

Bidentate Group 13 Lewis Acids with ortho-Phenylene and peri-Naphthalenediyl Backbones

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I

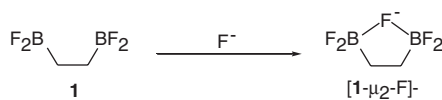
INTRODUCTION

The chemistry of polydentate Lewis acids^{1–3} is still in its infancy but is rapidly expanding to a number of areas including molecular and anion recognition, catalysis and crystal engineering. Conceptually, polydentate Lewis acids are often regarded as the charge reverse analogs of polydentate Lewis bases and are thus expected to act as polydentate ligands for electron-rich substrates.⁴ This analogy was recognized almost four decades ago by Shriver and Biallas who showed that methoxide anions are effectively chelated by 1,2-bis(difluoroboryl)ethane (**1**), a charge reverse analog of ethylenediamine (Scheme 1).⁵ Following this seminal contribution, a great deal of effort has been devoted to the synthesis and study of such polydentate Lewis acids. An important part of the compounds that have been investigated consists of polyfunctional organostannanes¹ and organomercurials.^{6–11} Despite the soft Lewis acidity of tin and mercury, these compounds exhibit remarkable properties and have been used as receptors for anions as well as for small electron-rich molecules. For example, while the 1,2-distannyllbenzene **2**¹² or the mercuraborand **3**¹³ readily complex chloride anions, trinuclear mercury derivatives such as trimeric perfluoro-*ortho*-phenylene **4** can be used as receptors for organic substrates including acetone (Scheme 2).¹⁴ Aiming at more powerful Lewis acids, a great deal of effort has been devoted to the preparation of polydentate Lewis acids that contain hard Lewis acidic elements of group 13.^{15,16} Despite their greater sensitivity toward hydrolysis and oxidation, several polydentate group 13 derivatives have been successfully synthesized and investigated.

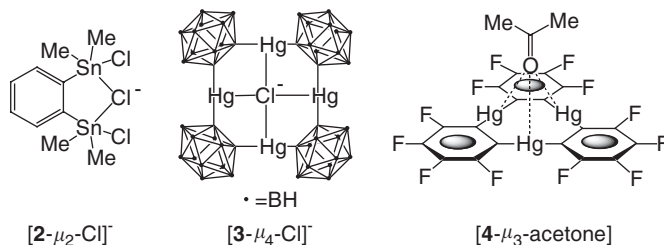
An important aspect of this research resides in the choice of the backbone that serves to hold the Lewis acidic site. In order to insure that the Lewis acidic sites

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SCHEME 1.



SCHEME 2.

remain available, it is important to choose a backbone that does not contain accessible Lewis basic sites such as oxygen or nitrogen atoms which could neutralize the Lewis acidic centers by intramolecular Lewis adduct formation or by through-bond π -electron donation. Moreover, as in the chemistry of polydentate Lewis bases, the structure of the backbone should serve to dictate the spatial orientation of the Lewis acidic centers as well as the overall rigidity or flexibility of the target polydentate Lewis acid. Since the occurrence of cooperative effects is entropically impaired with flexible systems, the preorganization of the Lewis acidic sites in a rigid molecular edifice is often preferred. Recent achievements in this area have centered on derivatives of *ortho*-substituted benzenes and *peri*-substituted naphthalenes. In this chapter, we will review the chemistry of bidentate Lewis acids containing two group 13 elements linked by an *ortho*-phenylene^{15,16} or a *peri*-naphthalenediyl backbone. This contribution follows an earlier review concerned with *peri*-naphthalenediyl group 13 derivatives.¹⁷

II

SYNTHESIS

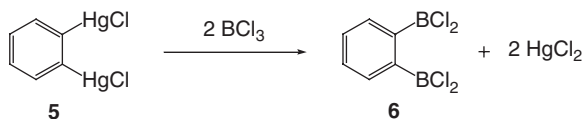
A. Boron Polydentate Lewis Acids

1. *Ortho*-Phenylene Boron Derivatives

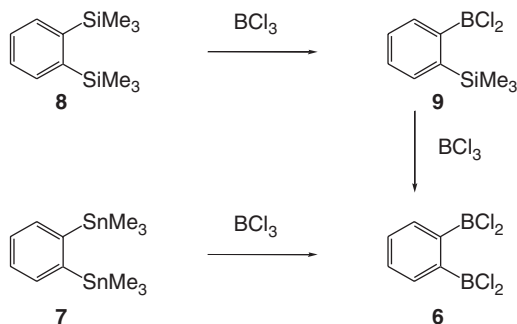
Bidentate boranes with an *o*-phenylene backbone constitute some of the simplest examples of polydentate Lewis acids with rigid backbones. They can be prepared by the reaction of boron halides with a 1,2-dimetallated benzene derivative. Thus, the reaction of 1,2-bis(chloromercurio)benzene (**5**) with boron trichloride affords 1,2-bis(dichloroboryl)benzene (**6**, Scheme 3).¹⁸

This compound (**6**) can also be obtained in one step by the reaction of 1,2-bis(trimethylstannyl)benzene (**7**) with an excess of boron trichloride at $-78\text{ }^{\circ}\text{C}$ in dichloromethane.¹⁹ It can also be prepared by the reaction of 1,2-bis(trimethylsilyl)benzene (**8**) with boron trichloride. In the latter, the reaction proceeds *via* the monoborylated intermediate **9** (Scheme 4).

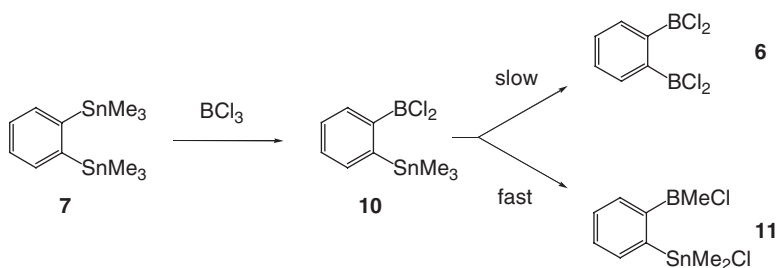
When the distannyl reagent **7** is employed, the fate of the reaction apparently depends on the reaction conditions. Indeed, Eisch observed that the reaction of **7** with boron trichloride at $-40\text{ }^{\circ}\text{C}$ in hydrocarbon solvent is not always selective and leads to the formation of both a monoborylated intermediate (**10**) that slowly converts into **6** (Scheme 5).²⁰ The outcome of these reactions is apparently further complicated by a fast methyl group transfer from the tin to the boron centers yielding the undesired monoborylated derivative **11**. Eisch also found that such reactions are not limited to the case of boron trihalide but can be performed with dialkyl boron halide starting materials. For example, the reaction of the distannane



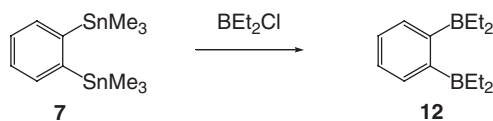
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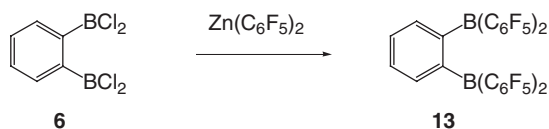
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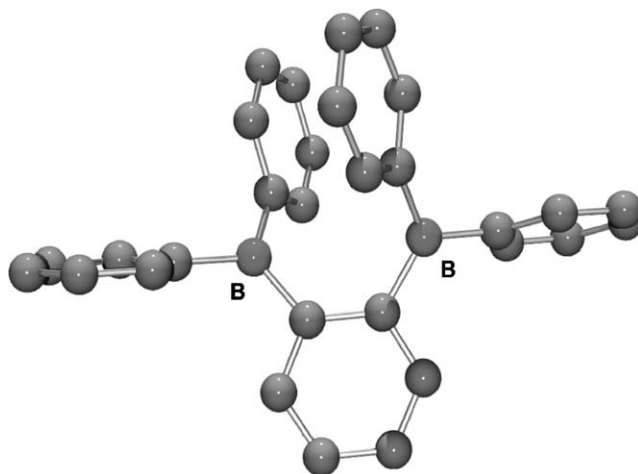
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SCHEME 6.

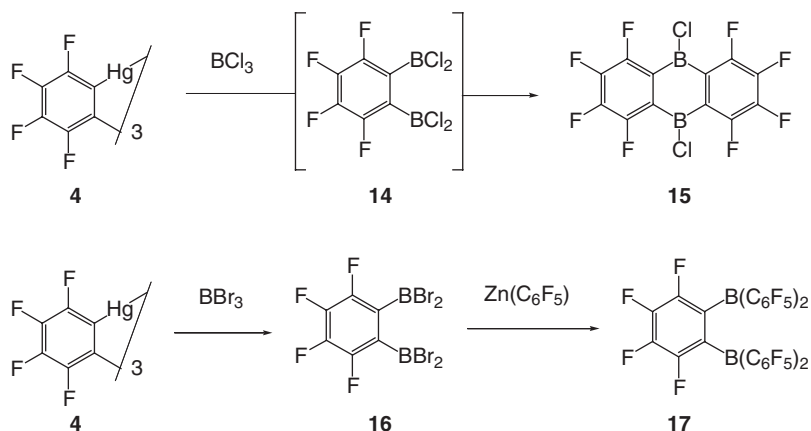


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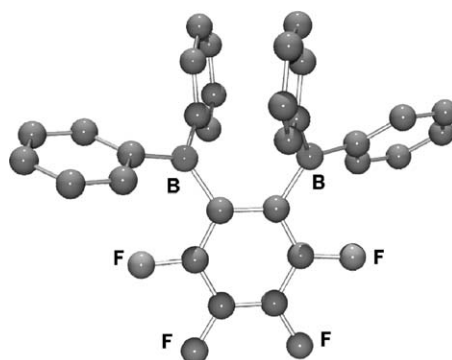
FIG. 1. Compound **13**. F-atoms from C_6F_5 groups omitted for clarity.

7 with diethylboron chloride is clean and affords high yields of 1,2-bis(diethylboryl)benzene (**12**, Scheme 6).

1,2-Bis(dichloroboryl)benzene (**6**) is an important starting material which lends itself to facile derivatization. As shown by Piers, it cleanly reacts with bis(pentafluorophenyl)zinc to afford the corresponding bidentate Lewis acid **13** (Scheme 7).²¹ The molecular structure of diborane **13** has been determined and is shown in Fig. 1. In this structure, the vicinal boron atoms are held at 3.26 Å and from one another and seem to be ideally positioned to cooperatively interact with monoatomic anions. The fully fluorinated version of this bidentate Lewis acid has also been prepared.²¹ Original efforts focused on the use of 1,2-bis(dichloroboryl)tetrafluorobenzene **14** as a starting material (Scheme 8). This compound could be observed in the early stage of the reaction of trimeric perfluoro-*o*-phenylenemercury (**4**) with boron trichloride, but was found to be unstable toward condensation into 9,10-dichloro-9,10-dihydro-9,10-diboraoctafluoroanthracene **15**. The successful synthesis of the fully fluorinated

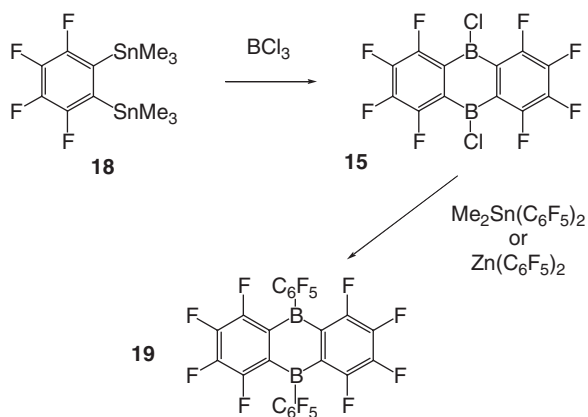


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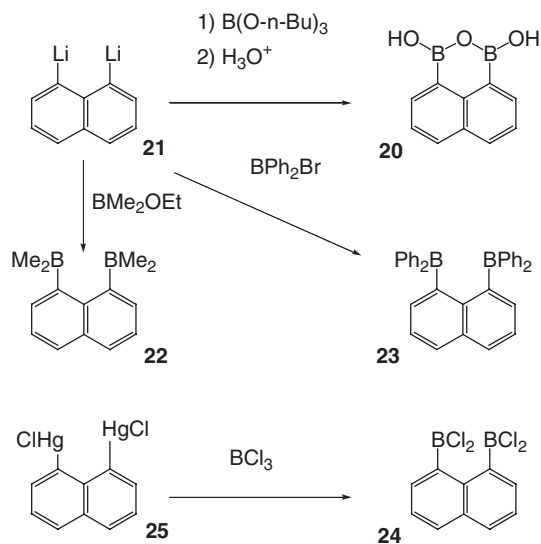
FIG. 2. Compound **17**. F-atoms from C_6F_5 groups omitted for clarity.

derivative employed the more stable 1,2-bis(dibromoboryl)tetrafluorobenzene **16**. This derivative was obtained from the reaction of the trinuclear organomercurial **4** with BBr_3 and was converted into **17** by treatment with bis(pentafluorophenyl)zinc. The structure of **17** (Fig. 2) has also been determined and closely resembles that of **13** (Fig. 1). However, this structure displays a significantly shorter distance of 3.14 Å between the two boron centers.

Distannyl derivatives have also been used as starting materials for the synthesis of fluorinated *ortho*-phenylene diboranes. The reaction of 1,2-bis(trimethylstannyl)tetrafluorobenzene (**18**)²² with BCl_3 affords 9,10-dichloro-9,10-dihydro-9,10-diboraoctafluoroanthracene (**15**) (Scheme 9).^{23,24} This compound can be further derivatized by treatment with bis(pentafluorophenyl)dimethyltin which affords the fully fluorinated 9,10-bis(pentafluorophenyl)-9,10-dihydro-9,10-diboraoctafluoroanthracene (**19**). This conversion can also be effected by the reaction of **15** with bis(pentafluorophenyl)zinc.²¹



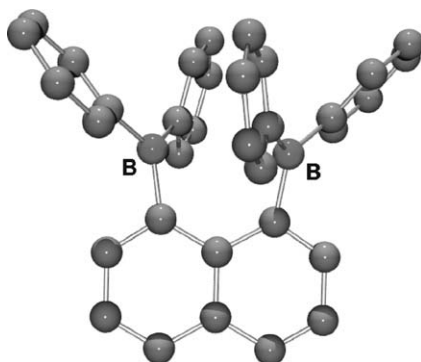
SCHEME 9.



SCHEME 10.

2. 1,8-Naphthalenediyl Boron Derivatives

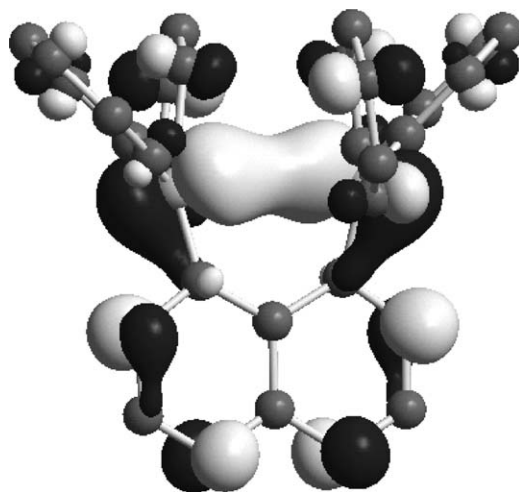
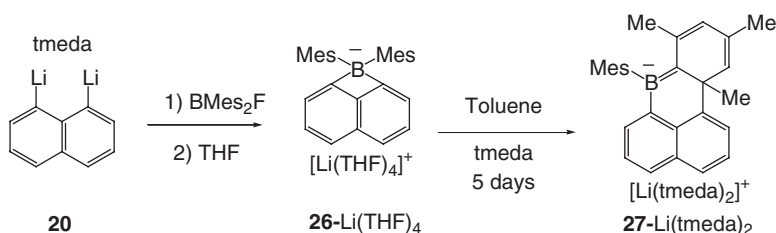
1,8-Diborylnaphthalenes constitute another class of rigid bidentate boranes. The first example of such derivatives were reported by Letsinger who prepared 1,8-naphthalenediboronic anhydride (**20**) from 1,8-dilithionaphthalene (**21**) and tris-*n*-butylborate followed by hydrolysis (Scheme 10).²⁵ While a variety of 1,8-diborylnaphthalenes are known,^{17,26} only a few of them have been investigated as bidentate Lewis acids. Symmetrical examples of such compounds include 1,8-bis(dimethylboryl)naphthalene **22**,²⁷⁻²⁹ 1,8-bis(diphenylboryl)naphthalene **23**³⁰ and 1,8-bis(dichloroboryl)naphthalene **24**.³¹ Compounds **22** and **23** have been prepared

FIG. 3. Structure of the diborane **23**.

by reacting the 1,8-dilithionaphthalene with an excess of the appropriate electrophile, while the tetrachloride **24** has been synthesized by the reaction of 1,8-bis(chloromercurio)naphthalene (**25**) with BCl_3 .³¹

Compound **24** is very sensitive to hydrolysis and affords the 1,8-naphthalene-diboronic anhydride **20** when exposed to moisture. Compound **22**, also referred to as hydride sponge, was prepared by the reaction of 1,8-dilithionaphthalene with dimethylboron ethoxide and isolated as a pale yellow oil.²⁷ A metathesis reaction involving the 1,8-dilithionaphthalene and diphenylboron bromide procedure was also used to generate 1,8-bis(diphenylboryl)-naphthalene **23**.³² The structure of this compound has been determined by X-ray diffraction (Fig. 3). As often encountered in the structure of *peri*-substituted naphthalene derivatives, the naphthalene backbone of this derivative 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, thus allowing for the occurrence of cooperative effects. The structure of this diborane has been computationally optimized using Density Functional Theory (DFT) methods (B3LYP, 6-31 + G* for the boron centers, 6-31G for all other atoms). The optimized geometry is close to that observed in the crystal. It is interesting to note that the Lowest Unoccupied Molecular Orbital (LUMO) bears strong contribution from the boron p_z orbitals which point toward one another (Fig. 4).

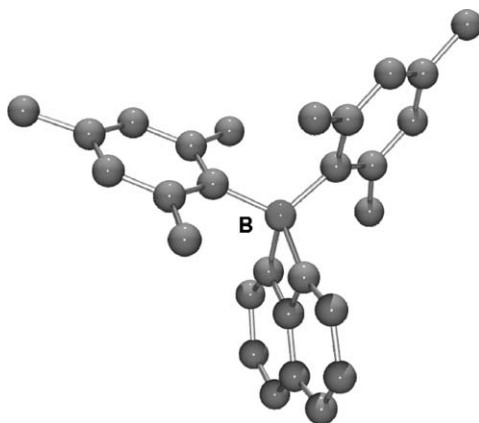
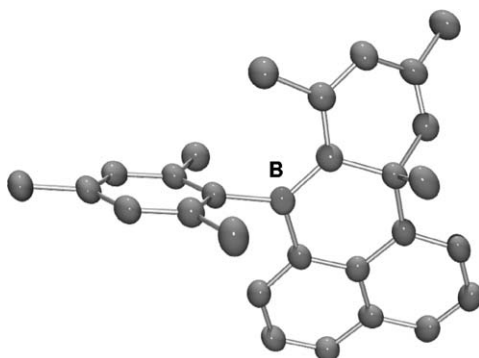
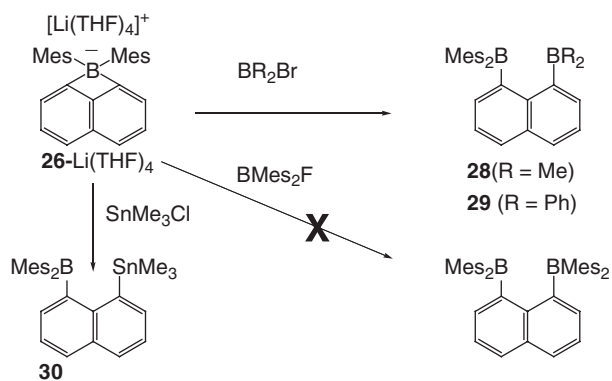
Unsymmetrically *peri*-substituted 1,8-diborylnaphthalenes have also been prepared and investigated as bidentate Lewis acids. The synthesis of such derivatives is non-trivial because it necessitates the sequential introduction of boryl moieties at the *peri*-positions of the naphthalene backbone. Thus far, this strategy has only been applied successfully on few occasions. The reaction of 1,8-dilithionaphthalenediylborate with one equivalent of dimesitylboronfluoride results in the formation of dimesityl-1,8-naphthalenediylborate **26** as a monoborylated naphthalene product (Scheme 11).³² This derivative is the only example of an anionic 1,8-boron-bridged naphthalene derivative. However, it is important to note that Siebert has reported the synthesis and structure of a neutral 1,8-boron-bridged naphthalene derivative which features a (*di-iso*-propylamino)boron moiety bridging the two naphthalene *peri*-carbon atoms.³³ A single-crystal analysis carried out on **26**-Li(py)₄ confirmed

FIG. 4. LUMO of diborane **23** obtained by DFT calculation.

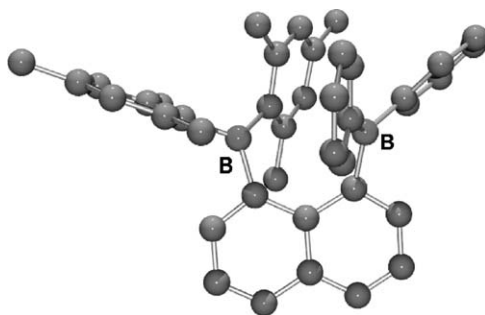
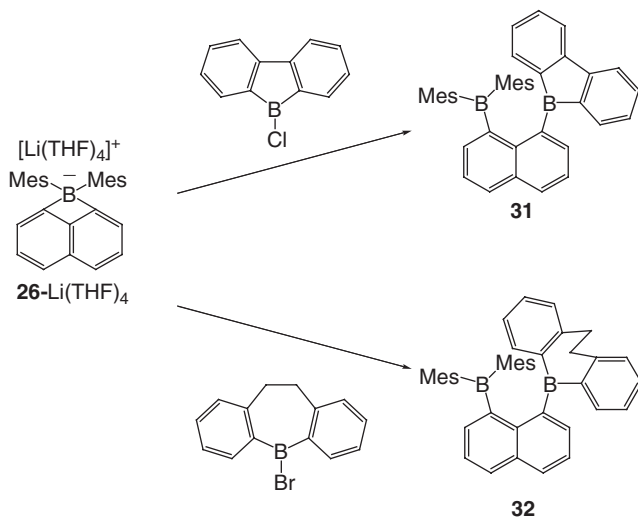
SCHEME 11.

the existence of a strained boracycle as indicated by the values of the endocyclic angles that show considerable contractions ($C-B-C = 80.5^\circ$, $C-C-C = 103.3^\circ$) (Fig. 5).³² Upon standing at room temperature in toluene for an extended period of time, **26** undergoes a ring expansion reaction to afford 8,10,11a-trimethyl-7-mesityl-11aH-7-borata-benzo[de]anthracene (**27**).³⁴ This isomerization reaction allows for a relief of the ring strain present in **26** at the expense of the aromaticity of one of the mesityl substituents. As shown by its crystal structure, compound **27** constitutes a rare example of a bora-alkene and features a carbon–boron double bond of 1.475(6) Å incorporated in a conjugated hexa-1-boratriene system (Fig. 6).

26-Li(THF)₄ undergoes ring opening reactions in the presence of various electrophiles including trimethylstannyl chloride³⁵ and diorganylboronhalides.^{32,34} Thus, reactions with dimethylboron bromide, diphenylboron bromide and trimethylstannyl chloride lead to high yields of 1-(dimesitylboryl)-8-(dimethylboryl)naphthalene (**28**),³⁵ 1-(dimesitylboryl)-8-(diphenylboryl)naphthalene (**29**),³² and 1-(dimesitylboryl)-8-(trimethylstannyl)naphthalene (**30**),³² respectively (Scheme 12). By contrast, reaction of **26** 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. Both **28** and **29** have been fully

FIG. 5. Structure of the borate anion **26**.FIG. 6. Structure of the borataalkene anion **27**.

SCHEME 12.

FIG. 7. Structure of the diborane **29**.

SCHEME 13.

characterized. The crystal structure of **29** indicates that the boron centers are separated by 3.35 Å (Fig. 7). This separation is greater than that observed in **23** and results from the increased steric demand of the boron substituents.

In order to allow for a closer approach of the boron centers, the introduction of flat cyclic boryl moieties with reduced steric hindrance has also been pursued. Thus, the reaction of **26** with 9-chloro-9-borafluorene and 5-bromo-10,11-dihydrodibenzo[b,f]borepin resulted in the formation of diboranes **31** and **32** which bear two different boryl moieties at the *peri*-positions of naphthalene (Scheme 13).³⁴ These diboranes have been characterized by multinuclear NMR spectroscopy and X-ray single-crystal analysis. In **31**, the boron center of the borafluorenyl moiety is π -coordinated by the *ipso*-carbon of a mesityl group with which it forms a contact of 2.730(3) Å (Fig. 8). As a result of this interaction, the boron center involved in this contact is slightly pyramidalized ($\Sigma_{\text{angle}} = 355.7^\circ$). In the case of **32** (Fig. 9), the distance between the boron center of the boracyclic moiety and the *ipso*-carbon of

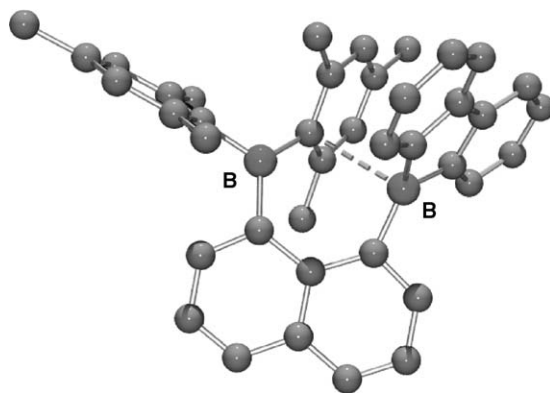


FIG. 8. Structure of the diborane **31** showing the short C_{ipso} -B interaction.

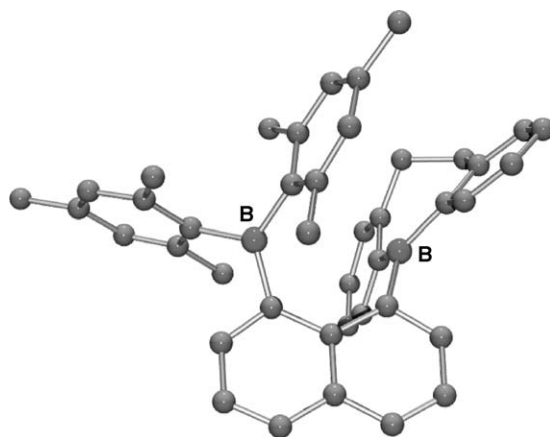
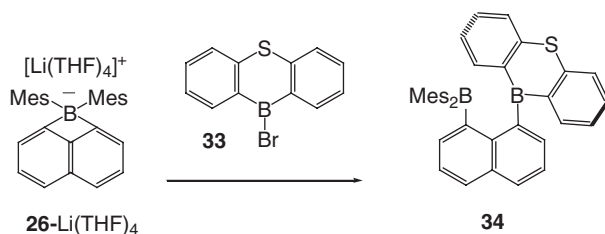


FIG. 9. Structure of the diborane **32**.

the mesityl group is much longer (3.15 Å) indicating a weaker interaction. The differences observed in the structures of **31** and **32** substantiate the increased Lewis acidity of the boron center of **31**. This increased acidity results from the anti-aromatic character of the 9-borafluorenyl moiety, which favors coordination events that remove the boron p-orbital from conjugation.^{36,37} The relief of strain energy in the borole ring upon boron pyramidalization also contributes to the increased acidity of the B(2) boron center.³⁷

In an effort to prepare bidentate boranes as colorimetric anion sensors, the incorporation of chromophoric boron moieties has also received attention. Reaction of 10-bromo-9-thia-10-boranthracene **33** with dimesityl-1,8-naphthalenediylborate **26** affords diborane **34** (Scheme 14).³⁸ This bright yellow diborane is soluble in chloroform, THF and pyridine. It has been fully characterized but its X-ray crystal structure could not be determined experimentally. Its structure was computationally optimized using DFT methods (B3LYP, 6-31+G* for the boron and sulfur



SCHEME 14.

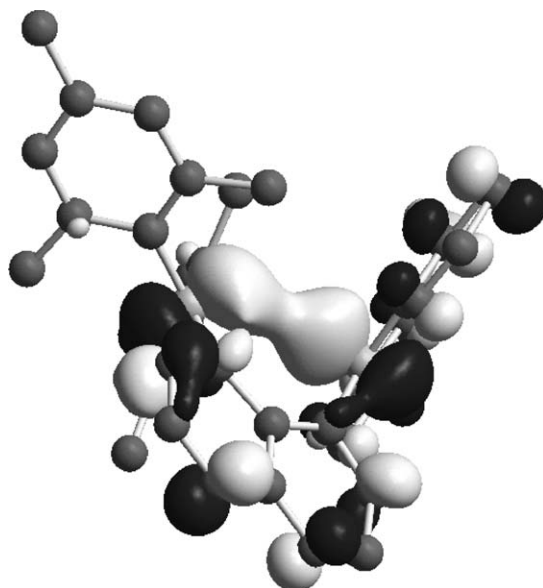
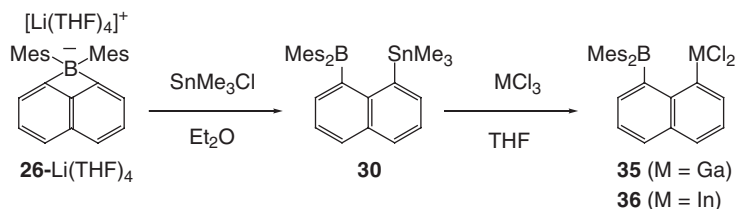


FIG. 10. DFT orbital picture showing the in-phase interaction of boron's empty p AO in the LUMO of **34**.

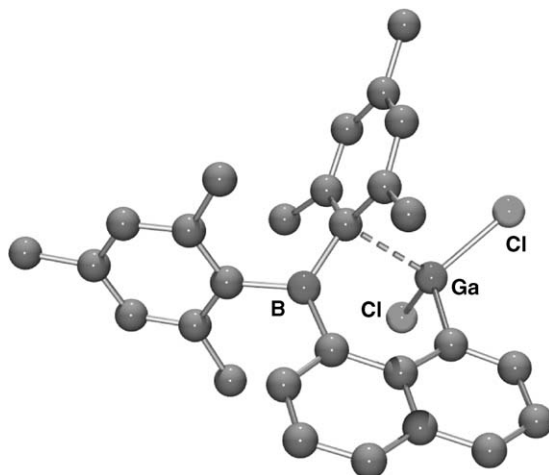
centers and 6-31G for all other atoms, Fig. 10). The optimized geometry is close to that observed for other diboranes bearing a dimesitylboryl group.^{32,34} Most importantly, examination of the DFT orbitals reveals that the boron p_z orbitals contribute to the LUMO and are oriented toward one another in a transannular fashion as observed for 1,8-bis(diphenylboryl)naphthalene.

The UV–Vis spectrum of **34** features a broad band centered at 363 nm, $\epsilon = 17,400 \text{ mol}^{-1} \text{ cm}^{-1}$. As indicated by a time-dependent DFT calculation, electronic excitations from the Highest Occupied Molecular Orbital (HOMO), HOMO-1 and HOMO-2 to the LUMO are the major contributors to this broad band.

Naphthalene-based bifunctional Lewis acids that involve boron and a heavier group 13 element have also been prepared starting from the boron/tin derivative **30** (Scheme 15).³⁵ Thus, the transmetalation reaction of **30** with gallium trichloride or indium trichloride in tetrahydrofuran (THF) results in high yields of 1-(dichlorogallium)-8-(dimesitylboron)naphthalenediyl **35** and 1-(dichloroindium)-8-(dimesitylboron)



SCHEME 15.

FIG. 11. Structure of **35** showing the short C_{ipso} -Ga interaction.

naphthalenediyl **36**. These boron/gallium and boron/indium heteronuclear bidentate Lewis acids have been characterized by multinuclear NMR, elemental analysis, and X-ray single-crystal analysis. Owing to the presence of a short contact between the *ipso*-carbon of a mesityl group and the heavy group 13 element ($C_{ipso}\text{-Ga} = 2.28 \text{ \AA}$, $C_{ipso}\text{-In} = 2.44 \text{ \AA}$), compounds **35** and **36** are best described as intramolecular π -arene complexes and were the first example of such complexes (Fig. 11).³⁹ As shown by ^1H and ^{13}C NMR spectroscopy, this π -interaction subsists in solution. For example, the methyl groups of the mesityl substituents give rise to six distinct resonances. Moreover, the ^{13}C NMR of the mesityl *ipso*-carbon atom coordinated to the heavy group 13 element ($\delta = 120.0$ for **35** and 125.2 for **36**) is shifted to high field when compared to trimesitylboron ($\delta = 144.8$ ppm) providing further proof for the existence of the π -interaction in solution.

B. Aluminum, Gallium and Indium Polydentate Lewis Acids

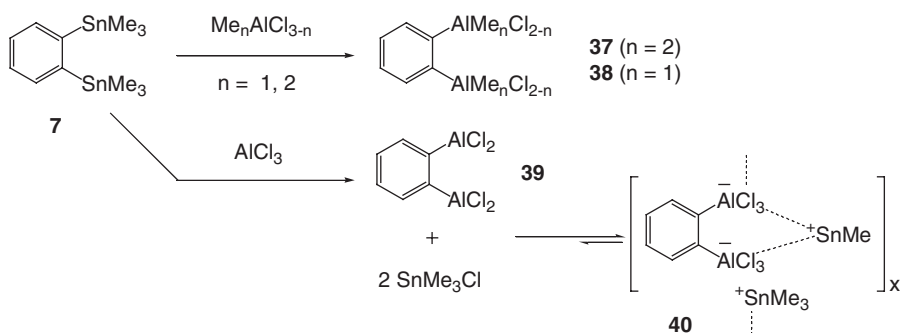
In comparison to their boron analogs, polydentate Lewis acids containing the heavier main group elements are generally scarce. This state of affairs certainly

reflects the synthetic difficulties that might be encountered in the design and preparation of such systems which typically exhibit high air and moisture sensitivity.

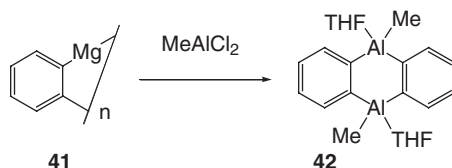
1. *Ortho*-Phenylene Aluminum, Gallium and Indium Derivatives

We note that while tin reagents have often been employed for the organoboron halides,^{19,20,23,24} the use of organostannanes as starting materials can also be applied to the synthesis of heavier group 13 derivatives. In the context of polyfunctional Lewis acid chemistry, this type of reaction has been employed for the preparation of *ortho*-phenylene aluminum derivatives. Thus, the reaction of 1,2-bis(trimethylstannyl)benzene **7** with dimethylaluminum chloride, methylaluminum dichloride or aluminum trichloride affords 1,2-bis(dimethylaluminum)phenylene **37**, 1,2-bis(chloro(methyl)aluminum)phenylene **38** and 1,2-bis(dichloroaluminum)phenylene **39**, respectively (Scheme 16).⁴⁰ Unfortunately, these compounds could not be crystallized and their identities have been inferred from NMR data only. In the case of **39**, the aluminum derivative could not be separated from trimethyltin chloride with which it reportedly forms a polymeric ion pair consisting of trimethylstannyl cations and bis(trichloroaluminate) anions **40**.

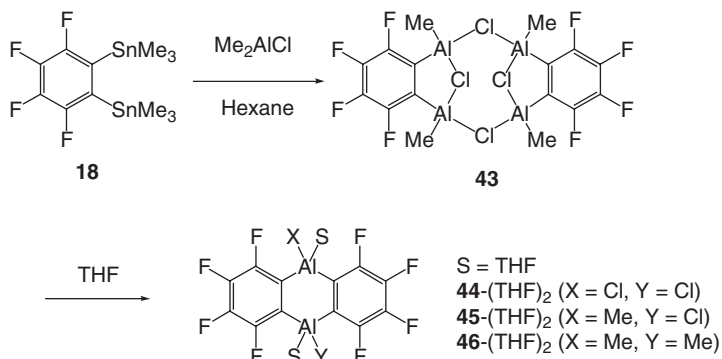
9,10-Dihydro-9,10-dialaanthracene derivatives have also been reported. As shown by Bickelhaupt, the reaction of *ortho*-phenylenemagnesium **41** with MeAlCl₂ leads to the formation of 9,10-dimethyl-9,10-dihydro-9,10-dialaanthracene as a bis(THF) adduct (**42**, Scheme 17).⁴¹ When taken out of solution, crystals of this adduct proved unstable toward THF loss so that the crystal structure could not be determined.



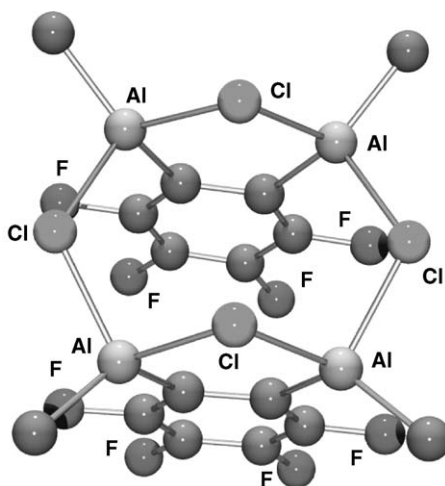
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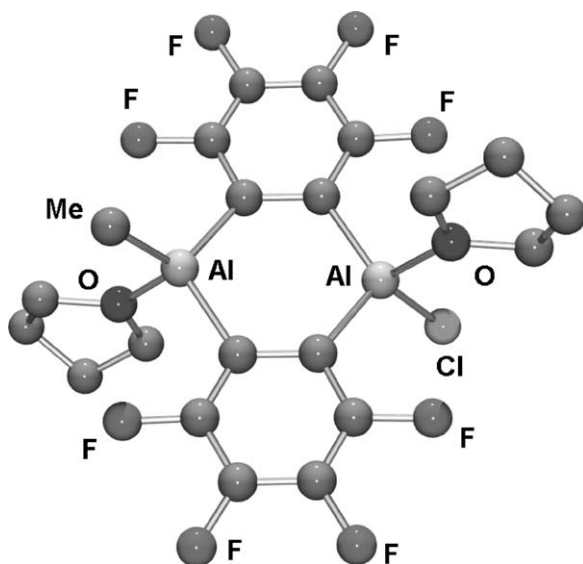
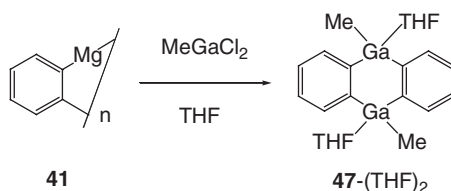
SCHEME 17.



SCHEME 18.

FIG. 12. Structure of **43**.

Efforts to prepare fluorinated analogs of these derivatives have also been made. When 1,2-bis(trimethylstannyl)tetrafluorobenzene (**18**) is allowed to react with dimethylaluminum chloride in hexane, the reaction follows a slightly different course than that observed in the case of 1,2-bis(trimethylstannyl)benzene (**18**) and affords 1,2-bis(chloromethylalumino)tetrafluorobenzene (**43**, Scheme 18). As indicated by X-ray analysis, the molecule has two 1,2-bis(alumino)tetrafluorobenzene units which are connected through an eight-membered (AlCl)₄ ring (Fig. 12).⁴² This compound is not stable when exposed to polar solvents such as THF which induces a ring closure reaction to produce a mixture of 9(X),10(Y)-9,10-diala-octafluoroanthracene species as bis(THF) adducts (X = Y = Cl (**44**), X = Cl, Y = CH₃ (**45**), X = Y = CH₃ (**46**)) as indicated by X-ray crystallography (Fig. 13) and ¹⁹F NMR spectroscopy carried out on the co-crystal of the three derivatives.⁴³ This cyclization reaction is similar to that observed in the case of 1,2-bis

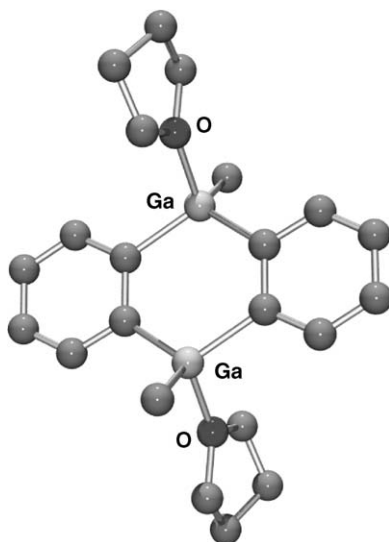
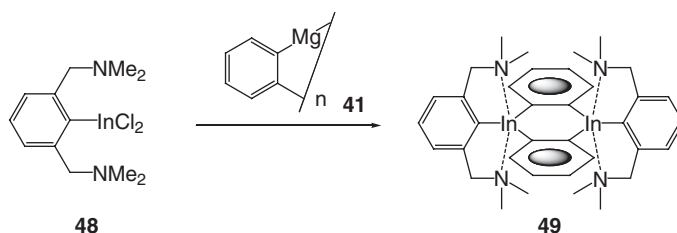
FIG. 13. Structure of the dialuminum derivative **45**-(THF)₂.

SCHEME 19.

(dichloroboryl)tetrafluorobenzene (**14**) which promptly converts into 9,10-dichloro-9,10-dihydro-9,10-diboraoctafluoroanthracene (**15**). Both aluminum atoms of **44–46** are in a distorted tetrahedral environment composed of the *ipso*-carbon atoms of the perfluorinated aromatic ring, the oxygen atom of a THF molecule and the disordered methyl group/chloride ion.

The same strategy has also been applied to the preparation of the corresponding digallium system.⁴¹ Reaction of *o*-phenylene magnesium (**41**) and MeGaCl₂ in THF affords 9,10-dimethyl-9,10-dihydro-9,10-digallaanthracene (**47**) as a bis(THF) adduct (Scheme 19, Fig. 14). The THF ligands could be readily displaced by pyridine to afford the corresponding bis(pyridine) adduct. The latter has been fully characterized. Its structure indicates the presence of two tetrahedrally coordinated gallium centers.⁴¹ In this regard, its structure is comparable to that of the 9,10-dialaanthracene-bis(THF) adducts **44–46**.

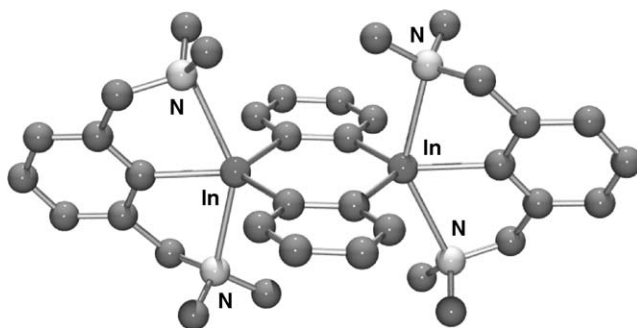
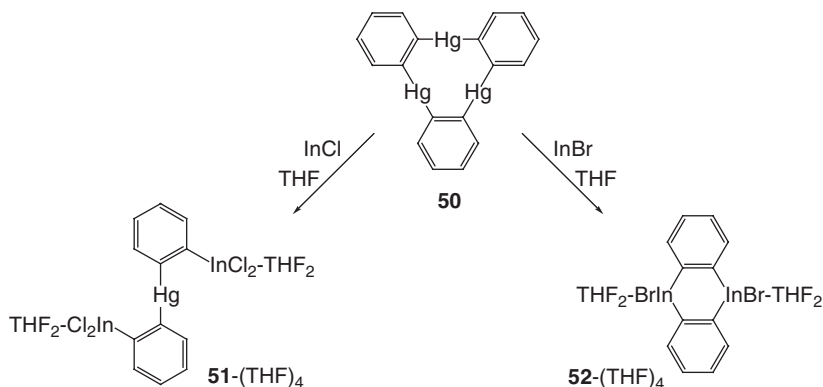
Ortho-phenylene-diindium complexes constitute a well-developed class of derivatives. The indium analog of **42** and **47** has been prepared by the reaction of *o*-phenylene magnesium with methyl indium dichloride.⁴³ The same reaction carried

FIG. 14. Structure of **47**-(THF)₂.

SCHEME 20.

out with 2,6-bis(dimethylaminomethyl)phenylindium dichloride (**48**) instead of methyl indium dichloride also affords the corresponding bimetallic complex **49** which could be isolated in fairly high yield (Scheme 20).⁴⁴ Its crystal structure confirms that each indium center is pentacoordinated (Fig. 15). Because of the constraints imposed by the ligand structure, the coordination geometry of each indium center deviates from an ideal trigonal pyramidal arrangement. The most noticeable distortion affects the N-In-N angle [143.5(2)°] which is much smaller than the expected 180°.

A series of *ortho*-phenylene-diindium complexes have also been prepared by transmetalation of the corresponding poly-mercury derivatives with indium(I) halides. Such transmetalation reactions are very advantageous; they proceed smoothly and yield mercury metal as a sole byproduct, which greatly facilitates the isolation of the target molecule.^{45,46} Trimeric *ortho*-phenylene-mercury (**50**)⁴⁷ is well-known to undergo such transmetalation. The preparation of *ortho*-dilithiobenzene, tetrameric *ortho*-phenylenemagnesium⁴⁸ and dimeric *ortho*-phenylenzinc⁴⁹ are representative examples that demonstrate the importance of this synthetic method. In

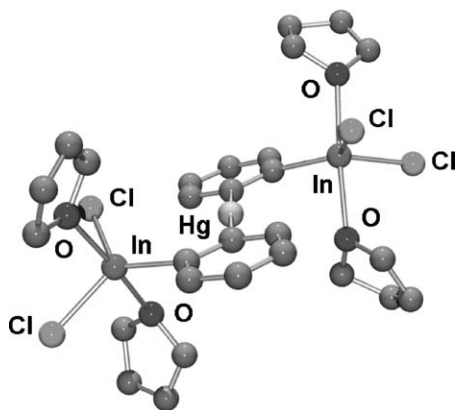
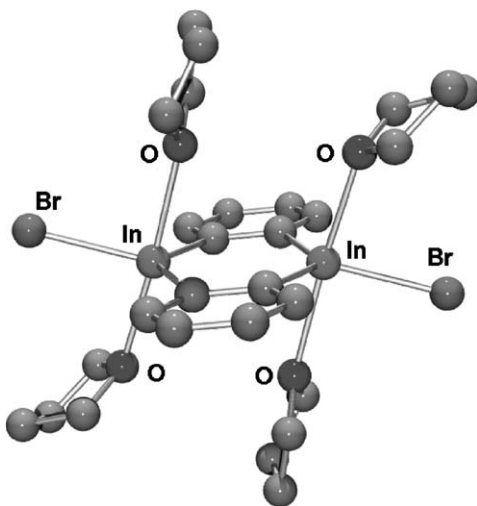
FIG. 15. Structure of **49**.

SCHEME 21.

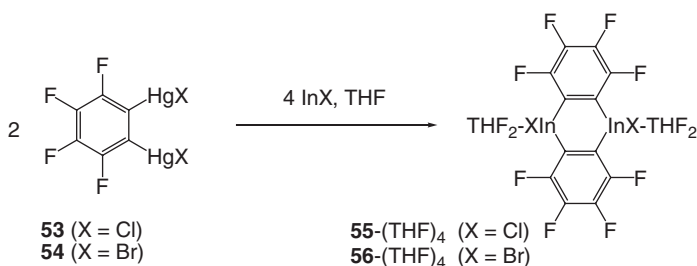
contrast to those clean transmetalations, the equimolar reaction of InCl with **50** takes an unexpected course and yields the heteronuclear trifunctional Lewis-acid **51** which has been isolated as a *tetrakis*(THF) adduct (Scheme 21).⁵⁰

The structure of **51**-(THF)₄ consists of two *ortho*-phenylene indium dichloride moieties linked through a central Hg atom, giving rise to a pseudo-centric core (Fig. 16). The mercury atom is, as expected, linearly coordinated. Each indium atom is penta-coordinated in a trigonal-bipyramidal fashion with two THF molecules at the axial positions and two chloride ligands as well as a phenylene ring at the equatorial sites.

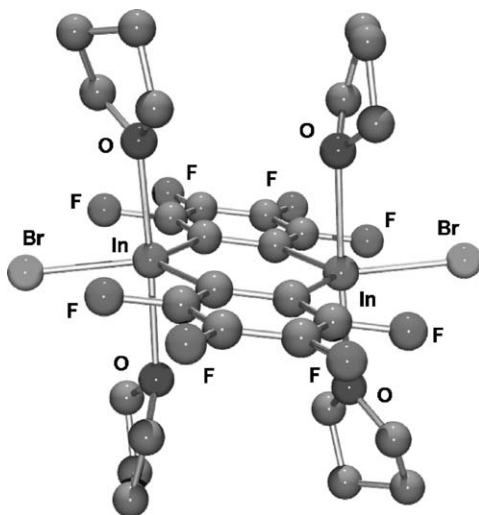
Unlike InCl, InBr reacts cleanly with **50** in THF to afford the *tetrakis*(THF) adducts of 9,10-dibromo-9,10-dihydro-9,10-diindaanthracene **52** in high yield (Scheme 21).⁵¹ Compound **52** crystallizes as a *tetrakis*(THF) adduct with two independent molecules in the unit cell. Both molecules are centrosymmetric (Fig. 17). Each indium atom is pentacoordinated in a trigonal-bipyramidal fashion, with two molecules of THF at the axial positions. Upon standing in a dry inert atmosphere, **52**-(THF)₄ readily loses two equivalents of THF to afford **52**-(THF)₂ as indicated by elemental analysis.

FIG. 16. Structure of **52**-(THF)₄.FIG. 17. Structure of **53**-(THF)₄.

In order to increase the Lewis acidity of the indium centers in compounds such as **52**, the preparation of derivatives that incorporate a tetrafluorophenylene backbone has also been pursued. 1,2-Bis(halomercuro)tetrafluorobenzene (halide = chloride (**53**) or bromide (**54**)) reacts with two equivalents of the corresponding indium(I) halide in THF at 25 °C to afford the *tetrakis*(THF) adduct of the respective 9,10-dihalo-9,10-dihydro-9,10-diinda-octafluoroanthracene (halide = chloride (**55**) or bromide (**56**)) (Scheme 22).⁵² Compound **56** is also prepared by the reaction of (*o*-C₆F₄Hg)₃ (**4**) with InBr in refluxing toluene followed by treatment with THF. The formation of the diindacycles **55** and **56** in the reaction of **53** and **54** with two equivalents of the corresponding indium(I) halide is surprising since, in principle, bis(indiumdihalide) complexes would be the expected products. This cyclization



SCHEME 22.

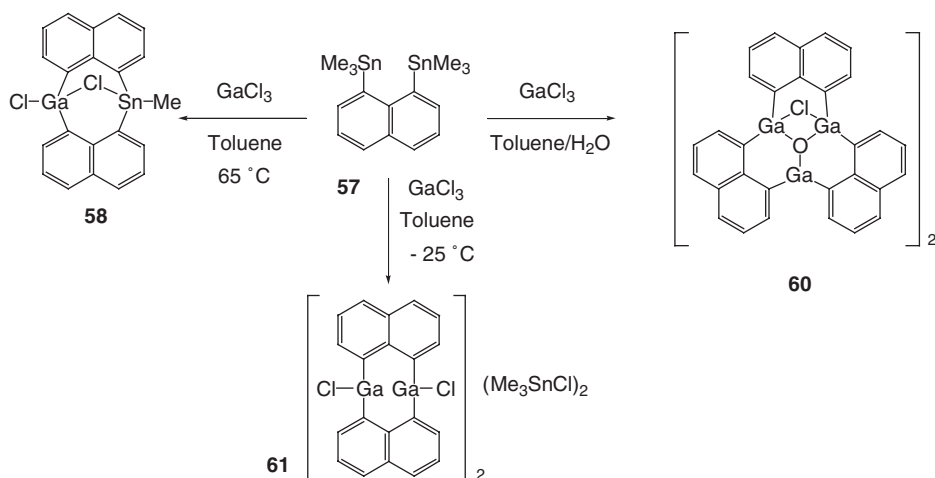
FIG. 18. Structure of $\mathbf{56}\text{-(THF)}_4$.

reaction is reminiscent of that encountered in the case of the tetrafluorophenylene dialuminum complex **43** which also undergoes a ring closure reaction in the presence of donor solvents.⁴³ Compounds **55** and **56** form stable *tetrakis*(THF) adducts which do not lose THF under normal conditions. Thus, their behavior is different from that of $\mathbf{52}\text{-(THF)}_4$, which was found to spontaneously lose two THF molecules at room temperature in an inert atmosphere. This reflects an increase in the Lewis acidity of the indium centers which can be associated with the presence of perfluorinated ligands. Structural studies have been undertaken on several adducts of these diindacycles (Fig. 18). While the structures resemble that of the perprotio-analog, the In–O bonds of $\mathbf{56}\text{-(THF)}_4$ are shorter by 0.08 Å than those of $\mathbf{52}\text{-(THF)}_4$ thus also reflecting the increased Lewis acidity of the indium centers.

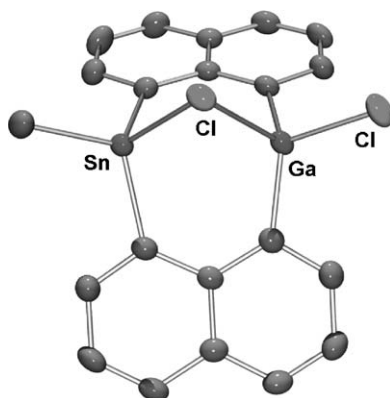
2. 1,8-Naphthalenediyl Gallium and Indium Derivatives

While no aluminum derivatives featuring the 1,8-naphthalenediyl backbone have ever been isolated, several gallium species have been successfully prepared. With the

exception of the mixed boron/gallium derivative **35** mentioned above,³⁵ 1,8-naphthalenediyl gallium derivatives have been prepared by transmetalation of 1,8-bis(trimethylstannyl)naphthalene **57** with GaCl₃.^{53,54} Under strictly anhydrous conditions and upon heating for 6 h at 65 °C, the reaction of **57** with GaCl₃ in toluene leads to high yields of bis(μ-1,8-naphthalenediyl)(μ-chloride)methyltin(IV)chlorogallium(III) (**58**) (Scheme 23).⁵³ Compound **58** adopts an unusual structure in that it features a folded eight-membered dimetallacycle in which the two metals are bridged by a chloride ligand (Fig. 19). Lowering the reaction temperature to -25 °C, leads to a decrease in the yield of **58** 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 [**59**-Me₃SnCl]₂.⁵⁴ The presence of a digallacycle unit in **59** indicates that the complete



SCHEME 23.

FIG. 19. Structure of **59**.

substitution of the stannyl groups of **57** is possible. As shown by ^1H NMR spectroscopy, $[\mathbf{59}\text{-Me}_3\text{SnCl}]_2$ does not retain its structure in pyridine solutions but rather dissociates to give $\text{Me}_3\text{SnCl}\cdot\text{py}$ and solvent-stabilized molecules of the digallacycle. In the presence of traces of water, the room temperature transmetallation reaction leads to a low yield of a third derivative **60** which consists of a 12-membered macrocycle containing three gallium atoms linked by 1,8-naphthalenediyl ligands and arranged about a central oxygen atom. The charge balance of **60** is achieved by the presence of a chloride atom that bridges two of the gallium centers. In the crystal, **60** exists as a dimer wherein the monomers are bridged *via* a Ga–O–Ga–O four-membered ring (Fig. 20). The three gallium atoms are separated by approximately 3 Å and form a nearly equilateral triangle.

In an effort to extend the use of organostannanes as starting materials for organoindium species, the reaction of **57** with InCl_3 in acetonitrile has been investigated (Scheme 24).⁵⁵ Remarkably, this reaction leads to the formation of the diindacycle bis(μ -1,8-naphthalenediyl)bis(chloroindium(III)) (**61**) which could be isolated as a *tetrakis*(pyridine) adduct by subsequent addition of pyridine. It is interesting to note that the *tetrakis*(THF) adduct of this diindacycle has been isolated in trace amounts in the reaction between InCl and 1,8-bis(chloromercurio)naphthalene (*vide infra*). The synthesis that uses the distannyl derivative **57** as a starting material appears to be a worthy alternative since it affords **61** in a 65% yield. Attempts to prepare a non-cyclic 1,8-(diindium)naphthalenediyl complex

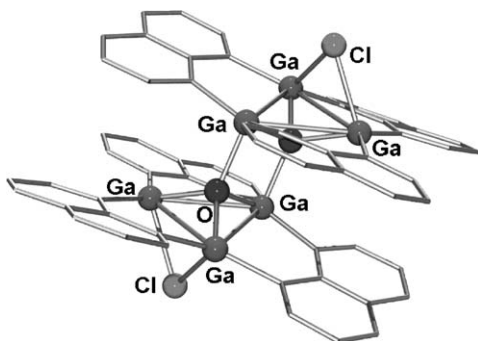
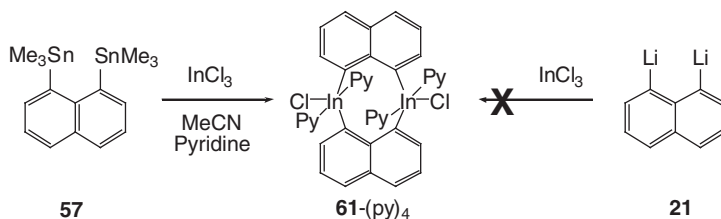
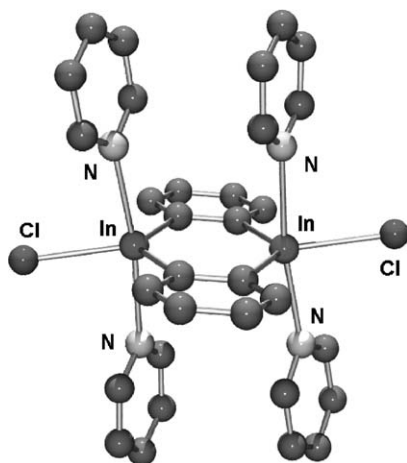
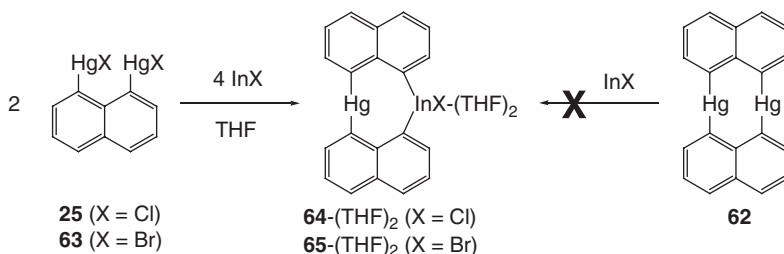


FIG. 20. Structure of **60**.



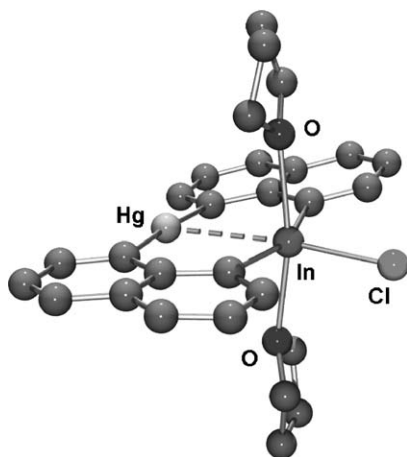
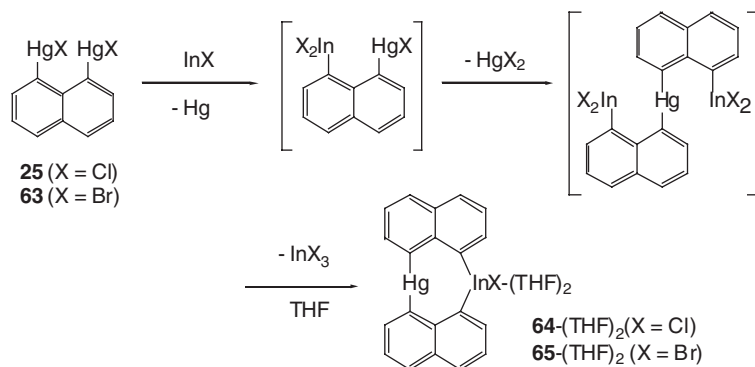
SCHEME 24.

FIG. 21. Structure of **60**-(py)₄.

SCHEME 25.

have not been successful. Even in the presence of an excess of InCl_3 , the reaction depicted in Scheme 24 always affords **61** as the only identifiable product. Attempts to prepare **61** by metathesis have also been pursued. As shown by ^1H NMR spectroscopy, treatment of InCl_3 with an equimolar amount of the 1,8-dilithio-naphthalene in Et_2O affords a 25% yield of the diindacycle. The indium centers of **61** are pentacoordinated in an approximate trigonal-bipyramidal fashion with pyridine ligands occupying the axial sites (Fig. 21). The indium coordination sphere undergoes strong distortions as shown by the value of the C–In–C angle (153.3°).

As for the synthesis of *ortho*-phenylene indium complexes, the transmetalation reactions of organomercurials with indium(I) halides have also been considered for the preparation of 1,8-naphthalenediyl diindium complexes. While the dimercury-cycle **62** fails to react with InBr , 1,8-bis(chloromercurio)naphthalene (**25**) and 1,8-bis(bromomercurio)naphthalene (**63**) react with their respective indium(I) halides to yield the mercura-indacycles **64** and **65** (Scheme 25) which have been isolated as bis(THF) adducts.⁵⁶ The indium center of **65**-(THF)₂ is penta-coordinated and

FIG. 22. Structure of **64**-(THF)₂.

SCHEME 26.

adopts a distorted trigonal–bipyramidal coordination sphere (Fig. 22). The main deviation from an ideal geometry occurs in the equatorial plane as indicated by the large C–In–C angles (150.9°). The most noticeable feature in the structure of **65**-(THF)₂ is the very short transannular Hg···In distance of 3.03 Å. There are no data available for Hg–In bonds. However, this distance is shorter than the sum of the van-der-Waals radii of the two metals (3.6 Å),⁵⁷ close to the sum of the metallic radii (3.12 Å) and just slightly greater than the sum of the Pauling covalent radii (2.94 Å).

The formation of **64** and **65** most probably involves transmetalation of only one mercury center followed by a series of ligand exchange processes leading to a ring closure as shown in Scheme 26. Considering the steric and geometrical constraints in **64** and **65**, such ring closure reactions are remarkable and seem to parallel those involved in the formation of the gallium/tin derivative **58**.⁵³

III

INTERACTION WITH LEWIS BASIC SUBSTRATES

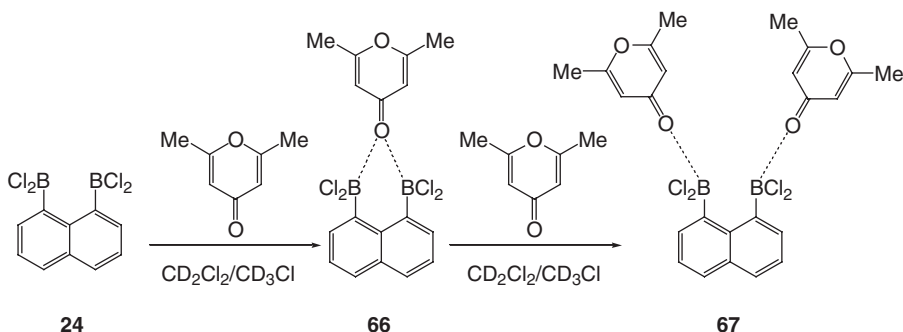
A. Complexation of Organic Substrates

1. Complexation of Organic Carbonyls

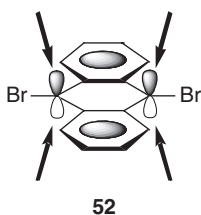
Several reports demonstrate that polyfunctional Lewis acids are valuable catalysts for reactions involving organic carbonyls such as aldehydes and ketones.^{58,59} It has been suggested that the high catalytic activity observed in these reactions is a result of the ability of the bifunctional Lewis acid to chelate the carbonyl oxygen atom. While the double coordination of formamides has been investigated in detail,^{8,10} the knowledge gathered on the chelation of ketones or aldehydes is somewhat limited.^{60–62} The Lewis acidic properties of the tetrachlorodiborane **24** have been investigated in solution. In addition to catalyzing Diels–Alder reactions,⁶³ this derivative forms identifiable complexes with dimethylpyranone (Scheme 27).⁶⁴ Thus, upon addition of one equivalent of dimethylpyranone, formation of the 1:1 complex **24**-(μ_2 -dimethylpyranone) (**66**) is observed. The identity of this complex has been confirmed by IR and ¹H 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 ¹H NMR chemical shifts suggest that the Lewis-acidic strength of **24** is close to that of BCl₃. The 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 (**67**).

2. Complexation of Diazines

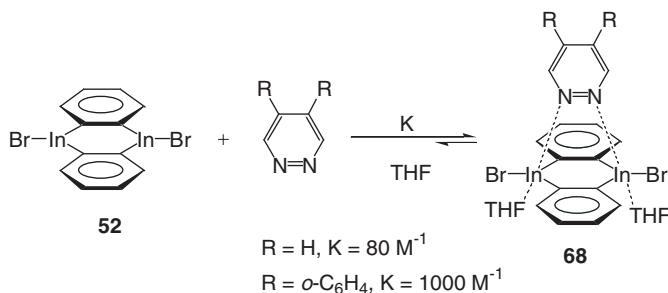
9,10-Dibromo-9,10-dihydro-9,10-diindaanthracene (**52**) contains two electrophilic indium centers positioned at the opposite apexes of a flat six-membered ring (Scheme 28). The specific arrangement of the two indium centers in this molecule indicates that the cooperative binding of bifunctional bases with adjacent basic sites might be attainable.



SCHEME 27.



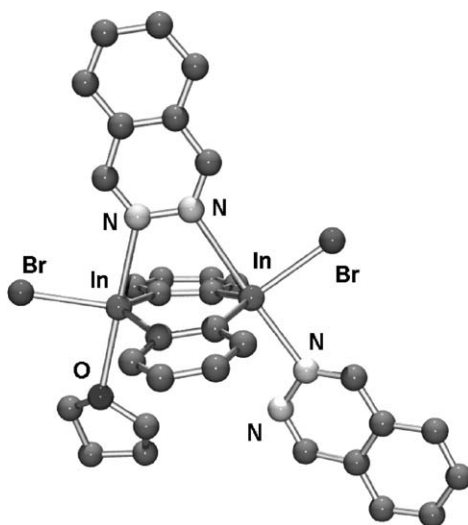
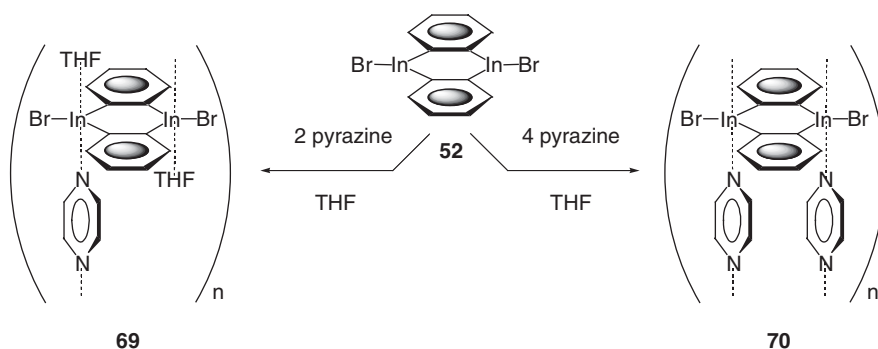
SCHEME 28.



SCHEME 29.

With this in mind, the coordination chemistry of **52** with different diazine structural isomers was investigated.⁶⁵ There were no detectable changes in the ¹H NMR spectrum of **52** in a THF-*d*₈ solution when either pyrazine or pyrimidine were added in 1:1 or 1:2 molar ratios, which suggested that only weak interactions might occur between **52** and these bases. In contrast, incremental addition of pyridazine or phthalazine to a THF-*d*₈ solution of **52** at 25 °C resulted in an upfield shift of the aromatic ¹H NMR resonances of the diindacycle **52** thus reflecting the formation of complexes between **52** and the 1,2-diazines. Analysis of the titration data clearly indicated the formation of 1:1 Lewis acid–diazine complexes **52**-pyridazine-(THF)₂ and **52**-phthalazine-(THF)₂ whose stability constants are equal to 80 (±10) and 1000 (±150) M⁻¹, respectively (Scheme 29). These data, as a whole, indicate that **52** is a selective receptor for 1,2-diazines.

While the 1:1 complex **52**-phthalazine-(THF)₂ seems to be the preferred species in solution, pale yellow crystals of the less soluble 1:2 complex **52**-(phthalazine)₂-(THF) (**68**) spontaneously formed from a saturated THF solution containing equimolar amounts of **52** and phthalazine. As shown in Fig. 23, the diindacycle acts as a ditopic receptor for one phthalazine molecule. Each indium atom adopts a trigonal–bipyramidal coordination geometry. The two nitrogen atoms of the chelated phthalazine molecule occupy one of the axial sites of each indium center. The coordination sphere of the indium atoms is completed by axial ligation of a THF or phthalazine molecule. These results indicate that, as a result of subtle structural variations, the indium p-orbitals of **52** can be brought to converge thus allowing chelation of bifunctional bases with adjacent electrophilic centers.

FIG. 23. Structure of **68**.

SCHEME 30.

Although only weak association takes place between compound **52** and pyrazine in solution, slow cooling of a THF solution of **52** containing one or two equivalents of pyrazine results in the crystallization of polymeric $[\mathbf{52}-(\text{THF})_2\text{-pyrazine}]_n$ (**69**) and $[\mathbf{52}\text{-pyrazine}_2]_n$ (**70**) (Scheme 30).⁶⁶ In **69**, the diindacyclic part of the complex is planar within experimental error (Fig. 24). Each indium atom is in a trigonal-bipyramidal coordination geometry. The axial positions are unsymmetrically occupied by one THF and one pyrazine molecule, respectively. The infinite chains run parallel to one another and do not form any short inter-chain contacts. The monomeric units $[\mathbf{52}-(\text{THF})_2\text{-pyrazine}]$ are linked through a single In–N linkage. All diindacycles are parallel to one another. In turn, chains of **69** are reminiscent of stairs in which the diindacycles would constitute the steps.

The stoichiometry of the assembly of **52** with pyrazine can be conveniently controlled. When the ratio of pyrazine:**52** was increased to four, crystals of a novel

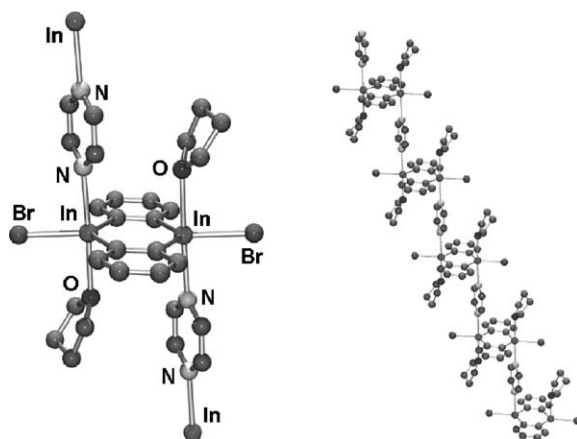


FIG. 24. Structure of **70**. Environment of a diindacyclic unit (left) and view of a portion of the coordination polymer (right).

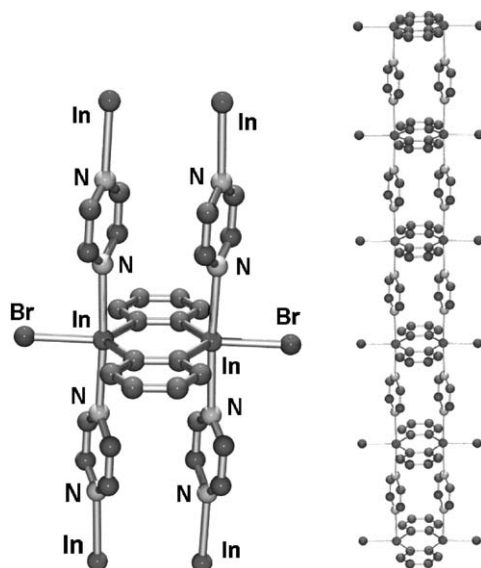


FIG. 25. Structure of **71**. Environment of a diindacyclic unit (left) and view of a portion of the coordination polymer (right). The interstitial THF molecules are not shown.

compound (**70**) spontaneously precipitated (Scheme 30). The ^1H NMR spectrum revealed the presence of two molecules of pyrazine and two molecules of THF per molecule of **52**. Compound **70** crystallizes with two interstitial THF molecules and consists of polymeric $[\mathbf{52}\text{-(pyrazine)}_2]_n$ (Fig. 25). Unlike in **69**, the monomeric units of **70** are assembled through two In–N linkages. Thus, chains of **70** resemble a ladder in which the diindacycles would constitute the rungs, while the $[\text{In-pyrazine}_2]_n$ sequences would constitute the parallel side-pieces (Fig. 25). The space

generated between each step of the ladder approaches closely the shape of a rectangle of $7.8 \times 3.6 \text{ \AA}$. The interstitial THF molecules are positioned half-way between the steps and do not penetrate the cavity deeply enough to be involved in short intermolecular contacts.

B. Complexation of Anions

1. 1,8-Naphthalenediyl-diboranes

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 (**22**) has been investigated as an anion receptor.^{27,28} In the presence of potassium hydride in THF, **22** forms a kinetically and thermodynamically stable 1:1 borohydride complex ($[\mathbf{22}\text{-}\mu_2\text{-H}]^-$) which fails to reduce benzaldehyde (Fig. 26, Scheme 31). In the crystal, both boron centers participate in a $3c\text{-}2e$ bond with the hydride anion, this situation being responsible for the unusual Lewis acidity of **22**. It is noteworthy that the presence of a hydride bridge allows for tetrahedralization of the boron centers, which are only separated by 2.54 \AA . In addition to abstracting hydrides from a variety of substrates such as monofunctional borohydride or zirconocene chloride hydride, **22** readily chelates fluoride and hydroxide anions when treated with $[\text{Me}_3\text{SiF}_2]^-[\text{S}(\text{NMe}_2)_3]^+$ and $\text{NEt}_3/\text{H}_2\text{O}/\text{PPH}_4\text{Cl}$, respectively. While complexation of small anions appears quantitative, **8** does not interact strongly with larger anions such as chloride and bromide.

By contrast, addition of PPNCl ($\text{PPN} = \text{bis}(\text{triphenylphosphineiminium})$) to **24** leads to the formation of the chloride chelate complex $[\mathbf{24}\text{-}\mu_2\text{-Cl}]^-$ (Scheme 32).³¹

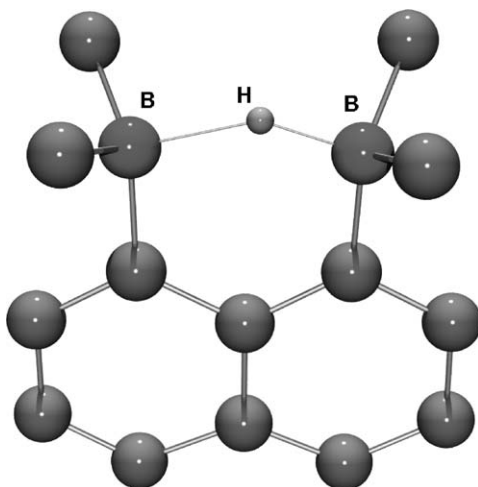
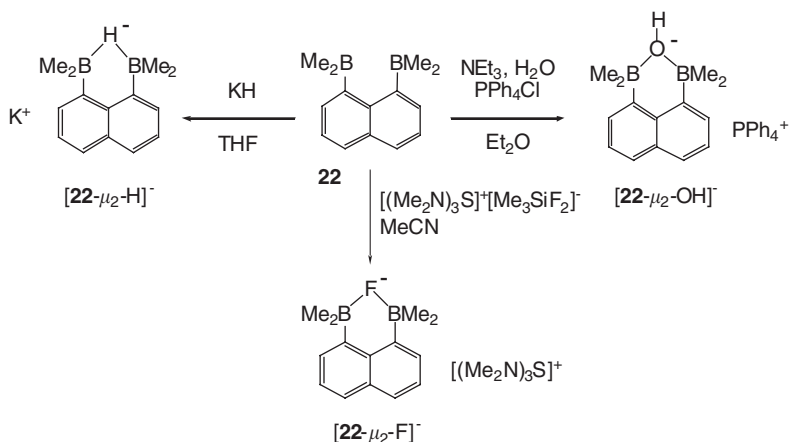
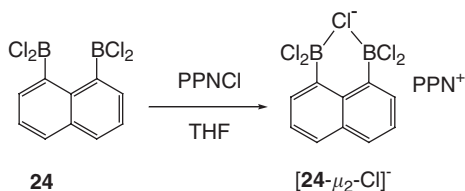


FIG. 26. Structure of $[\mathbf{22}\text{-}\mu_2\text{-H}]^-$.



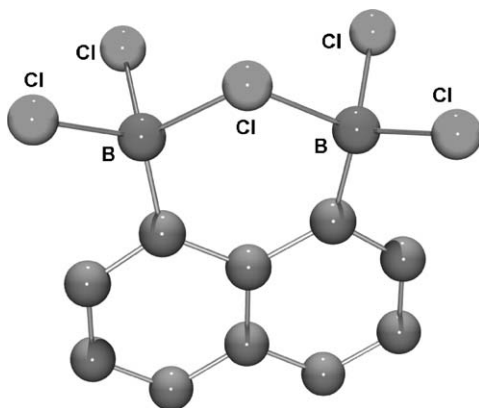
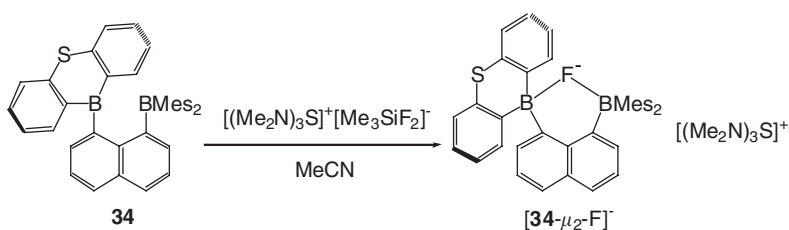
SCHEME 31.



SCHEME 32.

The ^{11}B NMR spectrum of this complex exhibits a peak at 13 ppm which is not affected by the addition of 10 equivalents of PhBCl_2 . This observation points to the greater thermodynamical stability of $[\text{24-}\mu_2\text{-Cl}]^-$ when compared to $[\text{PhBCl}_3]^-$. The crystal structure of the $[\text{Ph}_3\text{PNPPh}_3]^+$ (PPN) salt of $[\text{24-}\mu_2\text{-Cl}]^-$ has been determined and was found to be slightly disordered (Fig. 27). The chloride anion is coordinated to both boron centers with which it forms B–Cl bonds of av. 1.92(1) Å with a B–Cl–B angle of av. 105.8°. As shown by the puckered structure of the resulting 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.

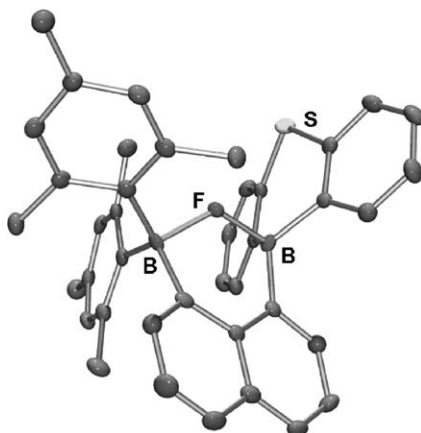
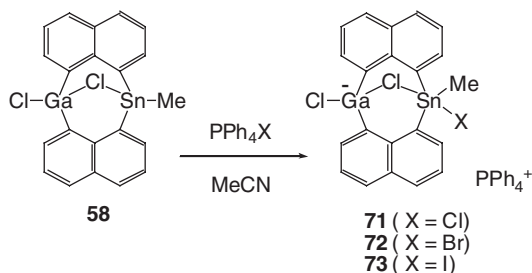
Taking into account the importance of the fluoride anion in the treatment of osteoporosis⁶⁷ and in dental care,⁶⁸ a great deal of effort is currently devoted to the design of selective fluoride sensors.^{69,70} Since 1,8-diborylnaphthalene species constitute ideal molecular recognition unit for fluoride, the bright yellow diborane **34** has been investigated as a colorimetric fluoride sensor.³⁸ In **34**, the boron center is incorporated in a chromophore so that its empty p-orbital strongly contributes to the LUMO of the molecule. Since the LUMO acts as the electron-accepting orbital in the transitions responsible for the yellow color of this molecule, any events leading to the disruption of the LUMO should greatly affect the absorption spectrum of compound **34** and should produce a colorimetric response. In the presence

FIG. 27. Structure of $[24-\mu_2\text{-Cl}]^-$.

SCHEME 33.

of $[\text{Me}_3\text{SiF}_2]^-[\text{S}(\text{NMe}_2)_3]^+$ in THF, compound **34** readily complexes fluoride anions (Scheme 33). This reaction is accompanied by a rapid loss of the yellow color and affords the anionic chelate complex $[34-\mu_2\text{-F}]^-$ which has been fully characterized. The ^{19}F NMR resonance of the bridging fluoride appears at -188 ppm. As confirmed by single-crystal X-ray analysis (Fig. 28), the fluorine atom is bound to both boron centers and forms B–F bonds of comparable lengths (F–B(1) 1.633(5) Å, F–B(2) 1.585(5) Å). The sum of the coordination angles ($\sum_{(\text{C}-\text{B}1-\text{C})} = 347.8^\circ$, $\sum_{(\text{C}-\text{B}1-\text{C})} = 341.2^\circ$) indicates that both boron centers are substantially pyramidalized.

As predicted, fluoride complexation leads to population of the LUMO of **34** and is logically accompanied by an instantaneous loss of the yellow color. Remarkably, no changes in the color of the solution or in the NMR of diborane **34** are observed in the presence of chloride, bromide or iodide anions indicating that the larger halides are not complexed. This finding corroborates earlier observations made by Katz on 1,8-bis(dimethylboryl)naphthalene (**22**).²⁸ Presumably, the size of the binding pocket provided by this bidentate borane can be held responsible for this selectivity. As determined by a UV–Vis titration experiment, **34** complexes fluoride anions with a binding constant of at least $5 \times 10^9 \text{ M}^{-1}$ which exceeds that observed for monofunctional borane receptors by 3–4 orders of magnitude.⁷⁰ The addition of water does not lead to decomplexation of the fluoride anion as typically observed

FIG. 28. Structure of $[34-\mu_2-F]^-$.

SCHEME 34.

for fluoride adducts of monofunctional boranes.⁷¹ These differences substantiate the chelating ability of **34** which leads to the formation of a thermodynamically more stable fluoride complex.

2. 1,8-Naphthalenediyl Gallium Species

The ability of 1,8-naphthalenediyl gallium derivatives to complex anions has also been studied.⁷² Treatment of bis(μ -1,8-naphthalenediyl)(μ -chloride)methyltin-chlorogallium **58** with one equivalent of tetraphenylphosphonium chloride, bromide and iodide in hot acetonitrile results, upon cooling, in the crystallization of the corresponding anionic adduct $[\mathbf{58-X}] [\text{PPh}_4]^+$ (**71**, X = Cl⁻; **72**, X = Br⁻; **73**, X = I⁻) (Scheme 34). The composition and structures of **71**–**73** have been confirmed by elemental analysis and single-crystal X-ray diffraction (Fig. 29). In all cases, the added halide coordinates to the tin center. Thus, unlike in **58**, the tin atom is surrounded by five ligands and adopts a distorted trigonal-bipyramidal geometry. Inspection of the structure of **71** indicates that the bridging chloride ligand (Cl(1)) shifts toward the gallium center upon coordination of an extra halide ligand

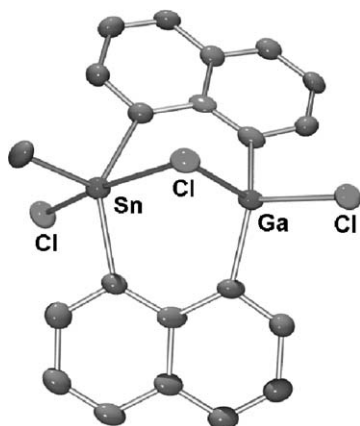
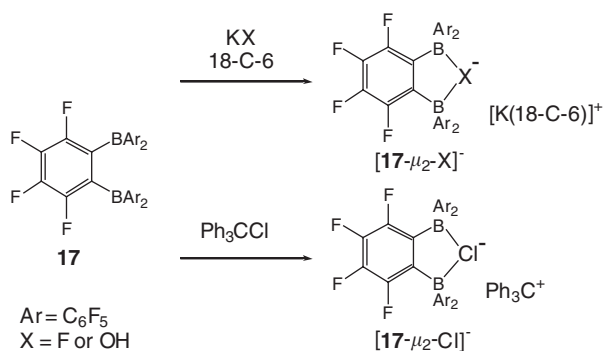


FIG. 29. Solid-state molecular structure of the anionic component of **71**.



SCHEME 35.

at tin. A similar effect is observed in **72** and **73**. These results indicate that the Lewis-acidic gallium and tin centers of **58** cooperate in the binding of anionic substrates. This synergy arises from the presence of a bridging chloride atom by which the gallium center transfers its Lewis acidity to the four-coordinate tin center. In other words, the primary Lewis-acidic site of **58** is the triorganotin chloride moiety whose electron deficiency is enhanced through partial abstraction of its chloride ligand by the neighboring gallium center.

3. *Ortho*-Phenylene Diboranes and Dialanes

Ortho-phenylene diboranes constitute another important class of polydentate Lewis acids which have been considered for the complexation of anions.^{16,15} In this context, most efforts have centered on the study of the ligative behavior of 1,2-bis(bis(pentafluorophenyl)boryl)tetrafluorobenzene (**17**). Similar to **22**, compound **17** forms chelate fluoride ($[\mathbf{17}\text{-}\mu_2\text{-F}]^-$) and hydroxide ($[\mathbf{17}\text{-}\mu_2\text{-OH}]^-$) complexes when treated with KF/18-C-6 and KOH/18-C-6, respectively (18-C-6 = 18-crown-6) (Scheme 35).²¹ The crystal structure of these anionic complexes has not been

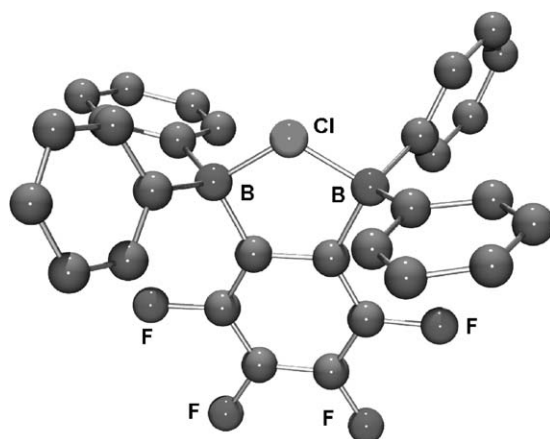
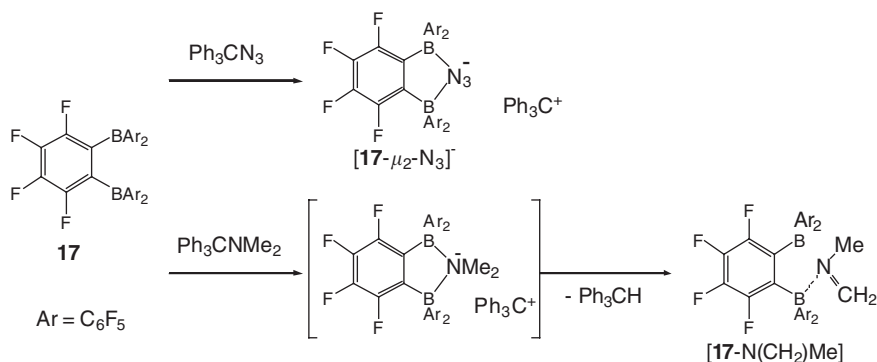


FIG. 30. Structure of $[17-\mu_2\text{-Cl}]^-$. F-atoms from C_6F_5 groups omitted for clarity.

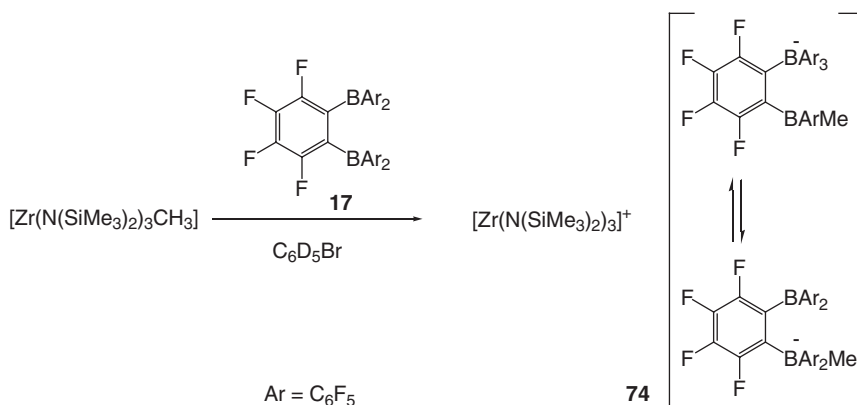
determined. However, NMR data unambiguously support the existence of symmetrical bridged structures. In the case of the fluoride complex $[17-\mu_2\text{-F}]^-$, the bridging fluoride atom gives rise to a ^{19}F NMR resonance at -167.2 ppm. This chemical shift is similar to that observed for the bridging fluoride in the 1,8-diborylnaphthalenes $[22-\mu_2\text{-F}]^-$ and $[34-\mu_2\text{-F}]^-$.^{27,38}

This anionic complex ($[17-\mu_2\text{-F}]^-$) has also been generated as a tritylium salt by the reaction of diborane **17** with $[\text{Ph}_3\text{C}]^+[\text{BF}_4]^-$.⁷³ The ability of **17** to abstract a fluoride from $[\text{BF}_4]^-$ is noteworthy and provides a measure of its Lewis acidic strength. The complexation of chloride has also been examined. Thus, reaction of **17** with Ph_3CCl leads to the formation of $[17-\mu_2\text{-Cl}]^-$ which has been isolated as the trityl salt.⁷⁴ The structure of this salt has been determined by single-crystal X-ray diffraction (Fig. 30). The chloride anion is essentially symmetrically coordinated to both boron centers with which it forms B–Cl bonds of 2.033(2) and 2.040(2) Å. The B–Cl–B angle of $94.34(6)^\circ$ is somewhat acute which suggests that chloride anion might be too large to comfortably sit in the bite provided by **14**. This angle is also more acute than that of 105.8° observed within the six-membered chelate ring of $[24-\mu_2\text{-Cl}]^-$. Bidentate **14** also abstracts chloride from PhMe_2CCl . Although no details are available, it has been reported that dialuminum complexes such as **37**, **38** and **39** are able to abstract the chloride ligand from Cp_2TiMeCl to afford the corresponding metallocenium salt which readily polymerizes ethylene.⁴⁰

In an effort to generate weakly coordinating anions for application in olefin polymerization catalysis, the complexation of alkoxide and phenoxide anion by **17** has also been studied.⁷³ Thus, the reaction of **17** with Ph_3COMe and $\text{Ph}_3\text{COC}_6\text{F}_5$ affords the corresponding complexes $[17-\mu_2\text{-OMe}]^-$ and $[17-\mu_2\text{-O}(\text{C}_6\text{F}_5)]^-$ which have been isolated as trityl salts (Scheme 36). In both cases, the ^{19}F NMR spectra are consistent with C_{2v} symmetry, therefore indicating that their chelate structures persist in solution. Both of these salts have been structurally characterized (Fig. 31). The bridging oxygen atom is trigonal planar in both complexes which contrast with the pyramidal structure of isoelectronic alkyloxonium $[\text{R}_3\text{O}]^+$ salts. The same



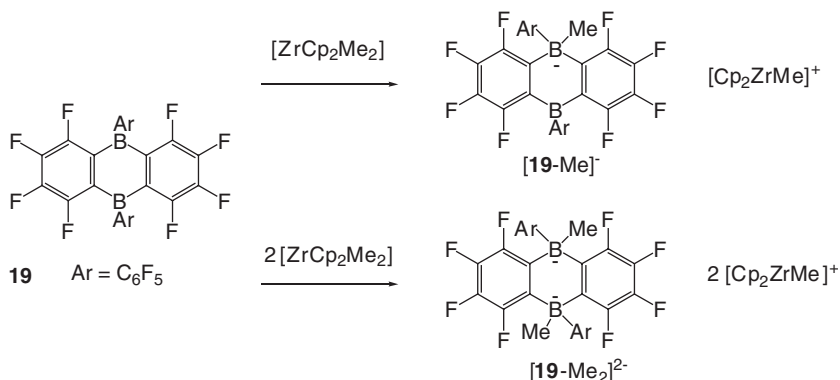
SCHEME 37.



SCHEME 38.

Fluorinated *ortho*-phenylene diboranes have also been considered as neutral methide abstractors. The reaction of **17** with [Zr(N(SiMe₃)₂)₃CH₃] in C₆D₅Br results in methide abstraction and formation of an ion pair containing the [Zr(N(SiMe₃)₂)₃]⁺ cation (Scheme 38).⁷⁵ By contrast with the anionic chelate complexes of **17** which all feature a bridged structure, methide complexation to **17** triggers a ligand redistribution reaction and subsequent formation of a non-bridged borate anion (**74**) as depicted in Scheme 38. In solution, anion **74** exists as a mixture of two structural isomers as indicated by NMR spectroscopy. Diborane **17** also reacts with Cp₂ZrMe₂ to afford the expected metallocenium which, however, slowly decomposes when kept for several days at room temperature in C₆D₅Br.

The fluorinated diboraanthracene **19** has also been investigated as a neutral methide abstractor for Cp₂ZrMe₂.^{23,24,75} Marks investigated the Lewis acidity of this bifunctional borane toward acetonitrile and demonstrated that this derivative is a stronger Lewis acid than B(C₆F₅)₃. Some of the factors contributing to the unusually high Lewis activity of this diborane include the nearly perpendicular conformation of the two C₆F₅ rings which prevents significant π-electron donation to



SCHEME 39.

the boron centers and, possibly, the antiaromatic character of the diboranthracene ring system which will favor any event leading to the removal of the boron empty orbital from conjugation with the *ortho*-phenylene π -electrons. In the presence of one or two equivalents of Cp_2ZrMe_2 , this diborane is able to abstract not only one but also two methide groups to form the corresponding anions (Scheme 39).^{23,24,75} The resulting anions have been characterized by NMR in CD_2Cl_2 . Both anions appear to have static structures on the NMR timescale.

IV

CONCLUSION

As presented in this review, a variety of synthetic strategies are now available for the synthesis of *ortho*-phenylene and *peri*-naphthalenediyl group 13 derivatives. Owing to the development of reliable synthetic strategies, bidentate boranes can be conveniently prepared with a relatively high degree of predictability. Moreover, these boron derivatives can be prepared with various substituents which can be used to control the Lewis acidic or chromophoric properties of the bifunctional boranes. By contrast, the composition and structure of the heavier group 13 *ortho*-phenylene and *peri*-naphthalenediyl derivatives have proved much harder to master. Many reactions are accompanied by unpredicted events such as spontaneous ring closure as in the case of the diindacycles **55**, **56** and **61**. Further complications sometimes result from incomplete substitutions as encountered in the gallium/tin derivative **58** and the mercuraindacycles **64** and **65**. The most attractive sets of properties so far discovered concerned that ability of the diboranes to complex small anions. The bright yellow diborane **34** serves as a sensor for fluoride anions. The charge neutrality of this sensor as well as the short space available between the boron centers makes this sensor highly selective for fluoride. It is also important to note that by virtue of its bidentate nature, the fluoride association constant is remarkably high and by far exceeds that measured for monofunctional borane receptors. The fluorinated diboranes also show a high affinity for anions. For example, the fully

fluorinated bidentate Lewis acid **17** forms extremely stable anionic complexes with pentafluorophenoxide. The resulting anion is remarkably robust and by virtue of its large size, weakly coordinating, a set of properties which makes it useful in olefin polymerization catalysis.

ACKNOWLEDGMENTS

We would like to thank the National Science Foundation (CAREER CHE-0094264), the Welch Foundation (Grant A-1423) and the Lavoisier from the French Ministry of Foreign Affairs (grant to M.M.).

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