Ox = Cl$^-$, Br$^-$, I$^-$, TEMPO$^-$, and Ph$_2$C$^{\cdot}$–O$^-$). The opposite process – reduction of the dpp-bian radical-anion to the dianion, which is accompanied by elimination of the organic radical and formation of **1**, is observed for the complexes (dpp-bian)$^{\cdot-}$MgR(Et$_2$O) (R = *i*Pr,[20a] *t*Bu, Me-All[20b]) in thf. The reactions of **1** with alkyl halides proceed in a different manner. Reduction of EtBr with **1** generates Br$^-$ and the ethyl radical. The bromide anion binds to magnesium, whereas the ethyl radical forms a C–C bond with the imino carbon atom of the dpp-bian ligand.[9e]

One of the modern synthetic approaches to the formation of carbon–heteroatom bonds is the addition reactions of the N–H, S–H, and S–S groups to double and triple C–C bonds of hydrocarbons.[21] Transition-metal-catalyzed bisthiolation of terminal alkynes proceeds by oxidative ad-

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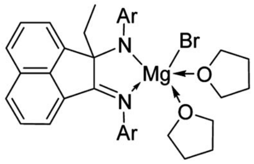


dition of disulfides to the zero-valent transition-metal complex, insertion of the alkyne to the M–S bond, and finally reductive elimination of the product.[22]

In this work, we have investigated oxidative addition reactions of disulfides to magnesium(II) and gallium(II) complexes of the redox-active dpp-bian ligand.

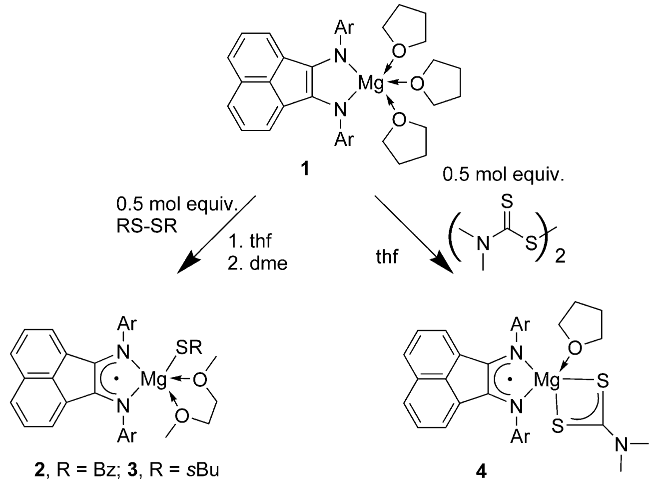
Results and Discussion

Reactions of (dpp-bian)Mg(thf)$_3$ (1) with RS–SR [R = Bz, *s*Bu, C(S)NMe$_2$]

One may expect that the reactions of equimolar amounts of complex **1** and disulfides RS–SR can proceed in two different directions: (i) as two-electron oxidative addition of disulfide resulting in bis(sulfido)magnesium coordinated to neutral dpp-bian, (dpp-bian)Mg(SR)$_2$; or (ii) similar to the above-mentioned reaction of complex **1** with EtBr, affording the (amido-imino)magnesium complex.

Addition of one molar equivalent of disulfides RS–SR [R = Bz, *s*Bu, or C(S)NMe$_2$] to complex **1** in thf caused in each case an immediate color change from deep green to orange. However, a workup of the reaction mixtures in all three cases afforded only free dpp-bian, thus indicating a transfer of two electrons from **1** to the sulfur substrates. Mg-containing products of these reactions, presumably Mg(SR)$_2$, have not been isolated. Although, as intended, the two-electron reduction of disulfides has been achieved by using an equimolar amount of complex **1** as reducing agent; unfortunately, the reactions proceeded with release of the redox-active ligand from magnesium. In contrast, reactions of **1** with 0.5 molar equivalents of RS–SR [R = Bz, *s*Bu, or C(S)NMe$_2$] in thf proceed with one-electron oxidation of the dpp-bian ligand in **1** to the radical-anion and result in the formation of compounds (dpp-bian)Mg(SBz)(dme) (**2**), (dpp-bian)Mg[S(*s*Bu)](dme) (**3**), and (dpp-bian)Mg[SC(S)NMe$_2$](thf) (**4**) (Scheme 1).

In the course of these reactions, the color of the solutions turns from deep green to cherry-red. In the case of dibenzyl disulfide and tetramethylthiuram disulfide, the reactions with **1** were complete within a few seconds at ambient temperature, whereas in the case of di-*sec*-butyl disulfide, heating at 80 °C for 30 min was required. Compounds **2** and **3** were isolated by crystallization from 1,2-dimethoxyethane in 69 and 72% yield, respectively, and compound **4** was crystallized from a toluene/hexane mixture (8:2) in 76% yield. Complexes **2**, **3**, and **4** have been characterized by elemental analysis, IR and ESR spectroscopy. Their molecular structures have been determined by single-crystal X-ray analysis. The deviation of elemental analysis results for **2**, **3**, and **4** from the calculated values can be explained by the oxygen and moisture sensitivity of the products.



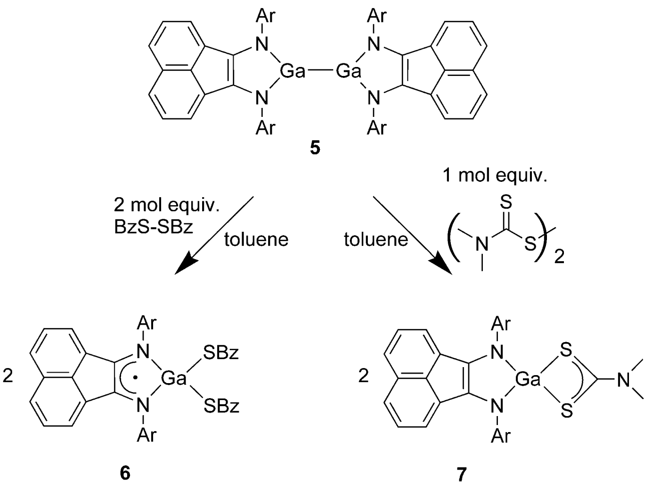
Scheme 1. Synthesis of compounds **2**, **3**, and **4**.

Complexes **2**–**4** are paramagnetic in the solid state as well as in solution. The room-temperature ESR spectra of **2**–**4** in toluene consist of quintets [**2**: g = 2.0031, $A(^{14}N)$ = 0.46 mT; **3**: g = 2.0030, $A(^{14}N)$ = 0.46 mT; **4**: g = 2.0037, $A(^{14}N)$ = 0.47 mT], thus indicating the presence of the dpp-bian radical-anion (S = 1/2) in these compounds. In the temperature range 330–130 K in solution, the signals do not change their shape.

IR spectra of **2**–**4** are also similar and prove that the complexes **2**–**4** consist of anionic dpp-bian ligands. The strongest absorptions in the IR spectrum of the free dpp-bian[23] ligand are the two C–N stretching vibrations at 1671 cm^{-1} and the split band at 1652 and 1642 cm^{-1}. In **2** and **3**, the C–N stretching vibrations are shifted to lower wavenumbers (**2**: 1538; **3**: 1532 cm^{-1}) relative to those of the free dpp-bian ligand and are indicative of sesquialteral C–N bonds in the dpp-bian radical-anion. The second band assigned to ν(C–N) in **2** and **3** and both C–N stretching bands in **4** overlap with nujol stretching vibrations. In the IR spectrum of **1**,[9a] which consists of the dpp-bian dianion, the most intense absorption (C–N single-bond stretching) is positioned at 1300 cm^{-1}. Very strong absorption at 704 cm^{-1} in the IR spectrum of **2** is attributed to the S–CH$_2$Ph stretching vibrations.

Reactions of (dpp-bian)Ga–Ga(dpp-bian) (5) with RS–SR [R = Bz, C(S)NMe$_2$]

Complex **5** consists of a direct gallium–gallium bond with metal atoms having formal oxidation state +2. Therefore, every (dpp-bian)$^{2-}$Ga^{2+} unit in **5** may give up two electrons without breaking the ligand-to-metal coordination resulting in the (dpp-bian)$^{\cdot-}$Ga^{3+} species, in which both the ligand and the metal are oxidized. The reaction of **5** with two molar equivalents of BzS–SBz proceeds in this way and produces monomeric and solvent-free compound (dpp-bian)Ga(SBz)$_2$ (**6**) (Scheme 2), which has been isolated as deep red crystals from toluene in 64% yield. A first indication for the oxidation of the dpp-bian dianion to the radical-anion in the course of this reaction is a color change of the reaction mixture from deep blue to red, which takes place within 2 h at 80 °C.



Scheme 2. Synthesis of compounds **6** and **7**.

The reaction of **5** with one molar equivalent of tetramethylthiuram disulfide proceeds with oxidation of the metal atoms in **5**, but the dpp-bian ligand preserves the dianionic state (Scheme 2). Accordingly, no essential color change in this reaction has been observed. Compound (dpp-bian)Ga[SC(S)NMe$_2$] (**7**) has been isolated as deep blue crystals in 57% yield by recrystallization from toluene.

As expected, compound **7** is diamagnetic, because it consists of the dpp-bian dianion ($S = 0$). Complex **7** reveals expected signals for the organic fragments in the ^{1}H NMR spectrum. Four methine protons of the isopropyl substituents are magnetically equivalent and give rise to a septet at $\delta = 3.66$ ppm. As in free dpp-bian and in all its metal complexes, the methyl groups of the isopropyl substituents are not equivalent, because of the restricted rotation around the Me$_2$(H)C–C$_6$H$_3$ bond. This non-equivalence of the CH$_3$ groups results in two doublet signals at 1.21 and 1.00 ppm. Two CH$_3$ groups of the sulfide ligand appear as a singlet signal at $\delta = 3.30$ ppm.

In toluene at ambient temperature, compound **6** reveals a well-resolved ESR signal (Figure 1a), thus indicating the presence of the dpp-bian radical-anion ($S = 1/2$) in this compound. The hyperfine structure of the signal is caused by the coupling of the unpaired electron to the gallium nucleus [$A(^{69}\text{Ga}) = 1.561$ mT and $A(^{71}\text{Ga}) = 1.983$ mT], to two nitrogen atoms [$A(^{14}\text{N}) = 0.495$ mT], and to four protons [$A(^{1}\text{H}) = 0.098$ mT]. The ^{1}H coupling constant is relatively small and may be attributed to coupling to methylene protons of two benzyl sulfide ligands rather than to interaction of the unpaired electron with the aromatic protons of the dpp-bian ligand.

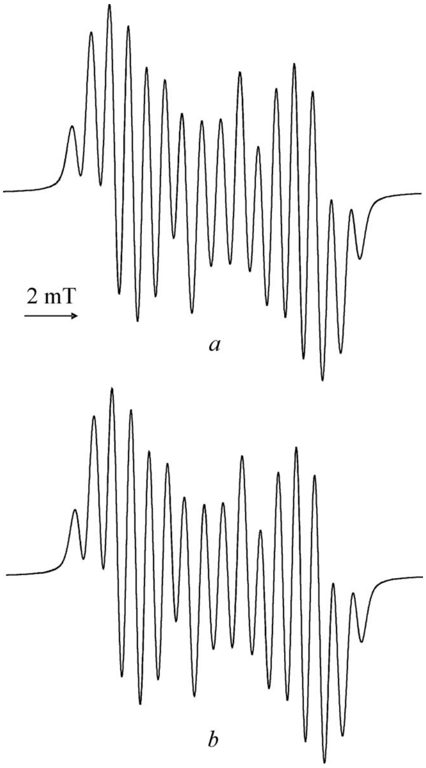


Figure 1. The ESR spectrum of complex **6** (toluene, 293 K): (a) experimental spectrum; (b) simulated spectrum [$g = 2.0026$, $A(^{69}\text{Ga}) = 1.561$ mT, $A(^{71}\text{Ga}) = 1.983$ mT, $A(^{14}\text{N}) = 0.495$ (2 N) mT, $A(^{1}\text{H}) = 0.098$ (4 H) mT].

Molecular Structures of Compounds 2–4, 6, and 7

The molecular structures of **2**, **3**, **4**, **6**, and **7** were determined by single-crystal X-ray diffraction and are depicted in Figures 2, 3, 4, 5, and 6, correspondingly. Selected bond lengths and bond angles are presented in Table 1, and the details of data collection and structure refinement are listed in Table 2. The unit cell of compound **4** consists of two crystallographically independent molecules, whose geometrical parameters are very much alike. Therefore, the bond lengths and angles for only one compound are discussed.

The search for the fragments Mg–S–C and Ga–S–C in the database of the CCDC resulted in 29 and 65 hits for Mg and Ga compounds, respectively. Many of the reported compounds consist of chelating ligand systems with an incorporated thiolate function. On the other hand, the Mg and Ga thiolates often form dimers through bridging thiolate groups. Hence, for the comparison and discussion of the molecular structures of **2**–**4**, **6**, and **7**, which are monomeric in the solid state, only monomeric compounds with terminal thiolate ligands have been selected from those reported. All the magnesium complexes of this sort consist of arylthiolate ligands and only one compound, (Ph$_3$CS)$_2$-Mg(15-crown-5),[24] can be considered as an (alkylthiolato)-magnesium complex. Note that the alkylthiolate is present in [CpMg(μ-S*t*Bu)(thf)]$_2$,[25] which is a dimer in the solid state.

Complexes **2**, **3**, and **4** represent five-coordinate species. The coordination environment of the metal atoms in **2** and

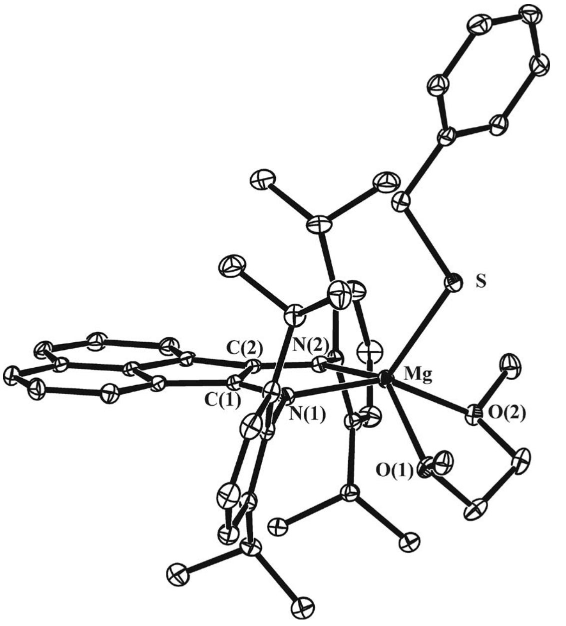


Figure 2. Molecular structure of **2**. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at 30% probability.

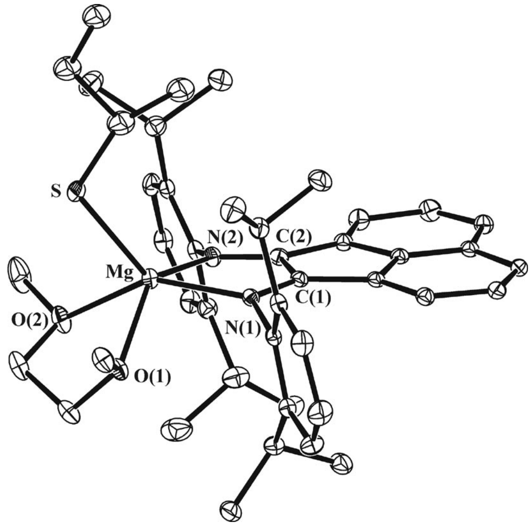


Figure 3. Molecular structure of **3**. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at 30% probability.

3 is distorted trigonal-bipyramidal, axial positions being occupied by atoms N(1) and O(2), those bonds to the metal are longer relative to the corresponding N(2) and O(1) bonds (Table 2). When differences in coordination number are considered, the magnesium–sulfur bond lengths in **2** [2.4170(7) Å] and **3** [2.3721(6) Å] compare well with those in (2,4,6-tBu$_3$C$_6$H$_2$S)$_2$Mg(Et$_2$O)$_2$ [av. 2.387(2) Å],[26] [2,6-(2,4,6-iPr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$S]$_2$Mg (2.328(1) Å],[27] (2,4,6-tBu$_3$C$_6$H$_2$S)Mg[N(SiMe$_3$)$_2$](thf)$_2$ [2.431(2) Å],[28] (PhS)$_2$-Mg(Py)$_4$ [2.6247(5) Å],[29] and (Ph$_3$CS)$_2$Mg(15-crown-5) [2.6607(8) Å].[24]

In dithiocarbamate derivative **4** (Figure 4), the coordination environment of magnesium is square-pyramidal, because there is no pronounced difference in the Mg–N as well as in the Mg–S bond lengths (Table 2). Thus, the basal plane is formed with two nitrogen and two sulfur atoms. The deviation of the magnesium atom from the this plane towards atom O(1) is 0.456 Å. The elongated Mg–S bonds [2.5208(8) and 2.5099(8) Å] in **4** relative to those in **2** and **3** indicate some delocalization of the negative charge between two sulfur atoms. The N(3)–C(37) bonds in dithiocarbamate ligand in free tetramethylthiuram disulfide [1.329(3) Å] [30] and in **4** [1.328(3) Å] are of the same length.

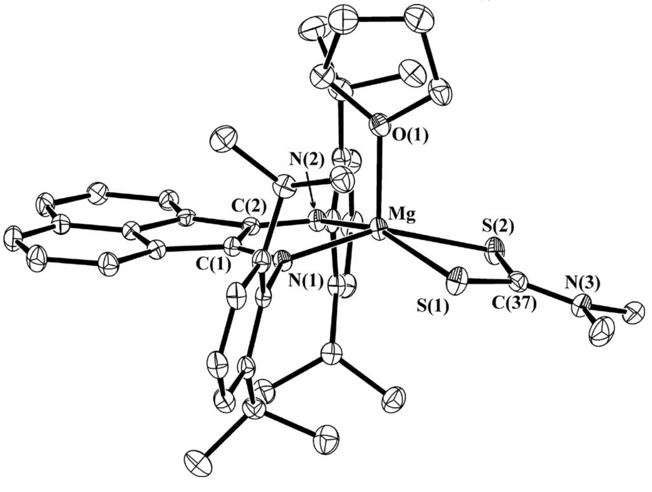


Figure 4. Molecular structure of **4**. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at 30% probability.

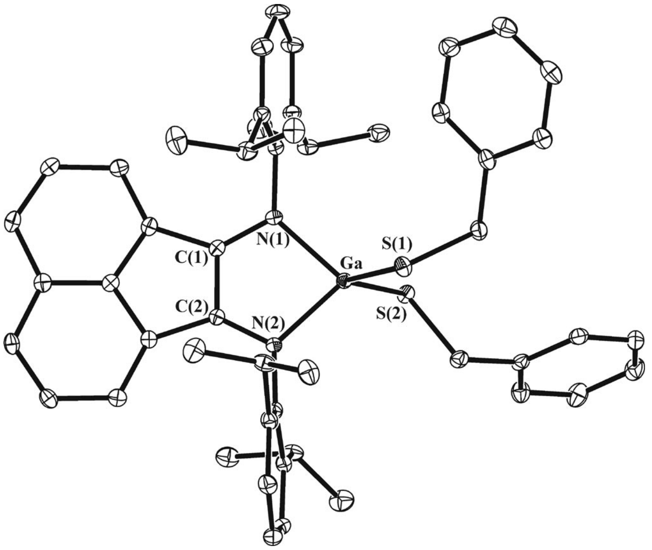


Figure 5. Molecular structure of **6**. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at 30% probability.

Gallium compounds **6** (Figure 5) and **7** (Figure 6) correspond to solvent-free four-coordinate species. Only eight monomeric gallium complexes that have terminal thiolate groups have been reported to date. Among them are four-coordinate alkylthiolates [(RS)$_4$Ga][R′$_4$N] (R = Et, R′ = nPr; R = Ph; R′ = Et),[31] (tBuS)$_3$Ga[N(H)Me$_2$],[32] (tBuS)$_2$-GaH(NMe$_3$)[33] and (tBuS)GaH$_2$(L) (L = quinuclidine),[33] as well as three-coordinate arylthiolates (2,4,6-tBu$_3$C$_6$H$_2$S)$_3$-Ga[34] and (2,4,6-tBu$_3$C$_6$H$_2$S)$_2$GaR (R = Me, nBu).[35] Also,

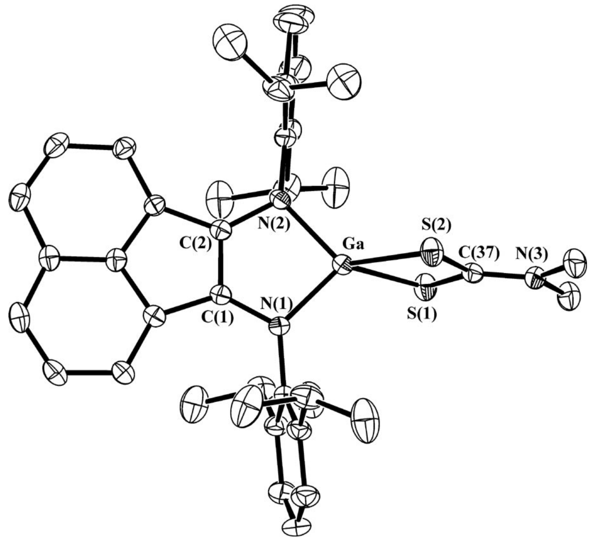


Figure 6. Molecular structure of **7**. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at 20% probability.

Table 1. Selected bond lengths [Å] and angles [°] for **2**, **3**, **4**, **6**, and **7**.

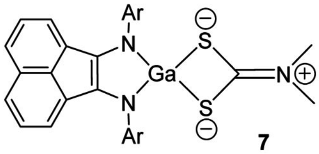
	2[a]	**3**[a]	**4**[a]	**6**[b]	**7**[b]
M–N(1)	2.1297(15)	2.1342(10)	2.1126(16)	1.9650(13)	1.8718(18)
M–N(2)	2.1079(16)	2.1294(10)	2.1187(16)	1.9732(13)	1.8826(17)
M–S(1)	2.4170(7)	2.3721(6)	2.5208(8)	2.2316(5)	2.3101(8)
M–S(2)			2.5099(8)	2.2397(4)	2.3132(7)
M–O(1)	2.1064(14)	2.1345(9)	2.0705(15)		
M–O(2)	2.1875(13)	2.1870(9)			
N(1)–C(1)	1.330(2)	1.3296(13)	1.328(2)	1.326(2)	1.385(3)
N(2)–C(2)	1.331(2)	1.3345(14)	1.327(2)	1.330(2)	1.397(3)
C(1)–C(2)	1.439(2)	1.4406(15)	1.451(2)	1.440(2)	1.373(3)
N(3)–C(37)			1.328(3)		1.308(3)
N(1)–M–N(2)	80.61(6)	80.83(4)	81.49(6)	85.75(5)	91.41(7)
O(1)–M–O(2)	75.40(5)	75.12(3)			
S(1)–M–S(2)			72.25(2)	112.780(17)	78.55(3)
N(1)–M–S(1)	114.95(4)	121.13(3)	98.03(5)	116.50(4)	120.96(6)
N(2)–M–S(1)	121.38(5)	119.94(3)	159.81(6)	111.84(4)	125.81(6)
N(1)–M–S(2)			153.27(6)	111.37(4)	121.49(6)
N(2)–M–S(2)			99.15(5)	116.11(4)	122.57(6)

[a] M = Mg. [b] M = Ga.

five gallium dithiocarbamates, $(Me_2NCS_2)_2GaCl$,[36] $(iPr_2NCS_2)_2GaCl$,[36] $(EtNCS_2)_2Ga(tBu)$,[37] $(EtNCS_2)_2Ga(OiPr)$,[37] and $(C_4H_4NCS_2)_3Ga$,[36] have been prepared and characterized by X-ray crystallography. Related tris(*O*-ethylxanthato-S,S′)gallium, $(EtOCS_2)_3Ga$, has also been reported.[38]

In compound **6**, two Ga–S distances are very close [2.2316(5) and 2.2397(4) Å] but somewhat shorter than those in the alkylthiolates $[(EtS)_4Ga]^-$ (av. 2.257 Å),[31] $(tBuS)_3Ga[N(H)Me_2]$ (av. 2.251 Å),[32] $(tBuS)_2GaH(NMe_3)$ (av. 2.257 Å),[33] and $(tBuS)GaH_2(L)$ (2.268 Å).[33] The S–Ga–S angle in **6** [112.78(1)°] is close to that in the bisthiolate derivative $(tBuS)_2GaH(NMe_3)$ [112.33(1)°],[33] indicating that the steric bulk of the dpp-bian ligand does not affect the bonding of the benzylthiolate groups to gallium in **6**. The angle between the planes N(1)–Ga–N(2) and S(1)–Ga–S(2) is 86.2°.

The bonding mode of the dithiocarbamate ligand to gallium in **7** is different from those in $(Me_2NCS_2)_2GaCl$,[36] $(iPr_2NCS_2)_2GaCl$,[36] $(EtNCS_2)_2Ga(tBu)$,[37] and $(EtNCS_2)_2Ga(OiPr)$.[37] In these four compounds, the two Ga–S distances within each dithiocarbamate ligand vary notably, as, for instance, in compound $(Me_2NCS_2)_2GaCl$ [(2.340(1)/2.440(1) and 2.348(1)/2.431(1) Å].[36] In compound $(EtNCS_2)_2Ga(tBu)$,[37] this difference is even larger (0.27 Å). In contrast, the Ga–S distances in **7** [2.3101(8) and 2.3132(7) Å] are almost the same. Note, that the N(3)–C(37) bond in **7** [1.308(3) Å] is shortened relative to those in tetramethylthiuram disulfide [1.329(3) Å][30] and in $(Me_2NCS_2)_2GaCl$ (av. 1.322 Å).[36] Thus, the dithiocarbamate ligand in complex **7** can be considered to some extent as a zwitterion.



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In the main-group metal complexes of the dpp-bian ligand, the metal–nitrogen distances decrease on going from the dpp-bian radical-anion to its dianion. For example, in monomeric four-coordinate aluminum complexes with the dpp-bian radical-anion, (dpp-bian)$AlMe_2$,[10a] and with the dpp-bian dianion, (dpp-bian)$AlMe(Et_2O)$,[10b] the Al–N distances are 1.949(2)/1.950(2) and 1.847(3)/1.848(3) Å, correspondingly. In **2**, **3**, and **4**, the Mg–N bond lengths (**2**: av. 2.119 Å; **3**: 2.132 Å; **4**: 2.116 Å) are similar but longer than the Mg–N bonds in the starting complex **1** (2.075 Å),[9a] indicating the presence of the dpp-bian radical-anion in **2**, **3**, and **4**.

In the four-coordinate gallium compounds **6** and **7**, the Ga–N distances are significantly different (**6**: av. 1.969 Å; **7**: 1.877 Å) and indicate the presence of the dpp-bian radical-anion in **6** and of the dpp-bian dianion in **7**.

The statement regarding the reduction state of the dpp-bian ligands in **2**–**4**, **6**, and **7** is further proved by an inspection of the bond lengths within the diimine moiety, since the dpp-bian ligand as well as other α-diimines in each reduction state (neutral, radical-anionic, and dianionic) have their own structural fingerprints. Population of the LUMO on going from neutral dpp-bian to its radical-anion and further to the dianion must result in shortening of the C(1)–C(2) bond and elongation of the C(1)–N(1) and C(2)–N(2) bonds. The distances C(1)–N(1) and C(2)–N(2) in **2**, **3**, **4**, and **6** (**2**: av. 1.331 Å; **3**: 1.332 Å; **4**: 1.328 Å; **6**: av. 1.328 Å) are longer than C–N bond lengths in free dpp-bian [both 1.282(4) Å][39] and in its Mo^0 complex (dpp-bian)$Mo(CO)_4$ (av. 1.296 Å)[40] but shorter than those in the dpp-bian dianion in **1** (av. 1.389 Å).[9a] Further, the C(1)–N(1) and C(2)–N(2) bonds in **2**, **3**, **4**, and **6** are very similar to those in the magnesium radical-anionic complexes (dpp-bian)MgI(dme) (av. 1.331 Å)[18] and $[(dpp\text{-}bian)MgCl(thf)]_2$ (av. 1.332 Å).[18] The C(1)–C(2) bond lenghts in **2**, **3**, **4**, and **6** [**2**: 1.439(2) Å; **3**: 1.441(1) Å; **4**: 1.451(2) Å; **6**: 1.440(2) Å] are approximately 0.05 Å longer than those in **1** [1.389(7) Å]

Table 2. Crystal data and structure refinement details for **2**, **3**, **4**, **6**, and **7**.

	2	**3**	**4**	**6**	**7**
Empirical formula	$C_{47}H_{57}MgN_2O_2S\cdot C_4H_{10}O_2$	$C_{44}H_{59}MgN_2O_2S$	$C_{43}H_{54}MgN_3OS_2$	$C_{50}H_{54}GaN_2S_2$	$C_{39}H_{46}GaN_3S_2\cdot C_7H_8$
M_r [g mol^{-1}]	828.44	704.30	717.32	816.79	782.76
Temperature [K]	100(2)	100(2)	100(2)	100(2)	298(2)
Crystal system	triclinic	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_12_12_1$	$P2_1/c$
a [Å]	11.5749(8)	13.1644(5)	11.2632(4)	12.0147(6)	16.437(4)
b [Å]	13.6720(10)	18.4079(7)	36.1982(13)	17.2459(9)	13.030(3)
c [Å]	16.2633(11)	17.5466(7)	20.4119(7)	21.0211(11)	20.334(4)
α [°]	74.3650(10)	90	90	90	90
β [°]	80.1750(10)	105.7560(10)	104.8040(10)	90	99.832(5)
γ [°]	71.9110(10)	90	90	90	90
Volume [Å^3]	2345.3(3)	4092.3(3)	8045.8(5)	4355.7(4)	4291.2(16)
Z	2	4	8	4	4
$\rho_{\text{calcd.}}$ [g cm^{-3}]	1.173	1.143	1.184	1.246	1.212
μ [mm^{-1}]	0.127	0.131	0.184	0.763	0.772
$F(000)$	894	1524	3080	1724	1656
Crystal size [mm]	0.57 × 0.40 × 0.18	0.30 × 0.25 × 0.10	0.63 × 0.53 × 0.34	0.35 × 0.17 × 0.09	0.60 × 0.25 × 0.09
$\theta_{\text{min}}/\theta_{\text{max}}$ [°]	2.16 to 26.00	2.05 to 26.00	1.98 to 25.00	1.94 to 27.50	2.03 to 26.00
Index ranges	$-14 \leq h \leq 14$	$-16 \leq h \leq 16$	$-11 \leq h \leq 13$	$-15 \leq h \leq 15$	$-20 \leq h \leq 20$
	$-16 \leq k \leq 16$	$-22 \leq k \leq 22$	$-39 \leq k \leq 43$	$-22 \leq k \leq 22$	$-16 \leq k \leq 16$
	$-19 \leq l \leq 20$	$-21 \leq l \leq 20$	$-24 \leq l \leq 24$	$-27 \leq l \leq 27$	$-25 \leq l \leq 25$
Reflections collected	19657	24433	44233	42010	36057
Independent reflections	9146	8040	14130	10003	8367
R_{int}	0.0242	0.0187	0.0360	0.0470	0.0578
Max./min. transmission	0.9774/0.9309	0.9870/0.9617	0.9401/0.8930	0.9345/0.7760	0.9337/0.6544
Data/restraints/parameters	9146/12/558	8040/4/455	14130/0/921	10003/2/644	8367/18/468
GOF on F^2	1.034	1.051	1.024	1.002	1.025
Final R indices	R_1 = 0.0459	R_1 = 0.0451	R_1 = 0.0525	R_1 = 0.0325	R_1 = 0.0558
[$I > 2\sigma(I)$]	wR_2 = 0.1139	wR_2 = 0.1189	wR_2 = 0.1231	wR_2 = 0.0714	wR_2 = 0.1294
R indices (all data)	R_1 = 0.0660	R_1 = 0.0535	R_1 = 0.0767	R_1 = 0.0430	R_1 = 0.0985
	wR_2 = 0.1214	wR_2 = 0.1240	wR_2 = 0.1318	wR_2 = 0.0747	wR_2 = 0.1426
Largest diff. peak/hole [e Å^{-3}]	0.961 and –0.548	0.712 and –0.666	0.606 and –0.349	0.554 and –0.283	0.426 and –0.258

but very close to those in (dpp-bian)MgI(dme) and [(dpp-bian)MgCl(thf)]$_2$ [1.438(5) and 1.445(4) Å, correspondingly].[18] In gallium complex **7**, the C–N and C–N bond alteration within the metallacycle is different from that in **6**. As a result of the dianionic character of the dpp-bian ligand in **7**, the C(1)–N(1) and C(2)–N(2) bonds [1.385(3) and 1.397(3) Å] are elongated, while the C(1)–C(2) bond [1.373(3) Å] is shortened relative to those in **6**.

Conclusions

The magnesium complex of redox-active acenaphthene-1,2-diimine, (dpp-bian)Mg(thf)$_3$ (**1**), may transfer one to two ligand electrons to disulfides. One-electron transfer reactions afford magnesium sulfide complexes with the radical-anionic dpp-bian ligand, whereas two electron-transfer processes lead to the release of dpp-bian. In contrast, each metal unit of digallane (dpp-bian)Ga–Ga(dpp-bian) (**5**) may transfer two electrons to substrates, e.g. disulfides without breaking the coordination of the dpp-bian ligand to the metal. In the course of such reactions, both the ligand and the metal are oxidized. Since digallane **5** consists of two redox-active centers – the ligand and the metal – one can expect that in deficiency of an oxidant the electron may be transferred to the substrate either from the metal center or from the ligand. The oxidation of only the gallium center is observed when complex **5** reacts with one molar equivalent of tetramethylthiuram disulfide. Our preliminary results show that the reactions of **5** with chlorine-containing oxidizing reagents occur with an oxidation of the dpp-bian ligand to the radical-anion and with preservation of the gallium–gallium bond in **5**.

Experimental Section

General Remarks: Starting compounds **1** and **5** as well as the newly prepared complexes **2**, **3**, **4**, **6**, and **7** are sensitive to oxygen and moisture. Therefore, all manipulations on the synthesis, isolation, and characterization of **2**, **3**, **4**, **6**, and **7** have been carried out in vacuo or under an atmosphere of nitrogen gas by using Schlenk techniques. The solvents were dried with sodium benzophenone. Melting points were determined in sealed capillary tubes. IR spectra were recorded with an INFRASPEK FSM-1201, and the ^{1}H NMR spectrum were obtained with a Bruker DPX-200 NMR spectrometer. The ESR spectra were recorded by using a Bruker EMX instrument equipped with an ER 041X microwave bridge. Complex **1** was prepared according to the literature procedure[9a] from 0.5 g (1.0 mmol) of dpp-bian and an excess of magnesium metal and used in situ for the preparation of complexes **2**, **3**, and **4**. The yields of **2**, **3**, and **4** were calculated on the basis of the dpp-bian used for synthesis of **1**. Compound **5** was prepared in a different manner from that originally reported:[12] a mixture of gallium metal (3.5 g, 50 mmol) and dpp-bian (0.5 g, 1 mmol) in toluene (20 mL) was refluxed for 12 h. In the course of the reaction, the color of the mixture turned from orange to deep blue. A deep-blue toluene solution of **5** was decanted from an excess of gallium, and the deep blue crystalline precipitate left behind together with the gallium metal was extracted with toluene (3 × 20 mL). A toluene suspension of **5** obtained as described was used in the further syntheses. The yields of **6** and **7** were calculated on the basis of the dpp-bian used for the preparation of **5**.

(dpp-bian)Mg(SBz)(dme) (2): To a solution of complex **1** {prepared in situ from dpp-bian [0.5 g (1.0 mmol)] and excess magnesium metal} in thf (30 mL) was added with stirring dibenzyl disulfide [0.12 g (0.5 mmol)]. The resultant mixture turned cherry-red instantly. In ca. 10 min, the solvent was evaporated under vacuum. The foamy residue was dissolved in dme (20 mL). Concentration under vacuum of the resulting dme solution gave **2** as deep-red prismatic crystals (0.57 g, 69 %). M.p. 282 °C. IR (nujol): $\tilde{\nu}$ = 1598 (m), 1538 (vs), 1357 (m), 1318 (m), 1294 (w), 1251 (s), 1185 (s), 1109 (s), 1094 (s), 1047 (s), 990 (m), 930 (m), 860 (vs), 820 (vs), 803 (m), 762 (vs), 704 (vs), 562 (m) cm^{-1}. ESR (toluene, 293 K): quintet, g = 2.0031, A_N = 0.46 mT. $C_{47}H_{57}MgN_2O_2S \cdot C_4H_{10}O_2$ (828.44): calcd. C 73.94, H 8.15; found C 74.63, H 7.38.

(dpp-bian)Mg[S(*s*Bu)](dme) (3): To a solution of complex **1** {prepared in situ from dpp-bian [0.5 g (1.0 mmol)] and excess magnesium metal} in thf (30 mL) was added di-*sec*-butyl disulfide [0.09 g (0.5 mmol)]. Within 30 min of reflux, the reaction mixture turned cherry-red. Volatiles were removed under vacuum. Crystallization of the residue from dme gave compound **3** as deep-red crystals (0.51 g, 72 %). M.p. 276 °C. IR (nujoil): $\tilde{\nu}$ = 1591 (m), 1532 (vs), 1319 (m), 1254 (m), 1215 (w), 1138 (w), 1181 (m), 1091 (m), 1048 (s), 867 (s), 857 (s), 820 (s), 807 (s), 789 (m), 772 (s), 765 (s), 669 (w), 606 (w), 544 (w) cm^{-1}. ESR (toluene, 293 K): quintet, g = 2.0030, A_N = 0.46 mT. $C_{44}H_{59}MgN_2O_2S$ (704.30): calcd. C 75.03, H 8.44; found C 75.28, H 7.99.

(dpp-bian)Mg[SC(S)NMe$_2$](thf) (4): Addition of tetramethylthiuram disulfide [0.12 g (0.5 mmol)] to a solution of complex **1** {prepared in situ from dpp-bian [0.5 g (1.0 mmol)] and excess magnesium metal} in thf (30 mL) caused an immediate color change from deep green to cherry-red. The solvent was evaporated in vacuo. Crystallization from a toluene/hexane mixture (8:2) afforded compound **4** as deep-red crystals (0.54 g, 76 %). M.p. 217 °C. IR (nujol): $\tilde{\nu}$ = 1592 (m), 1323 (w), 1275 (w), 1248 (s), 1179 (w), 1149 (w), 1115 (m), 1043 (w), 976 (m), 925 (m), 901 (w), 837 (m), 786 (s), 750 (vs) cm^{-1}. ESR (toluene, 293 K): quintet, g = 2.0037, A_N = 0.47 mT. $C_{43}H_{54}MgN_3OS_2$ (717.32): calcd. C 72.00, H 7.59; found C 71.23, H 8.06.

(dpp-bian)Ga(SBz)$_2$ (6): To a suspension of complex **5** {prepared in situ from dpp-bian [0.5 g (1.0 mmol)] and gallium metal [3.5 g (50 mmol)]} in toluene (30 mL) was added dibenzyl disulfide [0.24 g (1.0 mmol)]. Within 2 h at 80 °C, the reaction mixture turned red. Toluene was removed under vacuum, and the residue was dissolved in 1,2-dimethoxyethane. Compound **6** was isolated as deep red crystals (0.52 g, 64 %) from 1,2-dimethoxyethane. M.p. 194 °C. IR (nujol): $\tilde{\nu}$ = 1599 (m), 1540 (vs), 1494 (w), 1363 (w), 1318 (s), 1253 (m), 1214 (w), 1187 (m), 1147 (m), 1104 (w), 1070 (m), 1056 (w), 1040 (m), 950 (w), 934 (w), 891 (m), 876 (m), 824 (s), 803 (s), 765 (vs), 701 (vs), 642 (w), 594 (w), 565 (m), 547 (w), 470 (w), 465 (m), 412 (s) cm^{-1}. ESR (toluene, 293 K): multiplet, g = 2.0026, $A(^{69}Ga)$ = 1.561 mT, $A(^{71}Ga)$ = 1.983 mT, $A(^{14}N)$ = 0.495 (2 N) mT, $A(^{1}H)$ = 0.098 (4 H) mT. $C_{50}H_{54}GaN_2S_2$ (816.79): calcd. C 73.52, H 6.66; found C 73.12, H 6.43.

(dpp-bian)Ga[SC(S)NMe$_2$] (7): To a suspension of complex **5** {prepared in situ from dpp-bian [0.5 g (1.0 mmol)] and gallium metal [3.5 g (50 mmol)]} in toluene (30 mL) was added with stirring tetramethylthiuram disulfide [0.12 g (0.5 mmol)]. The color of the reaction mixture changed a little and became blue-green. Slow evaporation of the solvent in vacuo afforded complex **7** (0.39 g, 57 %) as deep blue crystals. M.p. 195 °C (dec). IR (nujoil): $\tilde{\nu}$ = 1554 (s), 1513 (s), 1438 (vs), 1403 (m), 1341 (vs), 1319 (w), 1264 (m), 1248 (m), 1180 (w), 1138 (w), 1112 (w), 1055 (w), 972 (m), 926 (m), 910 (m), 812 (m), 806 (m), 765 (vs), 732 (s), 696 (m), 651 (w), 622 (w), 569 (w), 521 (w), 464 (w), 420 (s) cm^{-1}. ^{1}H NMR (200 MHz, C_4D_8O, 20 °C): δ = 7.18 (s, 6 H, CH arom.), 6.94 (d, J = 8.3 Hz, 2 H, CH arom.), 6.73 (dd, J = 8.3, 6.8 Hz, 2 H, CH arom.), 5.81 (d, J = 6.8 Hz, 2 H, CH arom), 3.66 [sept., J = 6.8 Hz, 4 H, $CH(CH_3)_2$], 3.30 [s, 6 H, $N(CH_3)_2$], 1.21 [d, J = 6.8 Hz, 12 H, $CH(CH_3)CH_3$], 1.00 [d, J = 6.8 Hz, 12 H, $CH(CH_3)CH_3$] ppm. $C_{39}H_{46}GaN_3S_2 \cdot C_7H_8$ (782.76): calcd. C 70.58, H 6.95; found C 70.29, H 6.55.

Unfortunately, it is impossible to determine nitrogen content by elemental analysis in **2**–**4**, **6**, and **7** because of the presence of sulfur atoms.

Single-Crystal X-ray Structure Determination of 2, 3, 4, 6, and 7: The intensity data for **2**, **3**, **4**, and **6** were collected at 100 K, and for **7** at 293 K, with Bruker SMART APEX diffractometer using graphite-monochromated Mo-K_α (λ = 0.71073 Å) radiation. SADABS[41] was used to perform area-detector scaling and absorption corrections. The structures were solved by direct methods with SHELXS-97[42] and by full-matrix least-squares techniques against F_o^2 with SHELXL-97.[43] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in idealized positions, and their U_{iso} values were set to ride on the U_{eq} values of the parent carbon atoms [$U_{iso}(H) = 1.5U_{eq}$ for methyl carbon atoms and $1.2U_{eq}$ for other carbon atoms]. Experimental details are given in Table 1.

CCDC-732725 (**2**), -732726 (**3**), -732727 (**4**), -732728 (**6**) and -732729 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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