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Naphthalene derivatives *peri*-substituted by Group 13 elements

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Contents

Abstract

This review focuses on the chemistry of naphthalene derivatives substituted by Group 13 moieties at the *peri*-positions. Depending on the nature of the Group 13 elements, different synthetic approaches have been considered. 1,8-Diborylated naphthalene complexes are conveniently prepared by metathesis of boron halides or alkoxides with 1,8-dilithionaphthalene. Such complexes can also be obtained by ring opening reaction of 1,8-boron bridged naphthalene species. Owing to the proximity of the boryl moieties, these derivatives are often sterically congested. Gallium and indium derivatives have also been prepared. In this case, however, alternative synthetic approaches have been used. These derivatives can be obtained by reaction of $GaCl_3$ or $InCl_3$ with 1,8-bis(trimethylstannyl)naphthalene. The transmetalation reaction of indium(I) halides with 1,8-bis(halomercurio)naphthalene has also proved useful for the synthesis of naphthalenediylindium complexes. While the development of various applications is still being explored, the 1,8-diborylated naphthalene complexes serve as bidendate Lewis acidic hosts for neutral and anionic guests. Recently, such complexes have also served to provide a scaffold for the formation of radicals that feature intramolecular one-electron σ-bonds.

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Keywords: Naphthalene derivatives; Group 13; Lewis acids; Bifunctional

1. Introduction

The chemistry of polyfunctional Lewis acids [1] is rapidly expanding to a number of areas including molecular and anion recognition, catalysis, and crystal engineering. An important part of the compounds that have been investigated consists of polyfunctional organostannanes [2–9] and organomercurials [10–15]. Despite the soft Lewis acidity of tin and mercury, these compounds exhibit remarkable properties [16] and have been used as receptors for anions as well as for small electron rich molecules. More recently, synthetic advances made in the area of Group 13 chemistry have

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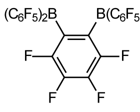
enabled the preparation of polyfunctional Lewis acids that contain several boron [17–24], aluminum [25–30], gallium [28] and indium centers [31–39]. Unlike their mercury and tin counterparts, these derivatives possess hard Lewis acidic elements, and therefore, exhibit distinct acceptor properties, especially in the binding of small anions and electron rich organic derivatives. As shown by a number of recent accounts, these compounds are becoming useful in the fields of catalysis [19–24,26,29], molecular recognition [18,27,35,38,40–42] and material synthesis [39,43]. An important aspect of this research resides in the choice of the organic backbone which dictates the spatial orientation of the Lewis acidic centers as well as the overall rigidity or flexibility of the structure. As in the chemistry of polydentate Lewis bases, the occurrence of cooperative effects is entropically impaired with flexible systems. Hence, the preorganization of the Lewis acidic sites in a rigid molecular edifice is often favored in the design of such compounds. Recent achievements in this area have centered on derivatives of *ortho*-subsituted benzenes and *peri*-substituted naphthalenes.

In this article, we will review the chemistry of naphthalene derivatives substituted by Group 13 moieties at the *peri*-positions. This review is not exhaustive and will emphasize results emanating from our laboratory. Before engaging into the core of the discussion and in order to set the context of the work presented herein, it is important to note that the *ortho*-phenylene backbone has often been incorporated into polyfunctional Group 13 complexes. For example, perfluorinated diboranes such as **1** and **2** have attracted a great deal of attention as activators for metallocene olefin polymerization catalysts [21,24] while diindacycles such as **3** have been used as building blocks for self-assembled coordination polymers [39].



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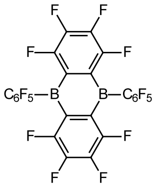

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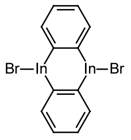

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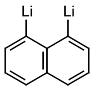
2. Synthesis

2.1. Starting materials for the synthesis of peri-substituted naphthalenes

1,8-Dilithionaphthalene (**4**), which can be conveniently synthesized by three literature procedures [18,44,45], is at the genesis of most of the chemistry described in this review. Like its magnesium analog [46], compound **4** serves as a starting material for *peri*-metalated naphthalene derivatives. It can also be converted into 1,8-bis(trimethylstannyl)naphthalene (**5**) [47] and 1,8-bis(chloromercurio)naphthalene (**6**) [48,49] which in turn are useful starting materials in the chemistry of Group 13-*peri*-substituted naphthalene derivatives.



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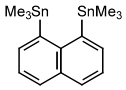

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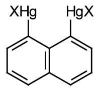
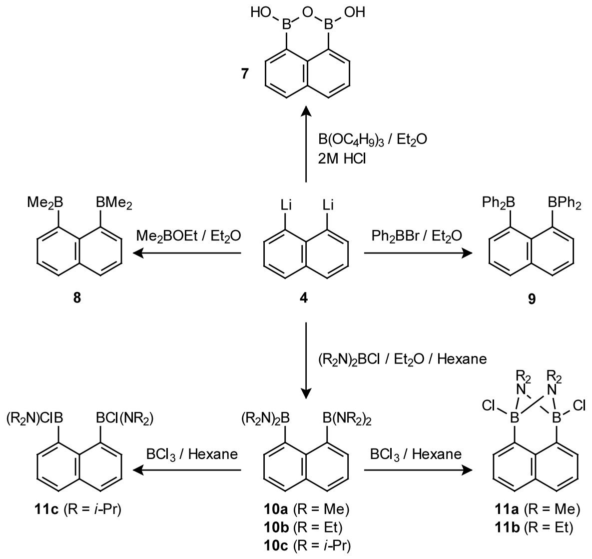


6a, X = Cl
6b, X = Br

2.2. Naphthalene derivatives substituted by boryl moieties at the peri-positions

The synthesis of 1,8-diborylnaphthalene derivatives was first reported by Letsinger who prepared 1,8-naphthalenediboronic anhydride (**7**) from **4** and tris-*n*-butylborate followed by hydrolysis (Scheme 1) [49]. Most 1,8-diborylnaphthalene derivatives known to date have also been prepared by metathesis reaction of **4** with boron halides or alkoxides (Scheme 1). These include dialkyl (**8**) [18,50,51], diaryl (**9**) (Fig. 1) [52] as well as diaminoboryl derivatives (**10a**–**c**) (Scheme 1) [53]. These compounds have been characterized by multinuclear NMR and X-ray single crystal analysis. As often encountered in the structure of *peri*-substituted naphthalene derivatives, the naphthalene backbone of these derivatives is subjected to distortions, which result from steric repulsions occurring between the proximal boryl moieties. The non-bonding boron–boron distances are close to 3 Å (Table 1), thus allowing for the occurrence of cooperative effects (vide infra). The bis(diamino-



Scheme 1.

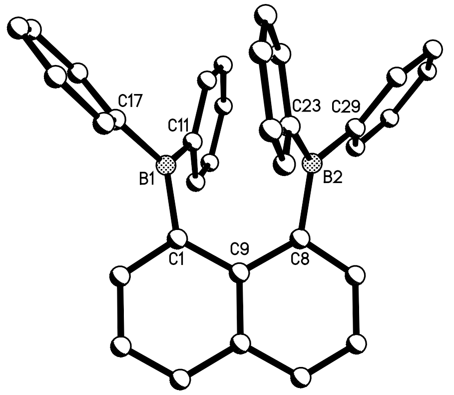


Fig. 1. Molecular structure of **9** in the crystal.

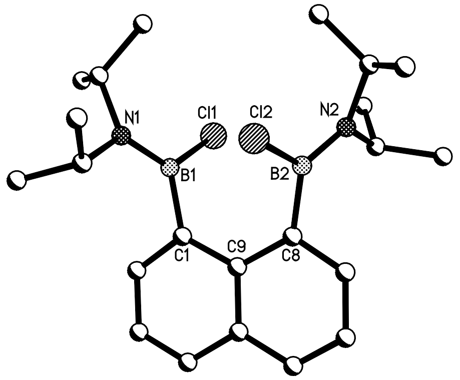
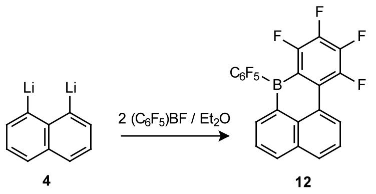
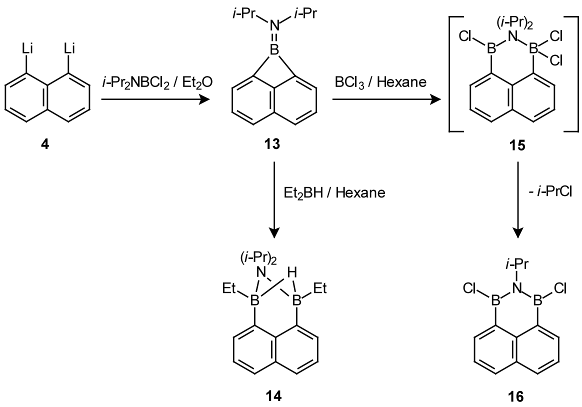


Fig. 2. Molecular structure of **11c** in the crystal.



Scheme 2.



Scheme 3.

boryl)-derivatives **10a**–**c** undergo ligand exchange with BCl_3 to afford the corresponding bis(aminochloroboryl)-compounds (**11a**–**c**) [53]. In the case of **11a**,**b**, ^{11}B-NMR suggests the formation of intramolecular B–N–B bridges. In the case of **11c** ($R = i$-Pr) however, the large steric bulk of the amido substituent prevents the formation of such bridges as confirmed by X-ray analysis (Fig. 2). In an attempt to prepare a fluorinated analog of the diborane **9**, the reaction of **4** with bis(pentafluorophenyl)boronfluoride has been studied. Surprisingly, this reaction does not lead to the formation of a diborane but affords 7-pentafluorophenyl-8,9,10,11-tetrafluoro-7-bora-7*H*-benzo[*de*]anthracene (**12**), which features a tricoordinated boron atom incorporated in a fused tetracyclic system with 16 π-electrons (Scheme 2) [54]. The formation of **12** can be rationalized by invoking the metathetical attachment of one bis(pentafluorophenyl)boryl group to the naphthalene backbone, followed by a nucleophilic substitution of an *ortho*-fluoride by the remaining carbanionic center. This anti-aromatic compound exhibits an irreversible reduction wave at -1.33 V (vs. SHE).

1,8-Boron bridged naphthalene derivatives are also known. Such compounds remain relatively scarce and have been reported on only two occasions [55,56]. The reaction of the dilithionaphthalene derivative **4** with one equivalent of (di-*iso*-propyl)aminodichloroborane leads to the formation of a naphtho[1,8-*bc*]boret (**13**) (Scheme 3) [55]. This compound, which features a strained four-membered boracycle has been characterized by single crystal X-ray analysis (Fig. 3). The acute C(1)–B–C(8) angle as well as distortions in the naphthalenediyl fragment are especially noteworthy (Table 2). As a result of ring-strain, this compound undergoes ring-opening reactions. For example, when treated with Et_2BH, a hydrido-bridged diborane is obtained (**14**) while reaction with BCl_3 leads to a heterocyclic compound (**16**), the formation of which likely proceeds through intermediate **15** (Scheme 3).

An anionic 1,8-boron bridged naphthalene derivative (**18**) has also been prepared by reaction of the dilithionaphthalene derivative **4** with one equivalent of dimesitylboronfluoride (**17**) (Scheme 4) [56]. The ^{11}B-NMR resonance observed at 2.3 ppm in d_8-THF is consistent with that typically observed for tetraarylborates such as

Table 1
Boron–boron distance in 1,8-diborylnaphthalene derivatives

Compound	**9**	**10a**	**11c**	**19**	**20**
B–B distance (Å)	3.003	3.034, 3.056	3.201	3.204	3.352

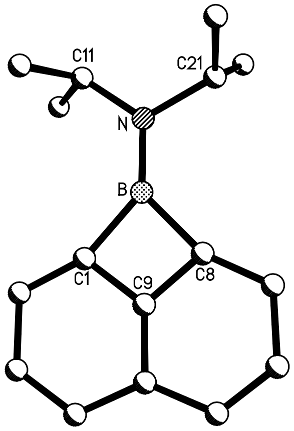
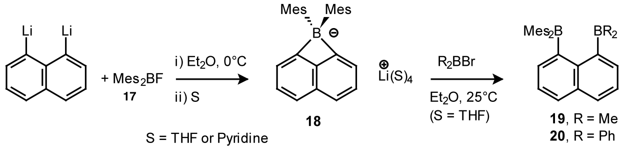


Fig. 3. Molecular structure of **13** in the crystal.

Table 2
Bond angles (°) observed in the 1,8-boron bridged naphthalenes **13** and **18**

Compounds	C(1)–B–C(8)	C(1)–C(9)–C(8)	C(9)–C(1)–B	C(9)–C(8)–B
13	86.2, 86.7	102.6, 103.0	85.6, 85.2	85.7, 85.1
18	80.5	103.3	87.6	88.6



Scheme 4.

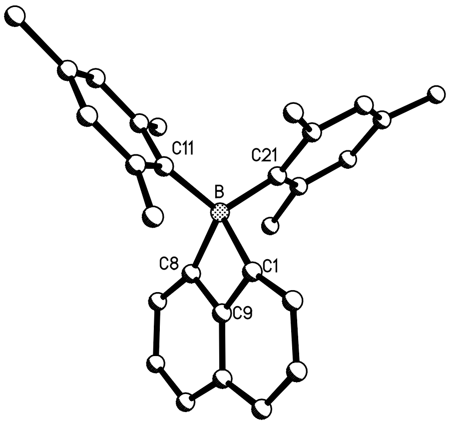


Fig. 4. Molecular structure of **18** in the crystal.

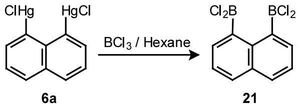
Ph_4B^- (δ −6 in d_8-THF). Compound **18** can be isolated as a crystalline Li(THF)$_4$ or Li(py)$_4$ salt, respectively. Single crystal X-ray analysis of the Li(py)$_4$ salt confirms the existence of a strained boracycle similar to that encountered in the structure of the naphtho[1,8-*bc*]boret **13** (Table 2, Fig. 4). It is important to note that the increased steric bulk of the boryl moiety in **18** leads to a decrease of the C(1)–B–C(8) angle (Table 2). **18**–Li(THF)$_4$ undergoes ring opening reactions in the presence of diorganylboronhalides [56]. Thus, reactions with dimethylboronbromide and diphenylboronbromide lead to high yields of 1-(dimesitylboryl)-8-(dimethylboryl)naphthalene (**19**) and 1-(dimesitylboryl)-8-(diphenylboryl)naphthalene (**20**), respectively, (Scheme 4). By contrast, reaction of **18** with dimesitylboronfluoride does not lead to the formation of 1,8-bis(dimesitylboryl)naphthalene, which likely results from the high steric demand of the mesityl substituents. Diboranes **19** and **20** have been characterized by multinuclear NMR spectroscopy. The ^{1}H-NMR spectrum of **19** and **20** indicates the existence of a rigid structure since four aryl protons and six distinct methyl groups are observed for the mesityl substituent. The methyl groups attached to the boron center of **19** give rise to two broad resonances, which coalesce at 50 °C. Compounds **19** and **20** are sterically crowded and feature intramolecular boron–boron distances that exceed 3 Å (Table 1).

Organomercurials have often been used as starting materials for organoboranes [57]. In such a fashion, compound **6a** reacts with BCl_3 to give high yield of 1,8-naphthalenediylbis(dichloroborane) (**21**) (Scheme 5) [58,59]. This compound is very sensitive to hydrolysis and affords the 1,8-naphthalenediboronic anhydride **7** when exposed to moisture.

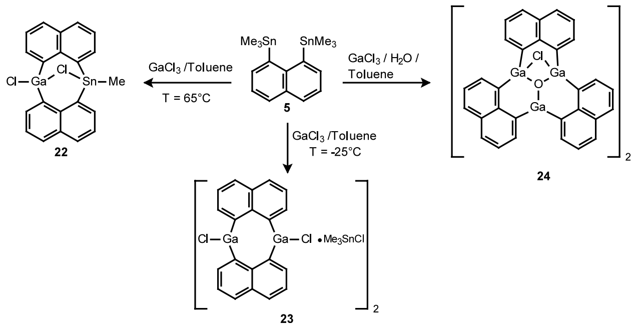
2.3. *Naphthalene derivatives substituted by gallium at the peri-positions*

Organotin reagents have often been employed for the arylation, vinylation and alkylation of boron halides [60–63]. Interestingly, however, application of this method to the case of heavier Group 13 derivatives appears much more limited [64,65]. Following some earlier work with aluminum [29,66], the reactions of organostannanes with $GaCl_3$ have been investigated as a means to prepare polyfunctional organogallium species.

The reaction of the distannyl derivative **5** and gallium trichloride in toluene leads to the formation of three products whose respective yields depend on the conditions of the reaction. Under strictly anhydrous conditions and upon heating for 6 h at 65 °C, this reaction leads to high yields of bis(μ-1,8-naphthalenediyl)(μ-chloride)methyltin(IV)chlorogallium(III) (**22**) (Scheme 6) [67]. Compound **22** adopts an unusual structure in that it features a folded eight-membered dimetallacycle in which the two metals are bridged by a chloride ligand.



Scheme 5.



Scheme 6.

Lowering the reaction temperature to −25 °C, leads to a decrease in the yield of **22** and the appearance of a new product which has been identified as an adduct formed between bis(μ-1,8-naphthalenediyl)bis(gallium(III)chloride) and trimethyltin chloride ([**23**·$Me_3SnCl]_2$) (Scheme 6) [68]. The presence of a digallacycle unit in **23** indicates that the complete substitution of the stannyl groups of **5** is possible. The solid state structure of [**23**·$Me_3SnCl]_2$ consists of a dimer in which the digallacycles are linked through chloride bridges to two pentacoordinated tin atoms (Fig. 5). With obtuse C–Ga–C angles (av. 133.3°), the gallium centers feature a distorted tetrahedral geometry resulting from the constraints imposed by the cyclic structure. The spontaneous ring closure observed in the formation of **22** and **23** is reminiscent of the formation of 7,7,14,14-tetramethyldinaphtho[1,8-*bc*:1′,8′-*fg*][1,5]distannocine observed when **5** is treated with dimethyltindichloride [7]. As shown by ^1H-NMR spectroscopy, [**23**·$Me_3SnCl]_2$ does not retain its structure in pyridine solutions but rather dissociates to give Me_3SnCl·py and solvent stabilized molecules of the digallacycle.

In the presence of traces of water, the room temperature transmetalation reaction leads to low yield of a third derivative (**24**) which consists of a 12-membered macrocycle containing three gallium atoms linked by 1,8-naphthalenediyl ligands and arranged about a central oxygen atom (Scheme 6) [68]. The charge balance of **24** is achieved by the presence of a chloride atom that bridges two of the gallium centers (Scheme 6). While excess water led to formation of naphthalene, the best yields in **24** were obtained for reaction mixtures containing the distannyl derivative **5**, $GaCl_3$, and H_2O in 0.06, 0.06, and 0.012 M concentration, respectively. In the crystal, **24** exists as a dimer wherein the monomers are bridged via a Ga–O–Ga–O four-membered ring (Fig. 6). The three gallium atoms are separated by ca. 3 Å and form a nearly equilateral triangle. The solution structure of **24** in d_8-THF has been investigated by pulse field gradient spin-echo (PGSE) methods and VT ^1H-NMR spectroscopy, which suggest the existence of an exchange between the monomeric and dimeric form of **24**. The high-temperature ^1H-NMR data suggest that upon dissociation into the monomer, the chloride anion undergoes rapid intramolecular exchange leading to an apparent three-fold molecular symmetry (Fig. 7). This proposal is in agreement with conductivity measurements, which indicate that THF solutions of **24** are non-ionic.

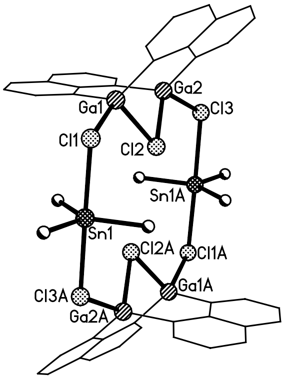


Fig. 5. Molecular structure of [**23**·$Me_3SnCl]_2$ in the crystal.

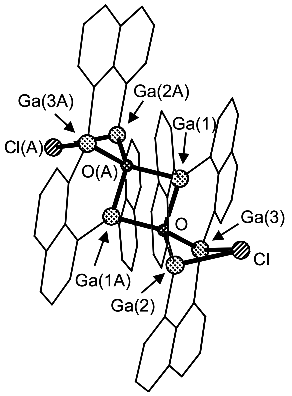


Fig. 6. Molecular structure of **24** in the crystal.

2.4. *Naphthalene derivatives substituted by indium at the peri-positions*

The transmetalation reaction of organomercurials with indium(I) halides constitutes an efficient method for the preparation of organoindium derivatives. Such reactions proceed smoothly and yield mercury metal as a sole by-product, which greatly facilitates the isolation of the products. Application of this strategy to the case of polyfunctional Lewis acids has proved to be equally successful, for example in the synthesis of the diindacycle **3** [34–37]. With this in mind, it appears logical that this methodology has been used for the synthesis of *peri*-substituted naphthalene derivatives of indium. While the dimercuracycle **25** [48] fails to react with InCl or InBr, the mercury compound **6a** as well as its bromo-analog **6b** react with their respective indium(I) halides to yield the mercura-indacycles **26** and **27** (Scheme 7) [69].

The formation of **26** and **27** most probably involves transmetalation of only one mercury center followed by

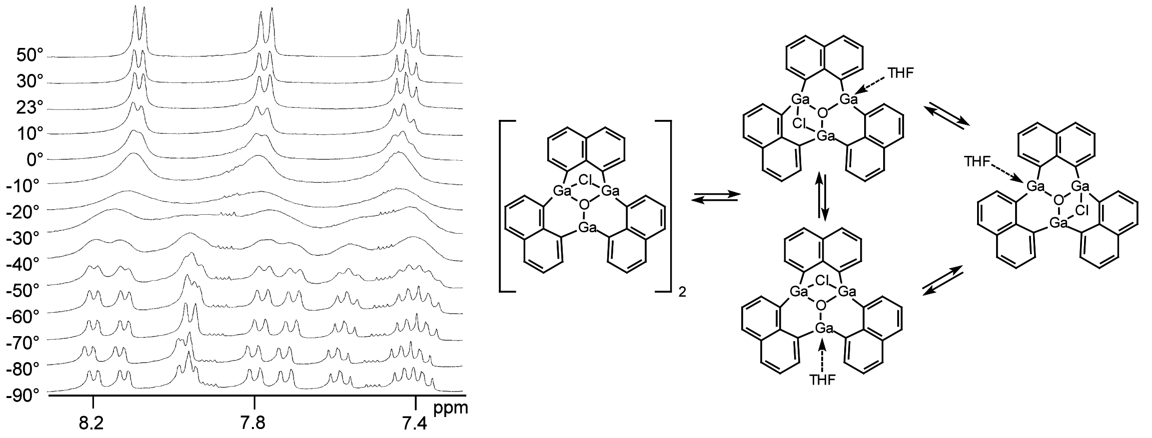
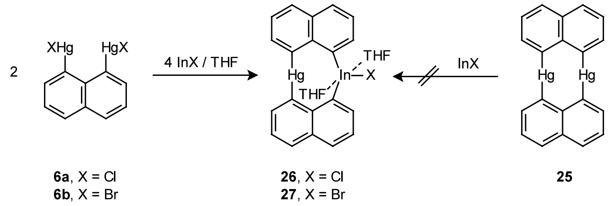
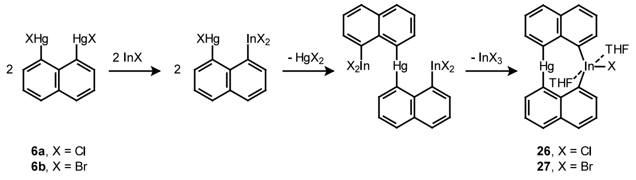


Fig. 7. Variable temperature ^{1}H-NMR spectrum of **24** in d_8-THF.



Scheme 7.



Scheme 8.

a series of ligand exchange processes leading to a ring closure as shown in Scheme 8. Considering the sterical and geometrical constraints in **26** and **27**, such ring closure reactions are remarkable and seem to parallel those involved in the formation of the gallium derivatives **22** and **23**. The formation of **26** is accompanied by several side reactions and partial disproportionation of InCl as shown by the isolation of **26** as a $(InCl_3(THF)_3)$ adduct. The indium centers of **26** and **27** are pentacoordinated and adopt a distorted trigonal bipyramidal coordination sphere (Fig. 8). The main deviation from an ideal geometry occurs in the equatorial plane as indicated by the large C–In–C angles (157.2° in **26** and 150.9° in **27**). The most noticeable feature in the structure of **26** and **27** is the very short transannular Hg···In distance of 3.01 and 3.03 Å, respectively. There are no data available for Hg–In bonds. However, these distances are shorter than the sum of the van-der-Waals radii of the two metals (3.6 Å) [70], close to the sum of the metallic radii (3.12 Å) and just slightly greater that the sum of the Pauling covalent radii (2.94 Å).

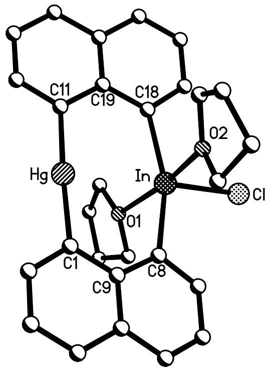
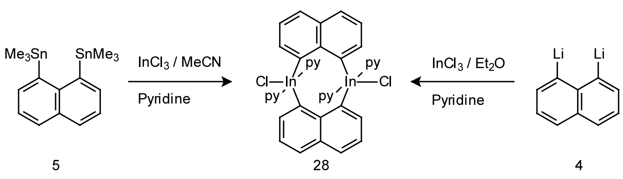


Fig. 8. Molecular structure of **26** in the crystal. The $(InCl_3(THF)_3)$ moiety is not shown for clarity.

The formation of heteronuclear complexes in the reaction depicted in Scheme 7 indicates that the reaction of the organomercury derivatives **6a**,**b** with indium monohalide is not adequate for the synthesis of 1,8-(diindium)naphthalenediyl complexes [69]. In an effort to discover alternative approaches to the synthesis of such complexes, the reaction of **5** with $InCl_3$ in acetonitrile has been investigated (Scheme 9). Following treatment with pyridine, this reaction yields the tetrakis(pyridine) adduct of bis(μ-1,8-naphthalenediyl)bis(chloroindium(III)) (**28**) [71]. It is interesting to note that the tetrakis(THF) adduct of this diindacycle has been isolated in trace amount in the reaction between InCl and 1,8-bis(chloromercurio)naphthalene. The synthesis that uses the distannyl derivative **5** as a starting material, therefore, appears as a worthy alternative since it affords **28** in a 65% yield. Attempts to prepare a non-cyclic 1,8-(diindium)naphthalenediyl complex have not been successful. Even in the presence



Scheme 9.

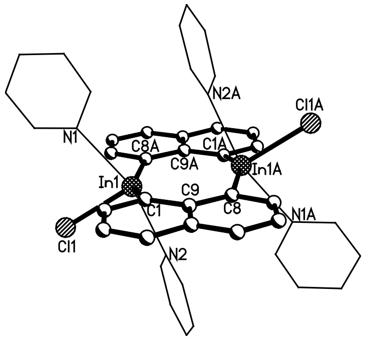


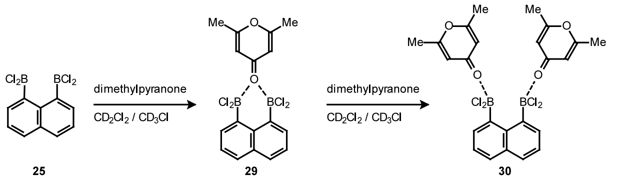
Fig. 9. Molecular structure of **28** in the crystal.

of an excess of $InCl_3$, the reaction depicted in Scheme 9 always affords **28** as the only identifiable product. Attempts to prepare **28** by metathesis have also been pursued. As shown by ^{1}H-NMR spectroscopy, treatment of $InCl_3$ with an equimolar amount of the dilithionaphthalene **4** in Et_2O affords a 25% yield of the diindacycle (Scheme 9). The indium centers of **28** are pentacoordinated in an approximate trigonal bipyramidal fashion with pyridine ligands occupying the axial sites (Fig. 9). The indium coordination sphere undergoes strong distortions as shown by the value of the C–In–C angle (153.3°) which is similar to that encountered in **26** and **27**.

3. Application

3.1. *Chelation of organic carbonyls*

Several reports demonstrate that polyfunctional Lewis acids are valuable catalysts for reactions involving organic carbonyls such as aldehydes and ketones [26,72,73]. The high catalytic activity observed in these reactions is likely to result from the ability of the bifunctional Lewis acid to chelate the carbonyl oxygen atom. On a few occasions, such phenomena have been observed in the activation of thioketones and thionoesters [74–76]. While the double coordination of formamides has been investigated in detail [77,78], the knowledge gathered on the chelation of ketones or aldehydes appears more limited [79–81]. The Lewis acidic properties of the tetrachlorodiborane **25** have been investigated in solution. In addition to catalyzing Diels–Alder reactions [82], this derivative forms identifiable complexes with dimethylpyranone (Scheme 10) [83]. Thus, upon addition of one equivalent of dimethylpyranone, formation of the 1:1 complex **25**-(μ_2-dimethylpyranone) (**29**) is observed. The identity of this complex has been confirmed by IR and ^{1}H-NMR spectroscopies, which are in agreement with the simultaneous coordination of the carbonyl functionality to both boron centers. Comparison of the IR stretching frequencies and ^{1}H-NMR chemical shifts suggest that the Lewis-acidic strength of **25** is close to that of BCl_3. Addition of one more equivalent of dimethylpyranone leads to the formation of a 2:1 complex in which there is coordination of one ketone per boron center (**30**).



Scheme 10.

3.2. *Anion complexation*

The strong basicity of 1,8-bis(dimethylamino)naphthalene (‘proton sponge’) results from the ability of this base to form a very stable conjugate acid in which the proton is simultaneously bonded to each nitrogen atom. Based on the expectation that the reverse-charge analogue of this species might exhibit unusual acidity, 1,8-bis(dimethylboryl)naphthalene (**8**) has been investigated [18,50]. In the presence of potassium hydride in THF, **8** forms a kinetically and thermodynamically stable 1:1 borohydride complex ([**8**–μ_2-H]$^-$) which fails to reduce benzaldehyde (Fig. 10, Scheme 11). In the crystal, both boron centers participate in a 3c–2e bond with the hydride anion, this situation being responsible for the unusual Lewis acidity of **8**. It is noteworthy that the presence of a hydride bridge allows for tetrahedralization of the boron centers, which are only separated by 2.54 Å. In addition to abstracting hydrides from a variety of substrates such as monofunctional borohydride or zirconocene chloride hydride, **8** readily chelates fluoride and hydroxide anions (Scheme 11) [18]. While complexation of small anions appears quantitative, **8** does not interact strongly with larger anions such as chloride and bromide. By contrast, addition of chloride anion to **21** leads to the formation of a chloride chelate complex ([**21**–μ_2-Cl]$^-$) that has been characterized by X-ray analysis (Fig. 11). As shown by the puckered structure of the resulting

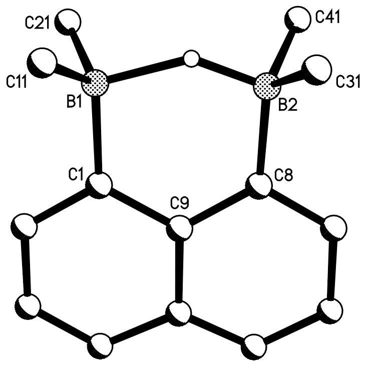
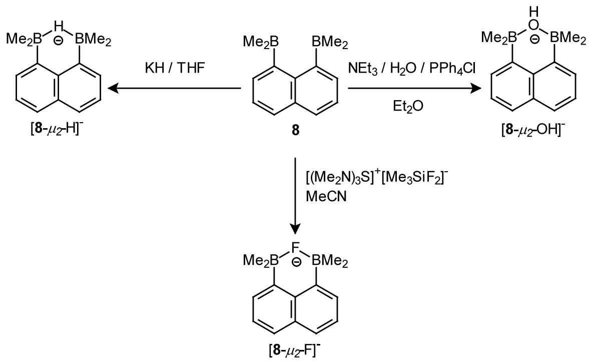


Fig. 10. Molecular structure of [**8**–μ_2-H]$^-$ in the crystal.



Scheme 11.

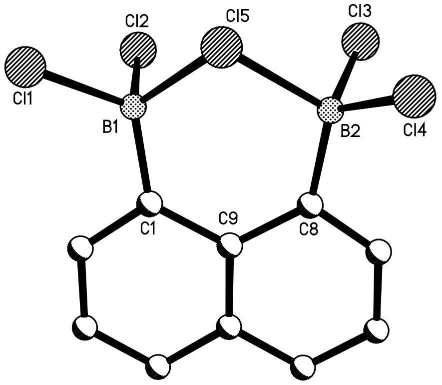


Fig. 11. Molecular structure of [**21**$-\mu_2$-Cl]$^-$ in the crystal.

chelate six-membered ring, the small space generated between the two boron centers is at the lower limit for accepting a large anion such as a chloride.

3.3. Formation of boron–boron one electron σ-bonds by reduction of 1,8-diborylnaphthalene derivatives

Single electron reduction of triorganoboranes leads to the formation of persistent radical anions [84–88]. While delocalization of the radical over the ligands accounts for the stability of these systems, EPR studies show that, in some instances, the unpaired electron is mainly localized at boron [89]. Reduction of diboranes of general formula $R_2B{-}BR_2$ has also been studied [90]. In this case, the unpaired electron occupies a π-bonding orbital formed by the overlap of the parallel boron p_z-orbitals. A less common situation is encountered when the unpaired electron occupies a boron–boron σ-bonding orbital. Although extremely rare, such complexes have occasionally been observed as transient low temperature species [91].

As previously suggested, the proximity of the boron centers in 1,8-diboryl-naphthalene derivatives should enable the intramolecular interactions of the boron p_z-orbitals [18]. A series of DFT calculations performed on diborane **9** confirmed this view [52] and showed that both boron empty p_z-orbitals contribute to the LUMO (Fig. 12). While reduction of **8** does not lead to any stable radicalar species [18], the cyclic voltammogram of **9** exhibits a reversible reduction wave at −1.81 V (vs. SHE). Upon treatment of THF solutions of **9** with potassium and 18-crown-6, dark purple solutions of **9**$^{\bullet -}$ are obtained (Scheme 12). The radicalar species **9**$^{\bullet -}$, present in solution, is stable for several hours at room temperature. The EPR spectrum of this radical exhibits a seven-line signal ($g = 2.002$, $a_B = 5.9$ G) in agreement with the hyperfine coupling of the electron spin with the two boron centers ($I = 3/2$) (Fig. 13). The multiplicity of the signal indicates that the semi-occupied molecular orbital (SOMO) involves orbitals at both boron centers. The magnitude of the coupling indicates that the boron orbitals are important contributors to the SOMO. All attempts to isolate **9**$^{\bullet -}$ in a crystalline form have been unsuccessful. However, DFT calculations suggest that upon reduction, the boron centers become slightly pyramidal and approach each other (B–B distance = 3.16 Å in **9** and 2.82 Å in **9**$^{\bullet -}$) to allow the formation of an intramolecular one electron σ-bond (Fig. 14) which can be viewed as resulting from the overlap of the formerly vacant boron p_z-orbitals.

4. Conclusion and future prospects

The chemistry of naphthalene derivatives substituted by Group 13 moieties at the *peri*-positions continues to be an area of active investigation. While a number of synthetic procedures have been developed for the preparation of boron derivatives, much progress is needed for controlling the composition and structure of the heavier Group 13 derivatives. Indeed, while *peri*-subsituted naphthalene complexes of aluminum are unknown, the gallium and indium complexes are cyclic and have been serendipitously prepared. It remains that some of these complexes feature appealing structure. In particular, the trinuclear gallium derivative **24** is a macrocyclic polyfunctional Lewis acid that could potentially function as a receptor for polyatomic anions.

The 1,8-diborylnaphthalene derivatives constitute remarkable complexing agents for small anions including hydride, fluoride and hydroxides. While the strength and irreversibility of the binding might preclude their use in sensors for anions, possible applications exist in the field of olefin polymerization catalysis where such complexes could serve as activators for metallocene catalysts.

Finally, the reduction of 1,8-diborylnaphthalene derivatives leads to the formation of radicals that feature intramolecular one-electron σ-bonds. Such ‘unsaturated’ bonds are unusual and will undoubtedly be subjected to further fundamental studies. It should also be noted that the extension of such bonding

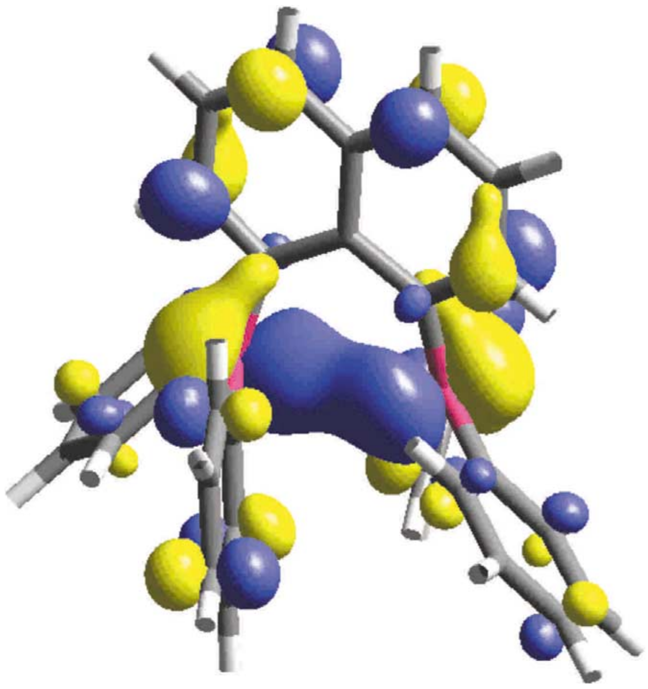
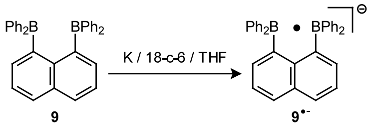


Fig. 12. DFT orbital picture showing the LUMO of $\mathbf{9}^{\bullet-}$.



Scheme 12.

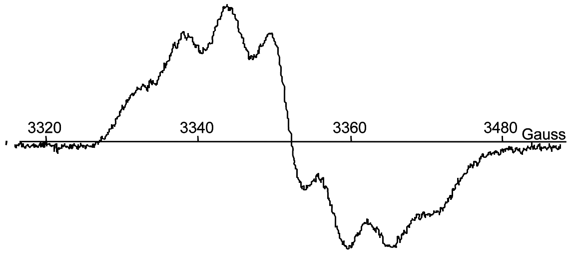


Fig. 13. X-band EPR spectrum of $\mathbf{9}^{\bullet-}$ in THF.

interactions over several centers could serve as a basis for the design of organic conductors [92].

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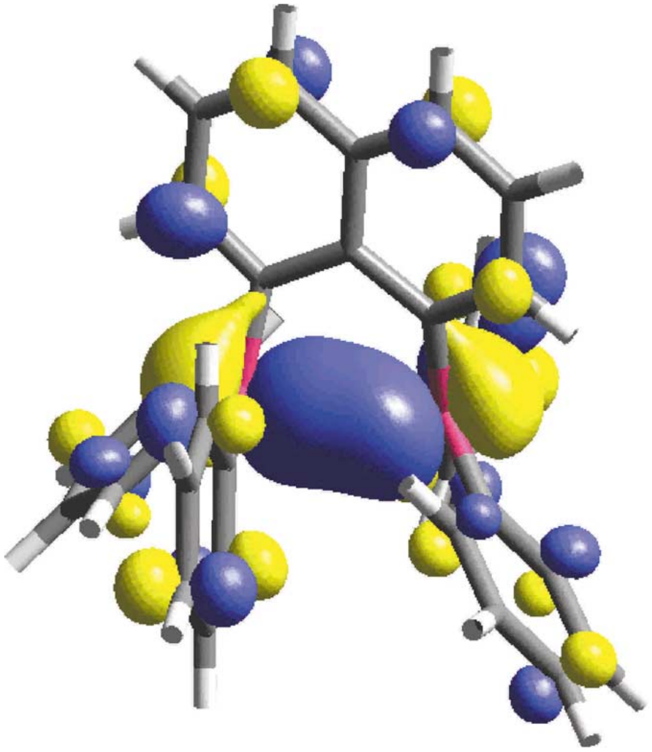

Fig. 14. DFT orbital picture showing the SOMO of $\mathbf{9}^{\bullet-}$.

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