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BOROXINE CHEMISTRY: FROM FUNDAMENTAL STUDIES TO APPLICATIONS IN SUPRAMOLECULAR AND SYNTHETIC ORGANIC CHEMISTRY

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Abstract – Organoboroxine chemistry has recently received much attention because the boroxine formation reaction is a powerful tool for the construction of organized architectures. The reversible nature of this reaction may result in new materials that possess unprecedented levels of structural organization due to facilitation through self-correction, and switchable properties can be imparted by the reaction's reversibility. In addition, the effectiveness of boroxines (especially arylboroxines) has been recognised in the field of organic synthesis. The chemical properties of boroxines are certainly of great interest in organic synthesis and in the creation of new organic compounds. In this review, I describe the development of various molecular architectures that originate from the fundamental properties and structures of boroxines; I also describe the use of boroxines as reagents and catalysts.

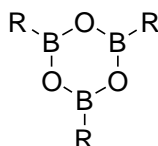
CONTENTS

1. Introduction
2. Structure and Lewis Acidity of Boroxine
3. Synthesis and Formation of Boroxine
 - 3-1. Synthesis of Boroxine
 - 3-2. Reversibility of Boroxine Formation and its Thermodynamic Stability: Experimental and Computational Considerations
 - 3-3. Formation of Hetero-Boroxine
4. Utility of Boroxines as a Reagent and a Catalyst in Organic Synthesis
 - 4-1. Utility of Boroxines as Vinyl and Aryl Sources in Organic Synthesis

- 4-2. Utility of Boroxine as a Catalyst in Organic Synthesis
5. Construction of Covalent Organic Frameworks by Boroxine Formation Reaction
6. Utility of Boroxines in Supramolecular Chemistry
 - 6-1. Ferrocenylboroxine Chemistry
 - 6-2. Utility of Boroxines in Polymer Chemistry
 - 6-3. Boroxine as an Electrolyte Material
 - 6-4. Two-Dimensional and Three-Dimensional Molecular Architectures Based on Boroxine in the Solid State
 - 6-5. Construction of Interlocked Molecule by the Boroxine Formation Reaction in Solution
7. Summary and Outlook

1. INTRODUCTION

Boroxine, a cyclic anhydride of three boronic acids, is a typical inorganic benzene (Figure 1), and the fundamental properties of boroxine have been studied from an early stage.¹ For example, the aromaticity of boroxine has been previously discussed because of the good stability of boroxine and the electronic character of oxygen and boron atoms, which possess two lone pairs and a sextet of electrons, respectively.² However, at present, it is accepted that triorganoboroxines have little aromatic character.³⁻⁸ In addition to these theoretical and fundamental investigations, boroxine has also been of interest to synthetic chemists as an alternative compound to boronic acid for performing the Suzuki–Miyaura coupling reaction.⁹ Subsequently, boroxine was found to have numerous uses in the field of organic synthesis. Lewis acidity, a fundamental property of boroxine, has also been studied.¹⁰ The utility of Lewis acidic boroxine has been demonstrated in materials science¹¹ (i.e. in materials for lithium-ion batteries) and in the construction of supramolecular structures. Recently, a turning point in boroxine chemistry was reported by the Yaghi group,¹² who demonstrated that the formation of boroxine is useful in the preparation of covalent organic frameworks.



boroxine

Figure 1

In this review, I will first present a general introduction of boroxine chemistry and describe a number of recent and previous studies I consider to be interesting. Second, I will discuss the applications of boroxine in the field of organic synthesis as a reagent and catalyst. Third, I will show that the boroxine structure and its formation process can play critical roles in the construction of supramolecular structures in

supramolecular chemistry and materials science. Especially well-known triarylboroxine chemistry will be mainly described. I would like to draw attention to excellent reviews on boron-containing organic compounds, including boronic acids,¹³ boronic esters¹⁴ as well as boroxines.¹⁵

2. STRUCTURE AND LEWIS ACIDITY OF BOROXINE

The crystal structure of triphenylboroxine **1a** was reported by Brock's group; the structure of the central boroxine skeleton was close to a flat and regular hexagon, and the bond angles in the boroxine ring were close to 120° (Figure 2).¹⁶ The three phenyl rings attached to three boron atoms were approximately coplanar with the boroxine ring and the coplanarity of the fourth ring of triphenylboroxine was similar to that of the triphenyltriazine (**2a**) structure (not 1,3,5-triphenylbenzene **2b**). It was expected the lone pairs of electrons on oxygen atoms to be less sterically demanding than the hydrogen atoms on the central benzene in triphenylbenzene.

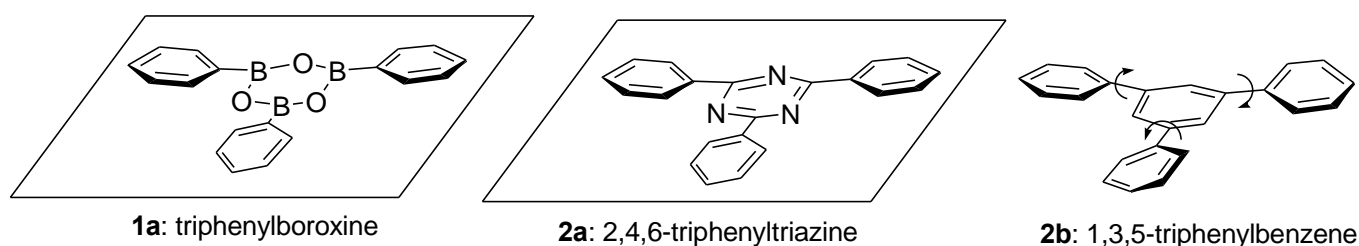


Figure 2. Coplanar structure of triphenylboroxine **1a**

Lewis acidity of boroxine has been reported by numerous researchers. In 1932 and 1933, Yabroff predicted the existence of a dianhydride of three boronic acid molecules and its adducts with several amines.^{17,18} However, the structure and nature of the bond between the amine and boroxine ring were not known with certainty. After several decades, structures of amine-adducted triphenylboroxines were proposed on the basis of IR and NMR spectrometry. Finally, Yalpani reported the X-ray crystal structure of phenylenediamine-adducted triphenylboroxines. In the solid state, for example, one 1,4-diazabicyclo[2.2.2]octane molecule was found to be directly involved in the adduct structure,¹⁹ and a 1:2 adduct of 1,4-diazabicyclo[2.2.2]octane with triphenylboroxine (boroxine ring/nitrogen atom = 1) was observed. The distance between the *N*-coordinated boron and carbon atoms (and oxygen atoms) was greater than that between the noncoordinated boron and carbon atoms (and oxygen atoms), and the O-B-C (*N*-coordinated) bond angle was 113° in the pyridine–phenylboroxine adduct.⁸ ¹H NMR investigations supported the formation of a 1:1 adduct of triphenylboroxine with quinuclidine but showed equivalence of three boron atoms in solution at room temperature. However, at low temperatures, the ¹H NMR signals split into two groups, which integrated in a 2:1 ratio. These NMR results showed that the coordination bond reversibly formed and that at room temperature, the rate was fast on the NMR time scale (Figure 3).

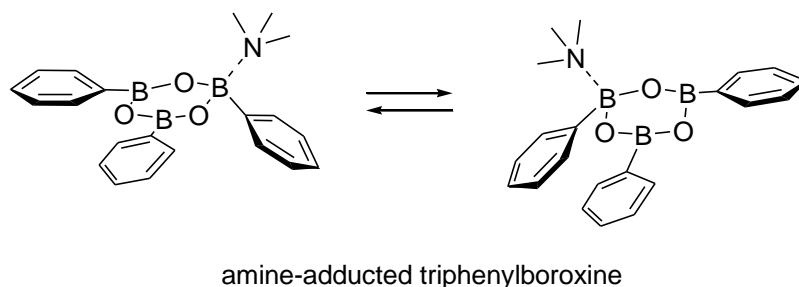


Figure 3. Complexation of triphenylboroxine and amine and its reversible coordination

The 7-azaindole (**3**) adduct of triphenylboroxine (**1a**) was studied by Wang's group.²⁰ The crystal structure of the adduct showed the presence of a hydrogen bond between the hydrogen of the azaindole NH and the oxygen of boroxine as well as B–N interactions (Figure 4). They performed variable temperature (VT) NMR experiments and showed that the activation energy of the intermolecular association–dissociation process of the azaindole and boroxine was 34 kJ/mol in CD₂Cl₂. This activation energy was lower than that of the pyridine–boroxine adduct (39 kJ/mol). The group attributed the low activation energy to the assistance of hydrogen bonding and the reduced base strength of the azaindole.

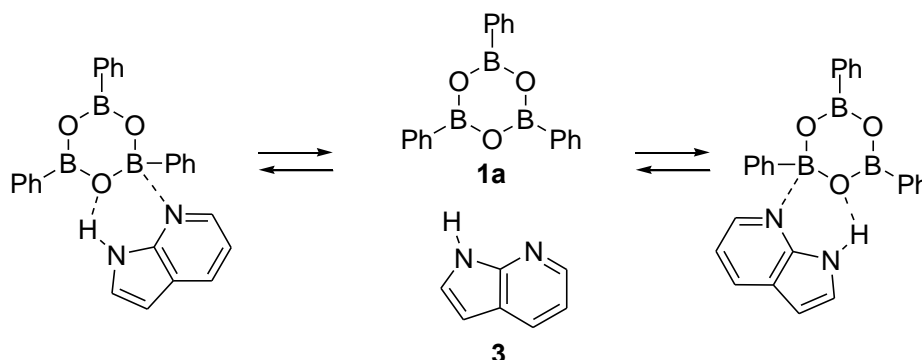
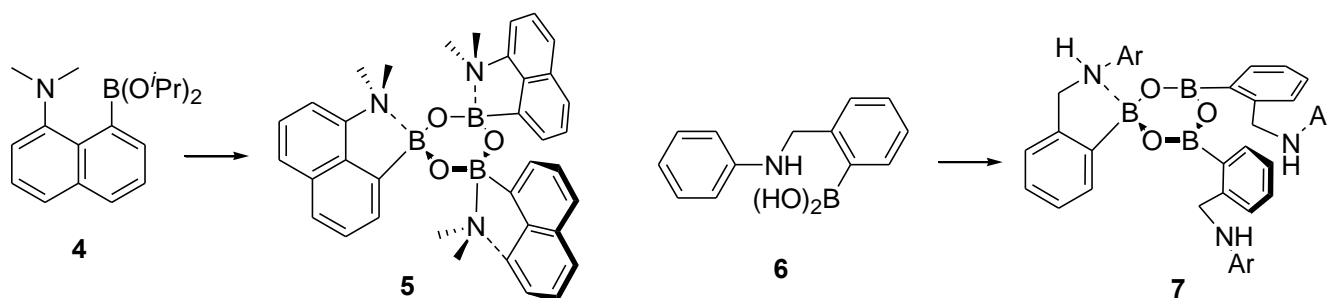


Figure 4. Association–dissociation process of 8-azaindole **3** and triphenylboroxine **1a**

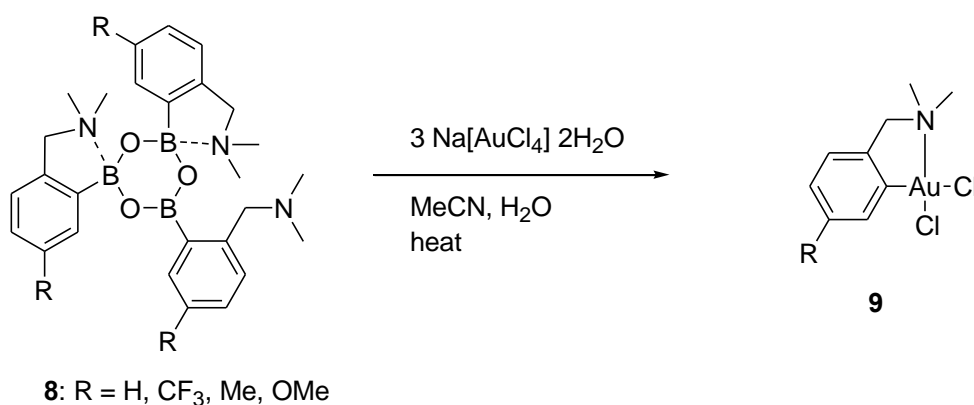
Whiting *et al.* reported the solid-state structure of the boroxine prepared from 1-*N,N*-dimethylamino-8-boronaphthalene **4** (Scheme 1, left).²¹ The X-ray structure of boroxine **5** revealed that all neighbouring nitrogen atoms forced intramolecular N–B interactions to occur, providing partial quaternisation at the boron centre. The weak nature of the N–B interactions was evidenced by a C–B–N bond angle of 92° and a C–N–B bond angle of 103°. Moreover, the fact that the naphthalene rings were nearly perpendicular to the boroxine core was interesting. However, proximal placement of the nitrogens of the amines does not always result in interactions with the borons of arylboroxines. When James *et al.* attempted to prepare a new boronic-acid-based saccharide sensor (**6**) bearing an aniline

moiety, they clarified the crystal structure of boroxine **7** (Scheme 1, right).²² In the solid state, only one of the units contained a B–N bond.



Scheme 1

Recently, Flower *et al.* successfully formed a gold(III)–carbon bond using amine-adducted boroxines **8** as precursors; the X-ray structures of **8** revealed two B–N bonds in the solid state (Scheme 2).^{23,24} Many catalytic reactions use proposed gold(I)/gold(III) redox systems to enable C–C coupling with arylboronic acids, and one of the proposed mechanisms involves transmetalation from the arylboronic acid to gold(III). Refluxing of a solution of intramolecular amine-adducted boroxines **8** and sodium tetrachloroaurate in an aqueous solution gave the corresponding gold(III) complexes **9**. They proposed that the boroxine hydrolysed in situ and that the free nitrogen coordinated to the gold centre prior to transmetalation.



Scheme 2

Recently, the interactions between halide anions and boroxine ring(s) were discussed by Mascali through computational studies.²⁵ He calculated the interaction energies and noncovalent bond distances for complexes **10** containing cylindrophanes and halogen anions (Figure 5, left). In all cases, these cylindrophanes could form stabilized complexes **10** with fluoride anions, and the boroxine-containing cylindrophane was suggested to exhibit particularly high selectivity for fluoride ions. More recently,

Frontera *et al.* reported a theoretical *ab initio* study of anion- π interactions in inorganic rings, including boroxine (Figure 5, right).²⁶ They also showed that interactions between boroxine and fluoride ions were favourable.

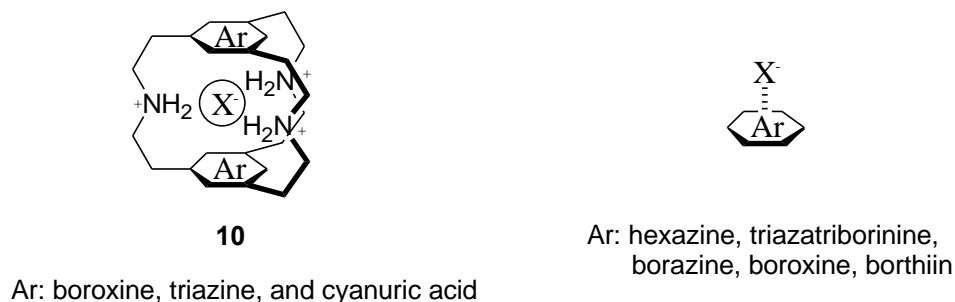


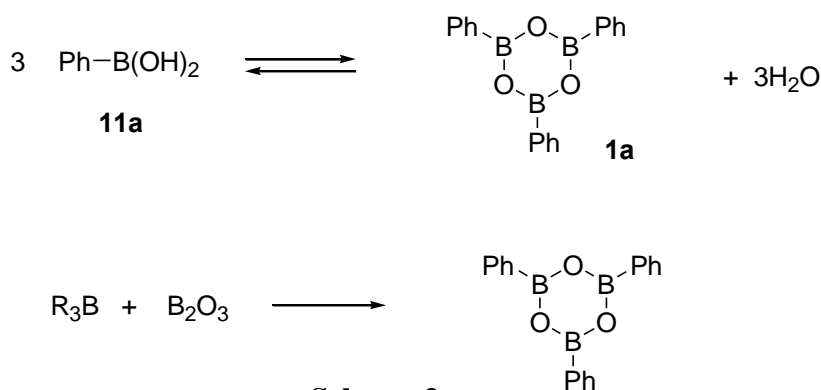
Figure 5

3. SYNTHESIS AND FORMATION OF BOROXINE

3-1. Synthesis of Boroxine

The conversion of boronic acid into the corresponding boroxine is well known; phenylboronic acid **11a** is dehydrated by simple heating (Scheme 3).^{27,28} Although the acid is stored in a bottle at room temperature, it gradually changes to the corresponding boroxine. In contrast, the recrystallisation of the boroxine from water can give the corresponding boronic acid. These phenomena show that the dehydration of the acid and the hydrolysis of the boroxine proceed reversibly in the absence of any additives.

Another method for the preparation of boroxine has also been reported. The reaction of triorganoboranes with boric oxide gives the corresponding boroxine in good yield, synthesis of trialkyl- and triphenylboroxines were reported (Scheme 3).²⁹

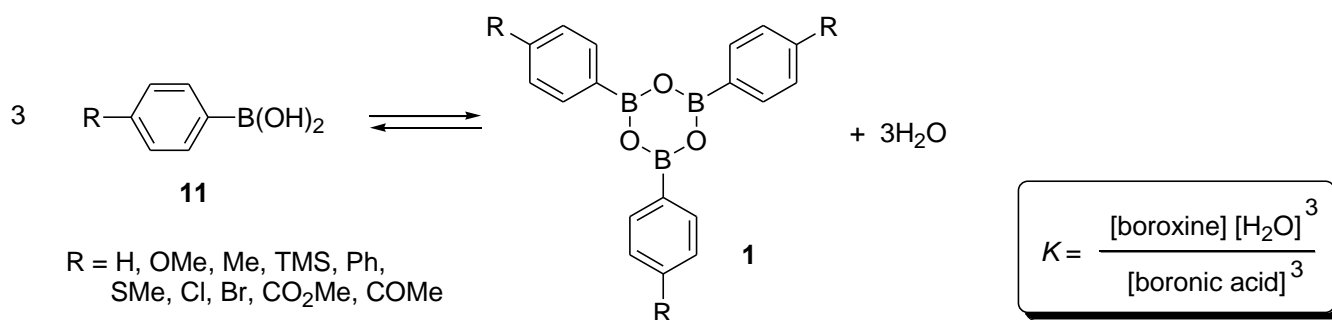


Scheme 3

3-2. Reversibility of Boroxine Formation and its Thermodynamic Stability: Experimental and Computational Considerations

The dehydration and hydrolysis processes proceed reversibly for boroxines, as shown in the previous section. Boroxines and boronic acids can be obtained under dehydration and aqueous conditions,

respectively. However, the equilibrium constants for these processes have not been discussed until quite recently. We have previously determined the equilibrium constants of arylboroxine formation (Scheme 4).³⁰ We prepared chloroform solutions of several arylboronic acids **11** that contained corresponding arylboroxines **1** with electron-donating or -withdrawing groups at the *para*-position in the benzene ring and systematically analysed their stability in the presence of water using NMR spectroscopy. The experiments revealed that both reversible reactions proceeded smoothly even at room temperature and that the electron-donating groups supported the formation of the arylboroxine. Furthermore, at first, the process involving the construction of rigid boroxines would appear to be entropically unfavourable. However, this process involves the release of three free water molecules from boronic acid to the bulk solvent. The formation of the boroxine incurs an enthalpic cost, but this cost is counteracted by a larger entropy gain.



Scheme 4

Kua and Iovine presented the results of calculations for triarylboroxine formation from boronic acids and the effects of *para*-substituents on the relative stabilities of the two species.³¹ Our experimental trend with respect to equilibrium constants of boroxine formation and their computational results were in good agreement. They also performed calculations for subsequent boroxine complexation by a nitrogen donor compound. Their calculations showed that all ΔH values were negative for amine-adducted boroxine formation and the adduct bearing electron-withdrawing substituents at the *para*-position are more enthalpically favourable among the reactions between substituted triphenylboroxine and ammonia, as expected from the Lewis acidities of the boroxines. The total ΔH values for the formation of ammonia-adducted arylboroxines from boronic acid monomers were still negative; however, the values for the adduct with electron-donating substituents (i.e. OMe) were close to zero. Furthermore, they discussed the fact that the mono-ammonia-adducted boroxine was enthalpically more stable than the diammonia-adducted boroxine. They validated the calculation through NMR experiments:³² the total free energies (from boronic acids to pyridine–boroxine adducts) were negative and the electron-withdrawing substituents had a more negative free energy change than the electron-donating substituents. They

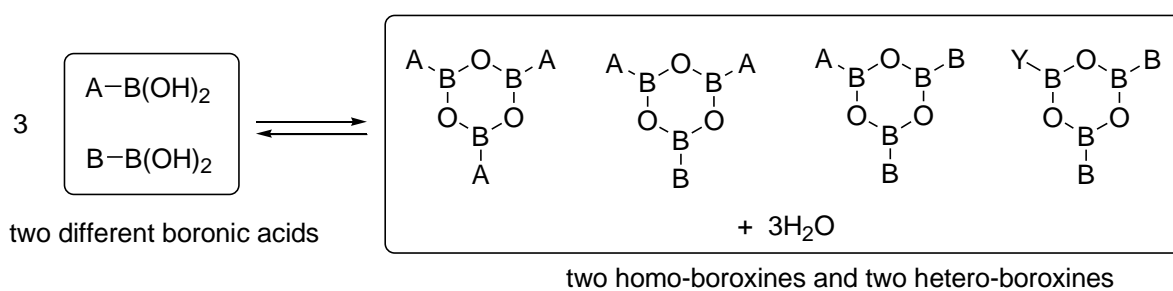
extended these studies to predict the possible intermediates and reported a computational study of the thermodynamics and kinetics of aliphatic boroxine and amine-boroxine complexation.^{33,34}

3-3. Formation of Hetero-Boroxine

After the thermodynamic stability of homo-arylboroxines was revealed by experimental and computational studies, in a previous study, we examined hetero-arylboroxines, which consist of different aromatic components.³⁵ The construction of hetero-boroxines appears to be straightforward when two boronic acids are mixed in a suitable solvent because the formation processes of both boroxine and boronic acid proceed reversibly. We used several symmetrical arylboronic acids **11b–e** and mixed two of them to analyse the resulting homo- and hetero-boroxines using ¹H NMR spectroscopy (Scheme 5). Integration of the signals of the seven species (two boronic acids, two homo-boroxines, two hetero-boroxines and water) present in the ¹H NMR spectra afforded the equilibrium constants (*K*) for the formation of four boroxines at several temperatures. These results showed that entropically driven forces and electron-donating groups in the *para*-position of the phenyl ring promoted the formation of hetero-boroxines, as in the case of homo-boroxines. Moreover, based on a statistical distribution of 1:3:3:1 for a mixture of equally stable members in a binary mixture of two boronic acids, the equilibrium constants of the hetero-boroxines were greater than those of the homo-boroxines. This concept (formation of four boroxines using two boronic acids) relies on the dynamic combinatorial library.

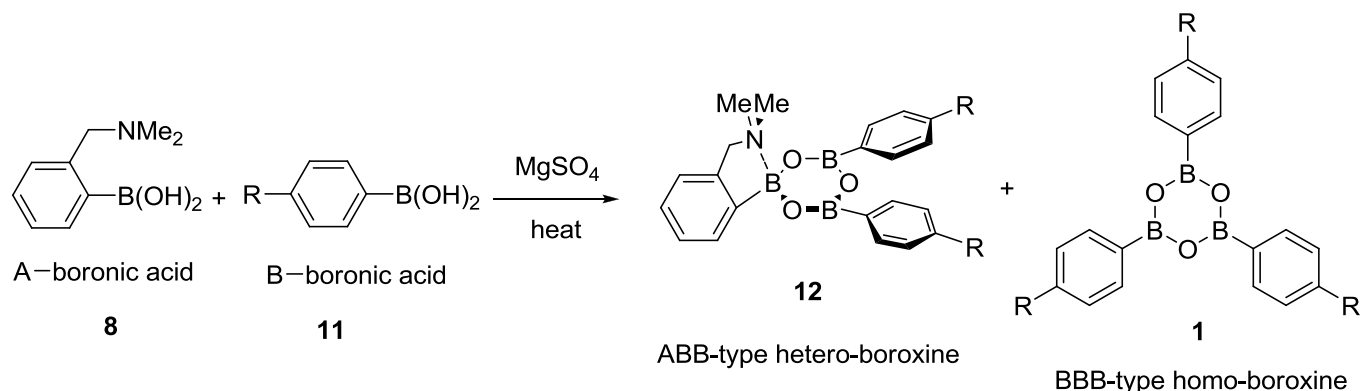
GC-MS experiments also showed the existence of four possible homo- and hetero-boroxines from the reaction of 3,5-dimethylphenylboronic acid **11b** and phenylboronic acid **11a** in the gas phase. The GC spectrum of their mixture in chloroform showed four abundant peaks based on the corresponding possible homo- and hetero-boroxines with no other distinct peaks. The monomeric boronic acid was most likely difficult to form under GC-MS conditions (i.e. high temperature and gas phase).

We accumulated thermodynamic parameters for numerous homo- and hetero-boroxine formation equilibria for one boronic acid **11** (Scheme 4) and two different boronic acids **11** (Scheme 5). Figure 6 presents *TΔS* plotted against ΔH .³⁶ The relationship between enthalpy and entropy thermodynamic terms (slope: 0.71, intercept: 0.97, R-value: 0.88) were obtained; this relationship represents the extent to which the entropic gain is decreased by the accompanying enthalpic loss, although a boroxine bearing an electron-donating group is enthalpically more stable than one bearing an electron-withdrawing substituent. This relationship suggests that the phenyl rings of a boroxine donate electrons to the electron-poor boron atoms (enthalpy term) and that restriction of the conformation on a boroxine that bears an electron-donating substituent may produce a large entropy loss due to the strong donation of the phenyl rings.



Invine and Kua advanced the progress of hetero-boroxine chemistry by selectively synthesising a hetero-boroxine (ABB-type) (Scheme 6).³⁷ As previously mentioned, arylboronic acids can smoothly form 1:1 amine–boroxine adducts, which are thermodynamically favoured over 2:1 or 3:1 adducts. Invine and Kua prepared arylboronic acid **8**, which contained an intramolecular ligand, and then mixed boronic acid **8** with excess amounts of normal arylboronic acid **11**. In this case, ABB-type hetero-boroxine **12** (1:1 adduct) would be more stable than other possible homo- and hetero-boroxines (i.e. BBB-type: unligated boroxine; AAA-type: 1:3 adduct; and AAB-type: 1:2 adduct). Boronic acid **8** was refluxed with two equivalents of arylboronic acids **11** in the presence of magnesium sulphate to afford a 9:1:1 mixture of **12**, **1** and boronic acid **11**.

The approach of Invine and Kua was based on the consideration of the thermodynamic stabilities of boroxine and the amine–boroxine adduct; they demonstrated how one specific hetero-boroxine could be selectively produced among four possible boroxines (i.e. they extracted the ABB-type boroxine among the AAA-, AAB-, ABB- and BBB-types). They also performed computational analyses. As expected, the ABB-type (**12**) was the most stable among the four possible boroxines. Further computational studies were performed, including a study of ABC-type unligated boroxines.³⁸



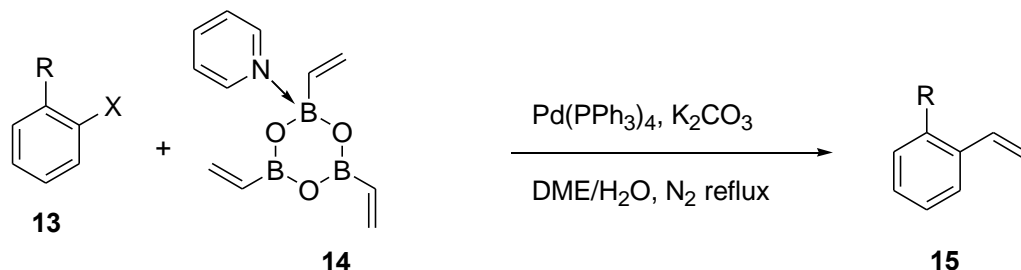
Scheme 6

4. UTILITY OF BOROXINES AS A REAGENT AND A CATALYST IN ORGANIC SYNTHESIS

4-1. Utility of Boroxines as Vinyl and Aryl Sources in Organic Synthesis

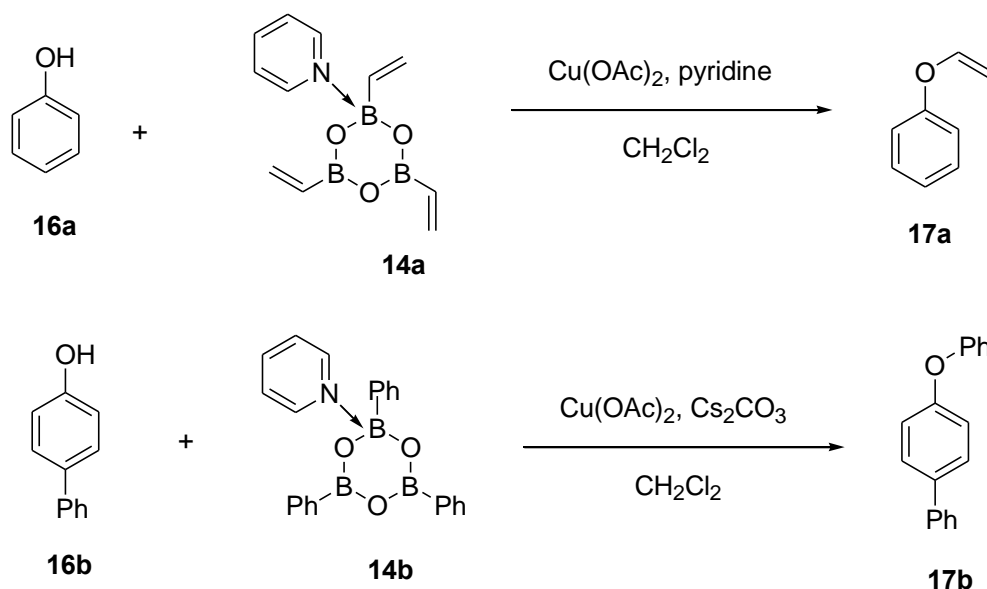
In organic synthesis, triarylboroxines are alternative reagents as aryl sources in the Suzuki–Miyaura coupling reaction. The Suzuki–Miyaura coupling reaction also appears to be a powerful method for the synthesis of substituted styrenes; however, when used as a potential vinylation reagent, vinylboronic acid tends to undergo uncontrollable polymerisation during the final stages of product isolation³⁹ and degrades over a time period of several days. O’Shea *et al.* converted vinylboronic acid into a bench-stable form that would still be capable of undergoing Suzuki–Miyaura-type coupling.⁴⁰ Vinylboronic acid was directly converted into its pyridine–boroxine adduct **14** as a solid prior to isolation, and the coupling of aryl

halides **13** with the pyridine–vinylboroxine adduct **14** afforded corresponding styrenes **15** in high yields under typical aqueous Suzuki–Miyaura coupling conditions (Scheme 7). They speculated that the vinylboronic acid could be generated in situ.



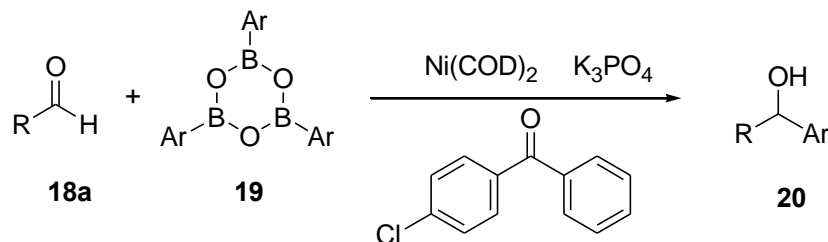
Scheme 7

O'Shea *et al.* reported another important synthetic utilisation of this pyridine–boroxine adduct **14a** as a vinylation reagent in a carbon–oxygen bond-forming reaction for generating aryl vinyl ethers **17a** (Scheme 8).⁴¹ Moreover, they prepared diaryl ether **17b** using phenol **16b** and pyridine–phenylboroxine adduct **14b** in the presence of a base instead of the pyridine–vinylboroxine adduct. When phenylboronic acid **11a** and phenylboroxine **1a** were used instead of pyridine adduct **14b**, the phenol gave a very low conversion to corresponding ether **17b**. They demonstrated the utility of the pyridine–boroxine adduct as a reagent for the *O*-vinylation and -arylation of phenols. They speculated that the structural consequences of the amine-to-boron coordination may be the key to a transmetalation step for the coupling reaction. Lam *et al.* described similar results for copper-promoted C–N and C–O bond cross-coupling with boroxine.⁴²



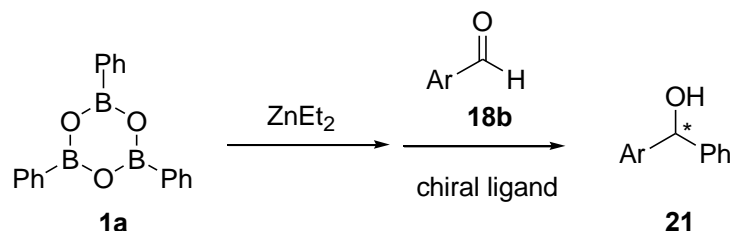
Scheme 8

The use of triarylboroxine **19** instead of boronic acid is effective in water-sensitive reactions because boronic acid generates water under ambient conditions, as discussed previously. Hu reported that Ni-catalysed addition reactions of boroxines **19** with aldehydes **18a** afforded corresponding alcohols **20** in the presence of 4-chlorobenzophenone in good yield (Scheme 9).⁴³



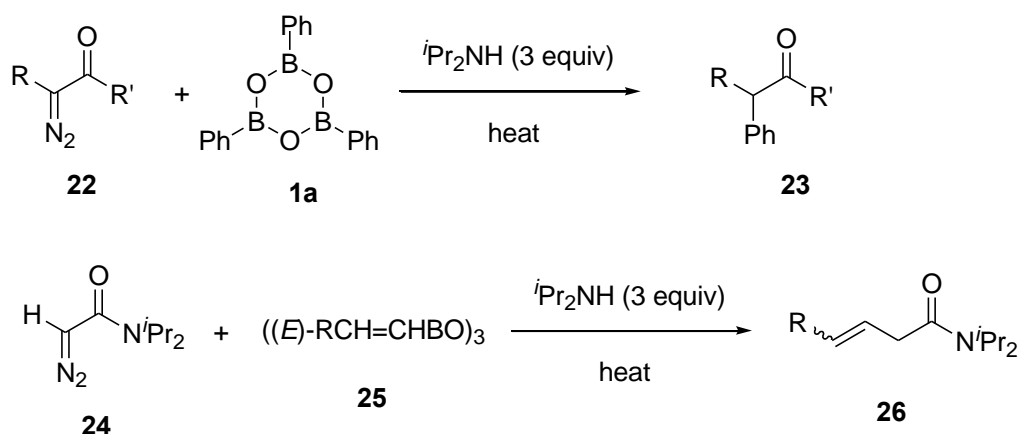
Scheme 9

Zhu demonstrated the utility of phenylboroxine **1a** as a phenyl source in the asymmetric transfer of aryl groups onto aromatic aldehydes **18b** (Scheme 10).⁴⁴ The use of phenylboroxine **1a** instead of phenylboronic acid **11a** in the preparation of a zinc reagent resulted in a slightly higher enantioselectivity of asymmetric biarylmethanols **21** and a shorter reaction time. Seto *et al.* developed a method of generating an aryl-zinc reagent from the corresponding arylboroxine and Et_2Zn for enantioselective addition to 3,4-dihydroisoquinoline *N*-oxide.⁴⁵

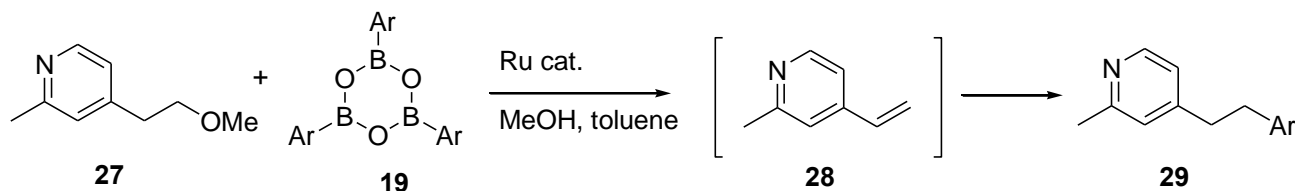


Scheme 10

Boroxines have also played useful roles in the arylation and vinylation of α -diazocarbonyl compounds **22** and **24** (Scheme 11).⁴⁶ At the outset of this investigation, Wang *et al.* used phenylboronic acid as an arylation reagent. The isolated yield of arylation product **23** was poor, and when phenyl pinacolborane was used instead of boronic acid, no arylation product was observed. The use of phenylboroxine **1a** instead of boronic acid improved the yields and reaction rate in the presence of amines. Finally, they found that the reaction could be significantly improved by an addition of base. The reaction of boroxines **25** with α -diazo amides **24** was employed under similar reaction conditions to prepare α -vinylation products **26** in moderate to good yields. The addition of diisopropylamine improved the product yield but substantially slowed the reaction. Wang *et al.* speculated that the role of the amine was to neutralise the reaction system to prevent acid-sensitive diazo substrate **24** from decomposing.

**Scheme 11**

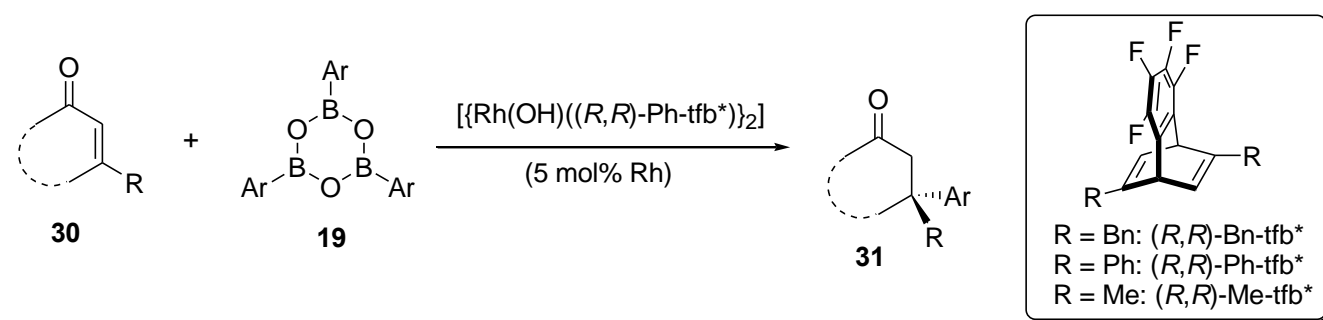
Kakiuchi reported the ruthenium-catalysed conversion of sp^3 C–O bonds in ethers to C–C bonds using triarylboroxines **19** (Scheme 12).⁴⁷ Although the detailed mechanism was unclear, they proposed a possible mechanism for the coupling reaction. First, dehydroalkoxylation of substrate **27** was facilitated by coordination between Lewis bases (pyridine nitrogen and ethereal oxygen) and a Lewis acid (a ruthenium or boron atom) and proceeded to give vinylpyridine **28**. The presence of methanol assisted the transmetalation of the aryl group from the boron atom to the ruthenium complex, and carbometallation of vinyl intermediate **28** followed by protodemetalation proceeded to afford arylation product **29**.

**Scheme 12**

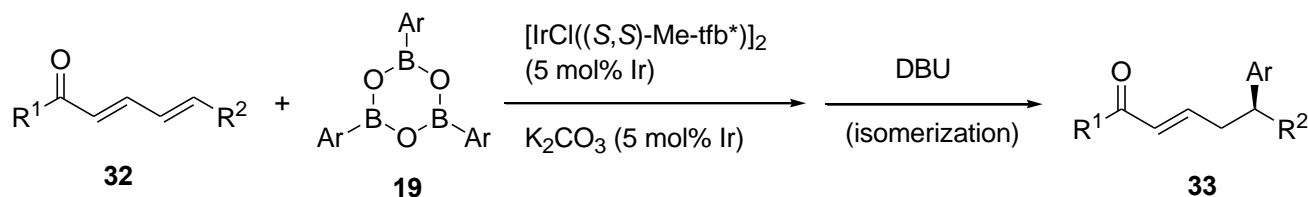
Moreover, Hayashi *et al.* discovered rhodium-catalysed asymmetric 1,4-addition of arylboroxines **19** to α,β -unsaturated ketones **30** (Scheme 13).⁴⁸ They found that $[\{\text{Rh}(\text{OH})(\text{ligand})\}_2]$ could effectively catalysed the addition of air-stable and readily available triarylboroxine **19**, and that $[\{\text{Rh}(\text{OH})((R,R)\text{-Bn-tfb}^*)\}_2]$ and $[\{\text{Rh}(\text{OH})((R,R)\text{-Ph-tfb}^*)\}_2]$ efficiently promote the reaction to afford the corresponding product **31** in high chemical yield with excellent enantioselectivity. Furthermore, acyclic enones reacted successfully under the same conditions (the enantioselectivities were somewhat lower).

Hayashi also reported iridium-catalyzed 1,6-addition of arylboroxines to $\alpha,\beta,\gamma,\delta$ -unsaturated carbonyl compounds.^{49a} Later they succeeded in the highly enantioselective 1,6-addition of arylboroxines **19** to $\alpha,\beta,\gamma,\delta$ -unsaturated carbonyl compounds **32** using $[\text{IrCl}((S,S)\text{-Me-tfb}^*)_2]$ as a catalyst (Scheme 14).^{49b}

Treatment of dienone **32** with boroxine **19** in the presence of K_2CO_3 gave a mixture of 1,6-adducts, which consist of (*E*)- and (*Z*)-isomers of β,γ -unsaturated enone and the conjugate enone **33**. After isomerization using DBU gave the enone **33** as the major isomer in high optical yield. This reaction can be applicable for the 1,6-addition to conjugate dienamides (**32**: $R^1 = NR_2$) and a dienolate (**32**: $R^1 = O^tBu$) with high enantioselectivity. Finally, they demonstrated the stereoselective synthesis of doubly phenylated ketone by using this 1,6-addition to $\alpha,\beta,\gamma,\delta$ -unsaturated ketone **32** followed by rhodium-catalysed asymmetric 1,4-addition of arylboroxines.



Scheme 13

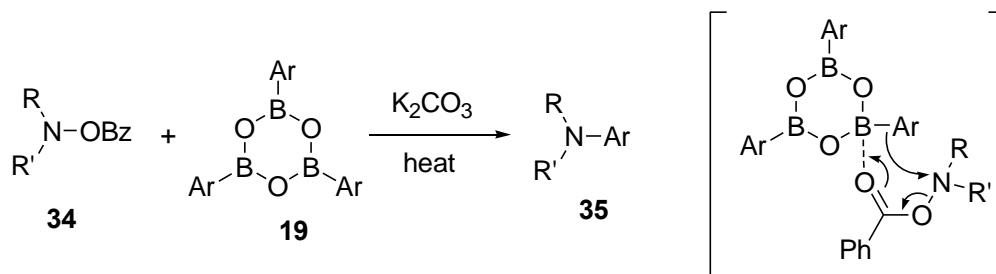


Scheme 14

Wang *et al.* developed a convenient strategy to construct $C(sp^2)\text{-N}$ bonds using arylboroxines **19** and *O*-benzoyl hydroxylamines **34** as coupling partners in the presence of a base (Scheme 15).⁵⁰ Treatment of primary and secondary amino benzoates **34** with a series of arylboroxines **19** with electron-donating and -withdrawing groups on aromatic rings furnished corresponding amines **35** in moderate to good yields. They proposed a direct substitution reaction mechanism to account for this transition-metal-free amination reaction. The reaction using a boronic acid instead of the boroxine gave the corresponding amination product in low yield.

As previously mentioned, a decade ago, boroxine was used as a precursor of boronic acid in synthetic organic chemistry. The fact that the addition of water to boroxine increases the amount of boronic acid resulted in improved yields and enantioselectivity of rhodium-catalysed asymmetric 1,4-additions.⁵¹ Another advantage of using boroxine in organic synthesis is that the exact amount of organoboron can be measured, as it is hard to isolate boronic acid as a single species (the acid gradually changes to the corresponding boroxine, as described in section 3-1). More recently, synthetic applications that exploit the

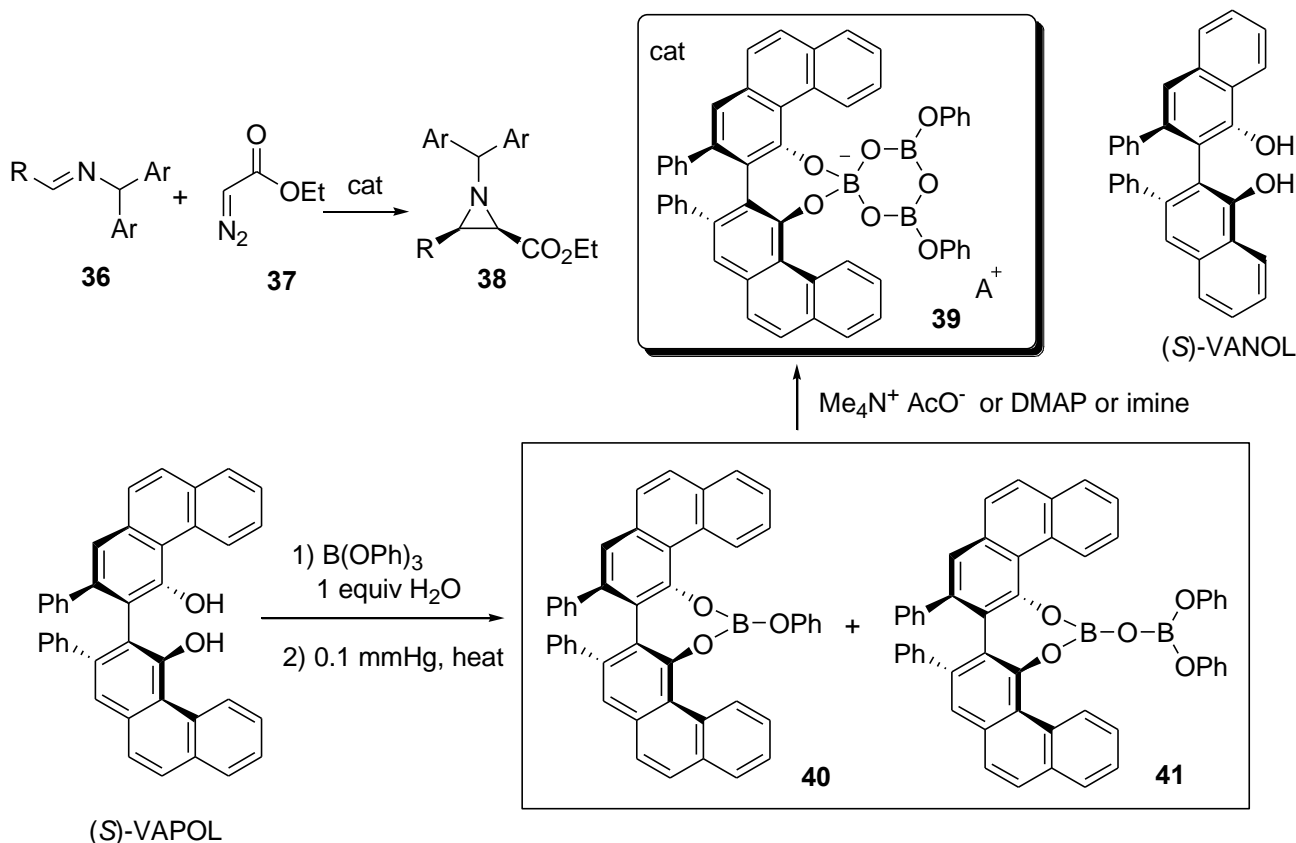
characteristic properties of boroxine have been reported, as discussed above. As an additional example, Fokin *et al.* reported the arylation of rhodium(II) azavinyl carbene with boronic acid.⁵² They hypothesised that the active arylating species was arylboroxine because the reaction was improved by the addition of CaCl_2 .



Scheme 15

4-2. Utility of Boroxine as a Catalyst in Organic Synthesis

Wulff *et al.* demonstrated the chiral-spiroborate-anion (boroxinate)-catalysed asymmetric aziridination of imines **36** using diazo compound **37** (Scheme 16).⁵³ They found that a VAPOL (or VANOL) and excess B(OPh)_3 catalytic system was efficient for the asymmetric synthesis of aziridine **38** and that heating a solution of VAPOL and excess B(OPh)_3 in the presence of one equiv of water afforded pyroborates **40** and **41**; their findings were supported by detailed ^1H and ^{11}B NMR spectra.⁵⁴ Their skilful NMR and

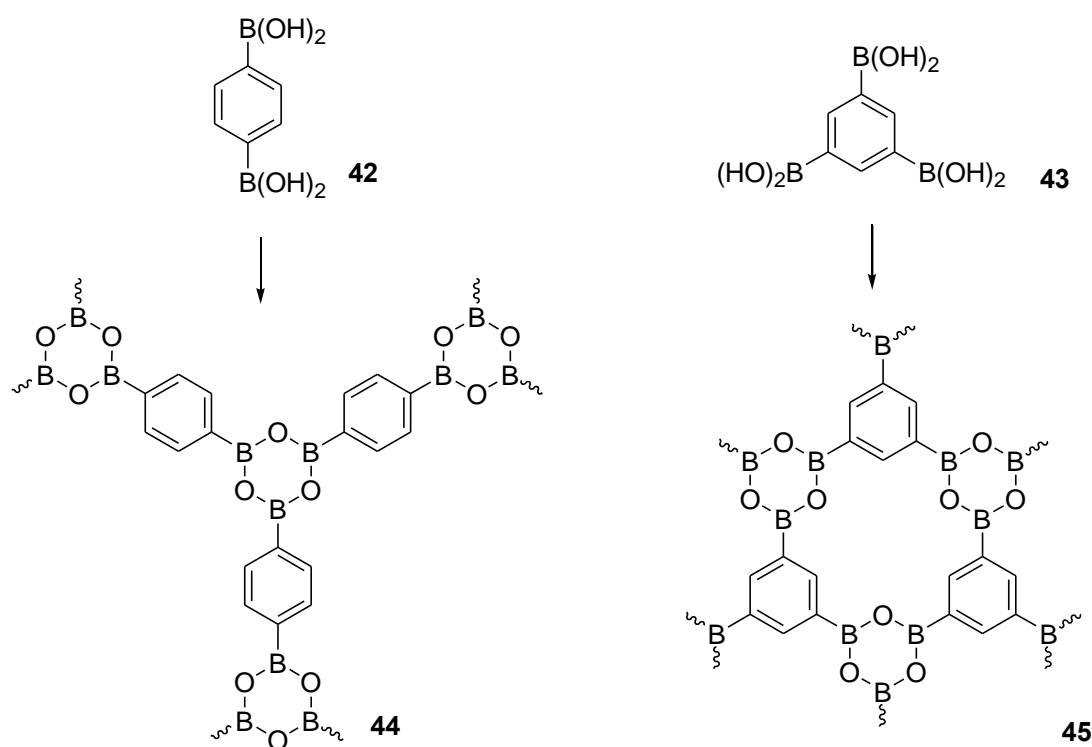


Scheme 16

X-ray analysis led to their conclusion that the real catalyst was chiral boroxinate **39**.⁵⁵ These analyses indicated a π - π stacking interaction between a phenanthrene ring of the VAPOL ligand and the pyridinium ion of the protonated DMAP when DMAP was added to the mixture of **40** and **41**. Moreover, a CH- π interaction between an *ortho*-hydrogen on the DMAP ring and one of the phenoxy rings of boroxine system was observed. Treatment of the mixture with imine **36** appeared to lead to the formation of the catalyst, which consisted of the boroxinate anion and the protonated form of imine **36** as a counter ion; these tentative assignments were based on ^{11}B and ^1H NMR spectra. Finally, X-ray diffraction analysis of boroxinate complex **39** (cation: protonated imine) revealed the interactions between the boroxinate anion and the protonated imine.⁵⁶ Wulff's group also reported this chiral-boroxinate-catalysed asymmetric heteroatom Diels-Alder reaction of an imine.⁵⁷

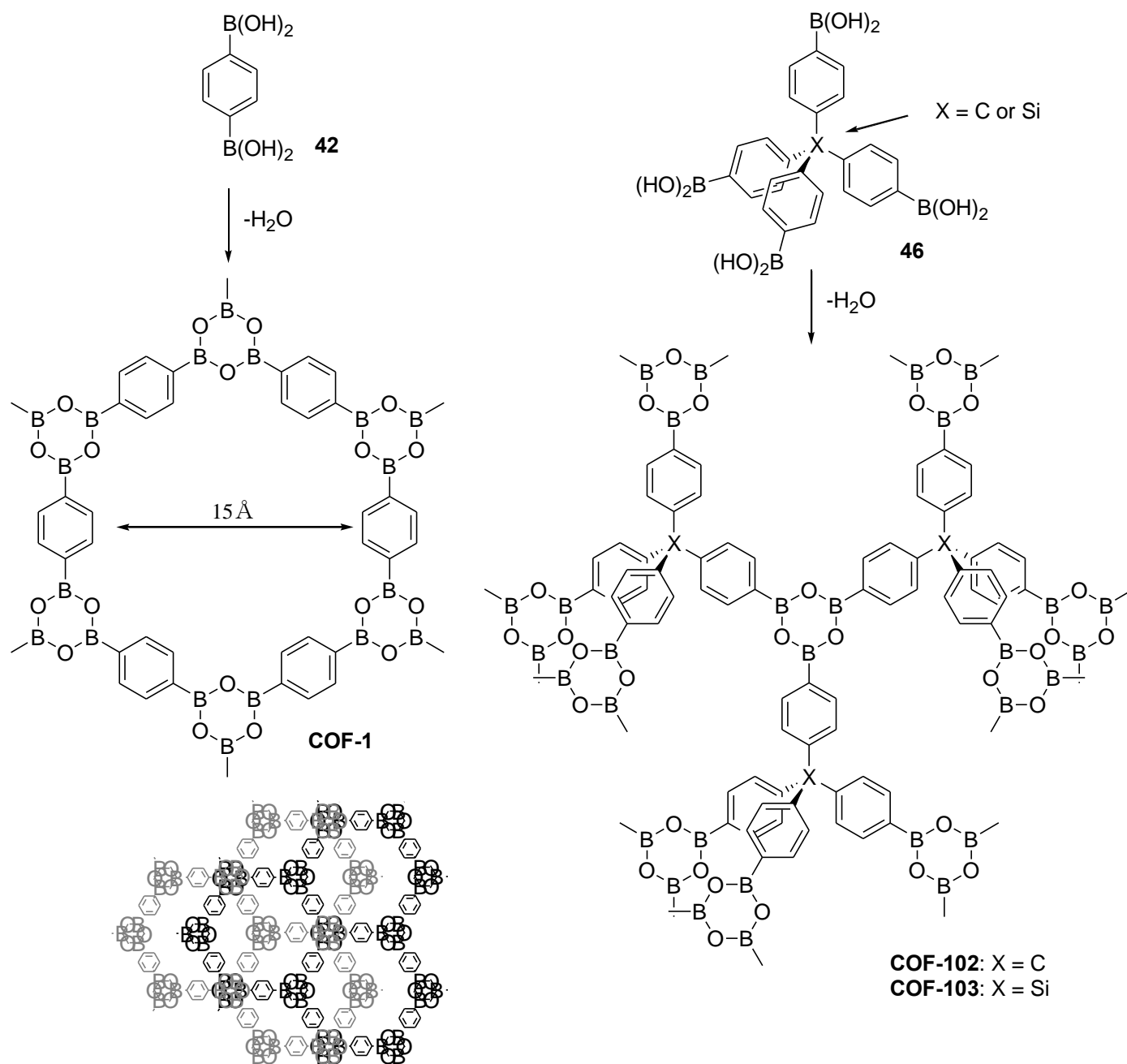
5. CONSTRUCTION OF COVALENT ORGANIC FRAMEWORKS BY BOROXINE FORMATION REACTION

Tour *et al.* expected boroxine networks **44** and **45** through dehydration reactions of organoboronic acids **42** and **43** and investigated the utility of this reaction in materials science in 1999 (Scheme 17).⁵⁸ They synthesised di- and triboronic acids from the corresponding di- and tribromobenzenes via a nickel-catalysed substitution reaction and blended diboronic acids **42** with polycarbonate resin, expecting a formation of boroxine networks **44**, which worked as a flame retardant, via the dehydration of the boronyl groups. Flame tests showed the effectiveness of diboronic acid **42** as a flame retardant.



Scheme 17

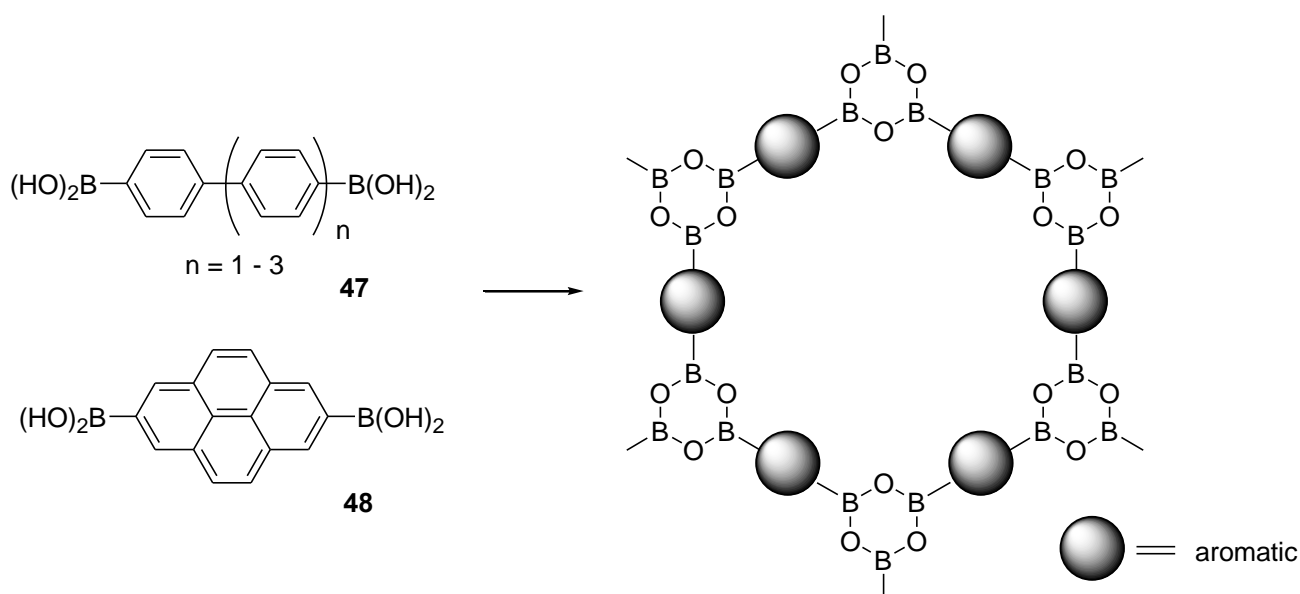
Two- and three-dimensional networks based on boroxines as covalent organic frameworks were reported by Yaghi in 2005.¹² The frameworks and their synthesis methodology have opened a new direction in the field of porous materials. Covalent organic frameworks are constructed from nonmetal building blocks via only stable covalent bonds. Therefore, thermally stable and lightweight covalent organic frameworks can be realised, and modification of the organic component of the building blocks can result in various sizes, shapes and properties of the porous materials in the frame. For example, the heating of a solution of diboronic acid **42** in mesitylene–dioxane afforded COF-1 (Scheme 18). IR and NMR spectroscopy were



Scheme 18

used to characterise the boroxine, and powder X-ray diffraction analysis of the crystals revealed the presence of organic sheets and a staggered packing arrangement, as shown on the left side of Scheme 18. The three phenyl rings attached to three boron atoms were approximately coplanar with the boroxine ring in the solid state, as mentioned in the introduction, and the coplanar conformation resulted in the sheet structure and its packing. The porosity of COF-1 was confirmed via N_2 gas-adsorption measurements; the total surface area was large (calculated to be $711 \text{ m}^2 \text{ g}^{-1}$). They subsequently synthesised three-dimensional covalent organic frameworks.⁵⁹ The dehydration of tetraboronic acids **46**, a tetrahedral building block, produced corresponding COF-102 (centre atom: carbon) and COF-103 (centre atom: silicon). The thermal stability of these COFs was confirmed via glass transition temperature (T_g) measurements, and the BET surface areas were 3472 and $4210 \text{ m}^2 \text{ g}^{-1}$ for COF-102 and COF-103, respectively. Furthermore, the Yaghi and Goddard groups considered these frameworks to be hydrogen⁶⁰ or methane⁶¹ storage materials.

Recently, Lackinger synthesised extended two-dimensional covalent organic frameworks via the on-surface condensation of boronic acids **47** and **48**.⁶² A series of isorecticular two-dimensional frameworks was created using diboronic acids, where the size of the organic backbone was incrementally varied from biphenyl to quaterphenyl (Scheme 19).



The construction of the COF structure on the surface was improved. Control of the formation of the two-dimensional COF was accomplished through manipulation with the tip of a scanning tunnelling microscope and electron irradiation.⁶³ Highly ordered surface covalent organic frameworks were obtained in the presence of a small amount of water ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was used as a water reservoir).⁶⁴ Water may

regulate the chemical equilibrium of the dehydration reaction to enable construction of the thermodynamically stable architecture, as was observed in solution.

6. UTILITY OF BOROXINES IN SUPRAMOLECULAR CHEMISTRY

A pioneering research of boroxine harmonised with materials science and supramolecular chemistry was published by Whitesides *et al.* in 1994.⁶⁵ They prepared self-assembled bilayers that consisted of ω -mercaptoalkylboroxine adsorbed onto gold in dry hydrocarbon solvents. The bilayer was hydrophobic, stable in air and 28 Å thick. It could be completely hydrolysed to a monolayer in aqueous ethanol to yield a hydrophilic 17-Å-thick SAM with boronic acid groups at its surface.

6-1. Ferrocenylboroxine Chemistry

Metal-containing boroxines have been used as a core for supermolecules. Ferrocenylboroxine **49** has been reported by Kotz⁶⁶ and independently and crystallographically characterised by Wagner and Herber.⁶⁷ Recently, Elschenbroich *et al.* extended the use of metal-containing boroxines to prepare tri([5]trovacenyl)boroxine **50**, which possesses three (η^7 -C₇H₇)V[η^5 -C₅H₄] groups as unsymmetrical paramagnetic components.⁶⁸ EPR experiments showed the coupling based on three ⁵¹V atoms, which is characteristic of three interacting ⁵¹V centres. Magnetic susceptibility of the boroxine, which is engaged in antiferromagnetic exchange, provided a value of $J = -1.04 \text{ cm}^{-1}$. More recently, ferrocene-bridged boroxine cyclophane **51** was prepared by Miljanic *et al.* The crystal structure revealed a rigid trigonal prism that contained a minimal boroxine-based covalent organic polyhedron (Figure 7).⁶⁹

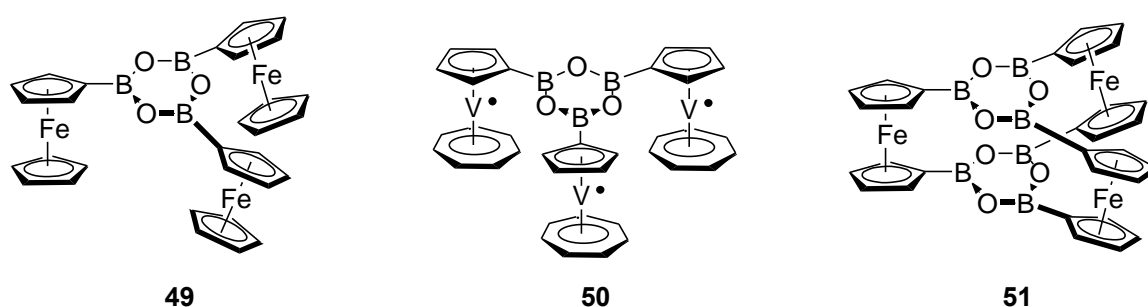


Figure 7

Jäkle's group prepared Lewis acidic, chiral ferrocenylborane derivatives⁷⁰ and later extended them to chiral ferrocenylboroxine **52**.⁷¹ X-ray analysis revealed that the boroxine adopted a double-propeller-like structure with three ferrocenyl and three naphthyl substituents on opposite sides of the central boroxine ring (Figure 8). The supramolecular organisation of the boroxine within the crystal was observed. Extended chainlike structures were found as a result of C–H π -interactions between one of the C–H

protons of each naphthalene moiety (i.e. the donor) and an unsubstituted cyclopentadienyl ring of the ferrocenes (i.e. the acceptor). These interactions generated an infinite triple-helical structure with chiral and hydrophobic pockets, which were surrounded by naphthalene and cyclopentadienyl rings. Two chloroform molecules (chloroform was used as a solvent) were trapped in each pocket, and intermolecular interactions occurred between the walls of the pocket and a chloroform molecule and between two chloroform molecules. The authors investigated the redox chemistry of the boroxine. Three well-separated waves based on three redox-active ferrocenyl moieties were observed in the cyclic voltammogram; these waves shifted to lower potentials upon the addition of DMAP as a Lewis base.

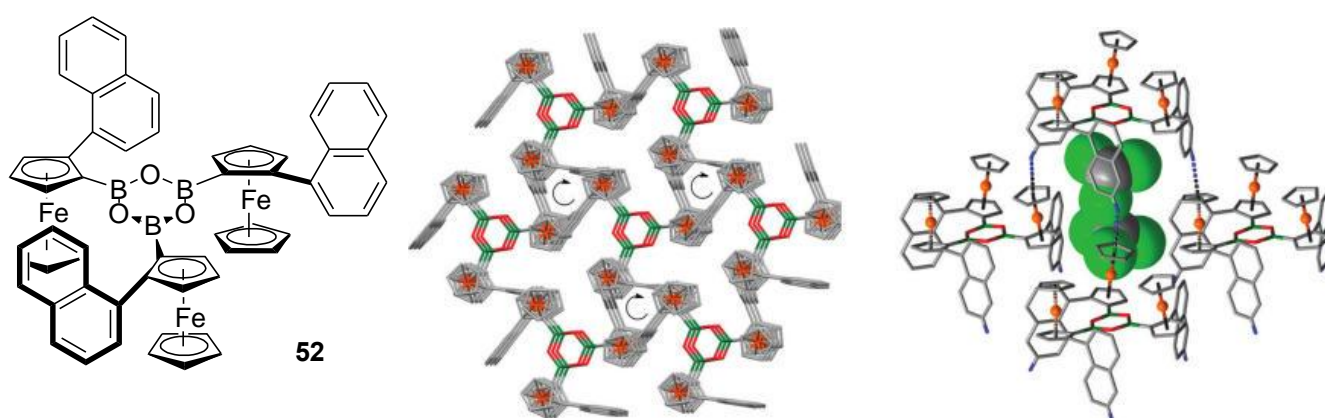


Figure 8. Monomeric structure and different views of the supramolecular structure of **52**. Centre: the view along the crystallographic *c*-axis (CHCl_3 molecules are omitted for clarity). Right: illustration of the pocket that contains two CHCl_3 molecules. (Modified reproduction from reference 71.)

6-2. Utility of Boroxines in Polymer Chemistry

The tripodal molecular architecture is an attractive motif for the construction of dendrimers. Iovine *et al.* synthesised branched boronic acid and subsequently treated the boronic acid with calcium chloride as a dehydration reagent to afford corresponding dendrimer-like boroxines **53** and **54** (Figure 9).⁷² Boroxines **53** and **54** were initially soluble in chloroform; however, they precipitated on standing probably because of the formation of π -stacked aggregates. Pyridine–boroxine adducts **53-py** and **54-py** were highly soluble in chloroform because the coordination of pyridine distorted the flat boroxine ring. NMR experiments revealed that the pyridine ligand was involved in fast exchange on the NMR time scale.

The noncovalent functionalisation of polymers is fascinating because self-assembly minimises complicated processes associated with modification of polymers and/or monomers and provides the parent polymer with reversible alternative physical and chemical properties. Iovine achieved polymer functionalisation using the complexation of pyridine and boroxine (Scheme 20).⁷³ Three different polystyrene-*co*-4-vinylpyridine (4-VP) polymers **55** that contained 22–90 mol% 4-VP were used in this study. NMR experiments suggested that the 4-fluorophenylboronic acid was efficiently converted into the

corresponding boroxine and that the boroxine ring was closed to fully associate with the pyridine rings. DSC results of polymers **56** (22 mol% 4-VP) with 4-VP/4-fluorophenylboroxine mole ratios that varied from 2.7:1 to 0.93:1 indicated that T_g increased from 117 to 134 °C (T_g of **55**: 101 °C). The increase in T_g was attributed to the complexation of the boroxine ring and pyridine, which produced a rigid and bulky side chain and decreased the polymer chain mobility. In TGA experiments, the parent polymer showed no significant weight loss until 400 °C. In contrast, degradation was detected at increasingly lower temperatures as the amount of 4-fluorophenylboroxine was increased.

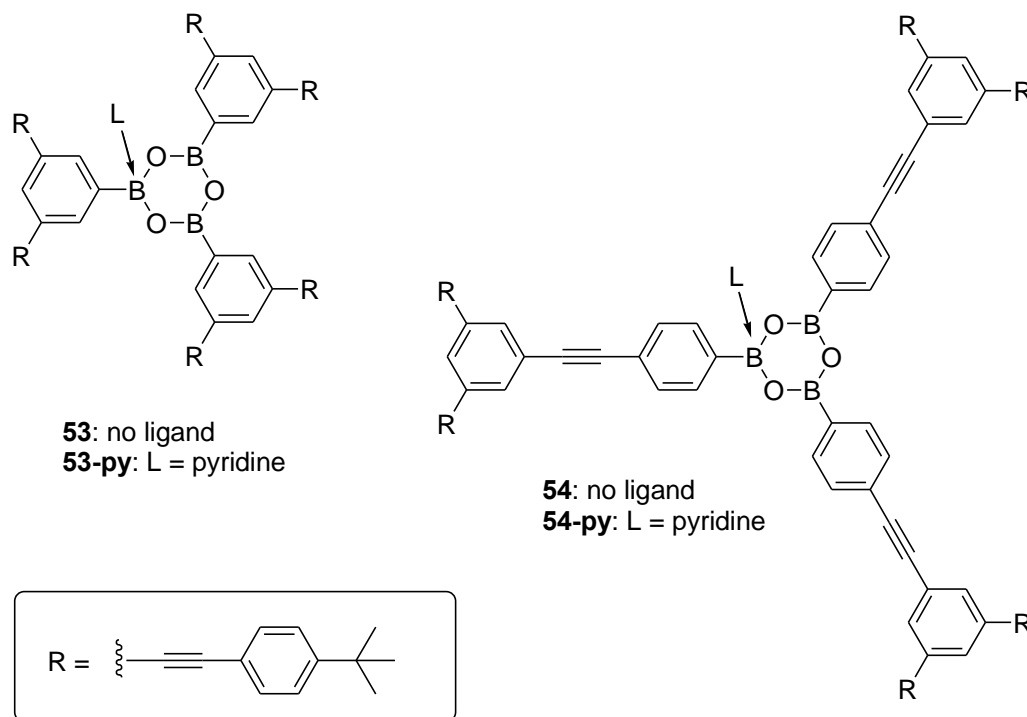
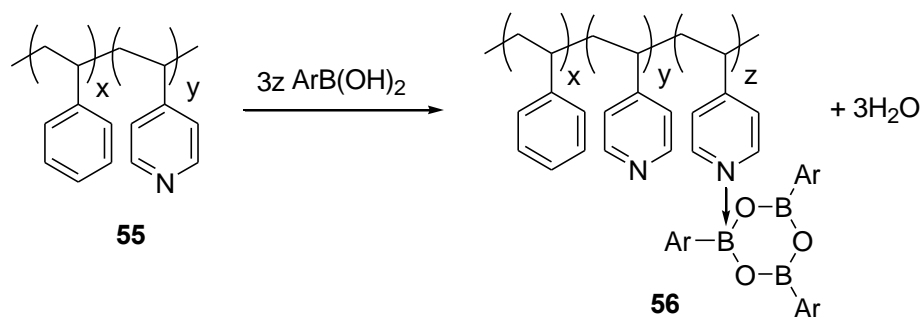


Figure 9

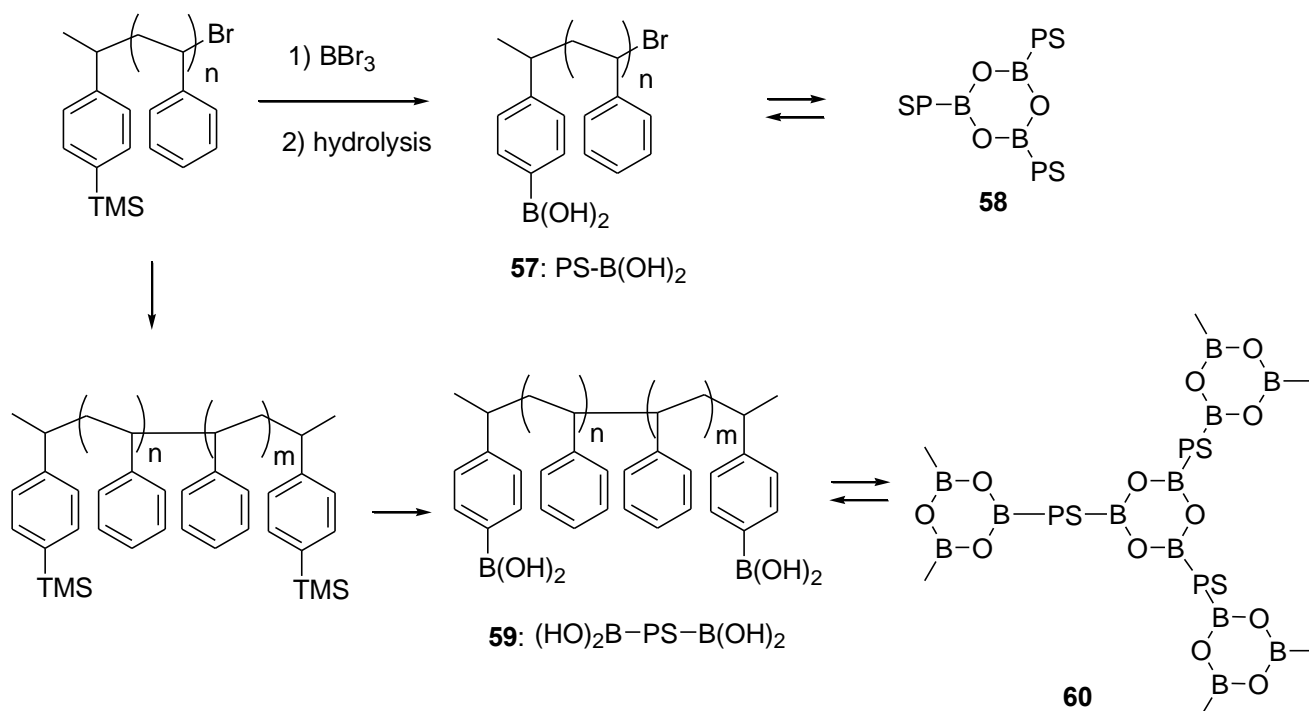


Scheme 20

Jäkle *et al.* prepared boron-end-functionalised polymers bearing a polystyryl main chain through polymerisation of styrene using a silylated initiator and exchange of the trimethylsilyl end group with

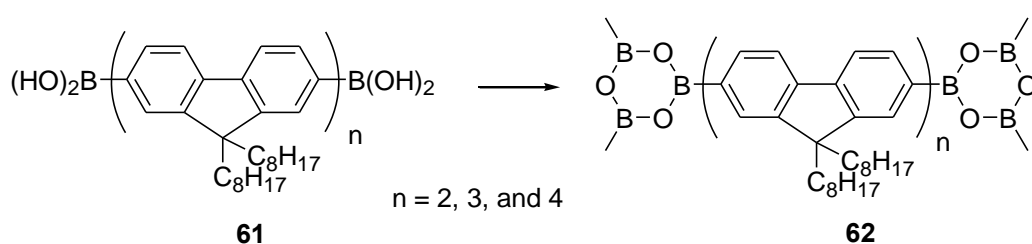
BBr_3 followed by hydrolysis (Scheme 21).⁷⁴ Ditelechelic organoboron polymer **59** could be manipulated through atom transfer radical coupling and the same transformation of the silyl group into a boronyl group. After monotelechelic polymer **57** (PS-B(OH)_2) was subjected to azeotropic distillation, boroxine-centred star polymer **58** was obtained. DSC analysis of the star polymer showed a significantly higher glass transition temperature ($T_g = 101\text{ }^\circ\text{C}$) for **58** compared to that of the PS-SiMe_3 precursor ($T_g = 80\text{ }^\circ\text{C}$). The authors confirmed the reversibility of the boroxine formation reaction; star polymer **58** could be readily transformed back to original polymer **57** through the addition of a small amount of water. However, upon azeotropic distillation of a benzene solution of ditelechelic polymer **59**, a white precipitate that was insoluble in anhydrous acetone was formed (Scheme 21). When a drop of water was added to a suspension of the solid in dry acetone, a clear solution was obtained. Because of the significantly higher glass transition temperature ($T_g = 112\text{ }^\circ\text{C}$) of **59** compared to the initial polymer $\text{Me}_3\text{Si-PS-SiMe}_3$ ($T_g = 95\text{ }^\circ\text{C}$) and because of its solubility, a network-like structure **60** with boroxine cross-links could be constructed.

Sumerlin also reported the synthesis of a three-armed star polymer via the covalent assembly of $(\text{HO})_2\text{B-PS}$ through boroxine linkages supported by complexation by boroxine–amine interactions.⁷⁵ A boroxine-core star polymer bearing a polycaprolactone residue was reported by the Iovine group.⁷⁶ Because thermal dehydration of the boronic acid was ineffective in this case, the authors induced the ligand-facilitated trimerisation of boronic acids using either pyridine or 7-azaindole as the Lewis base.



Scheme 21

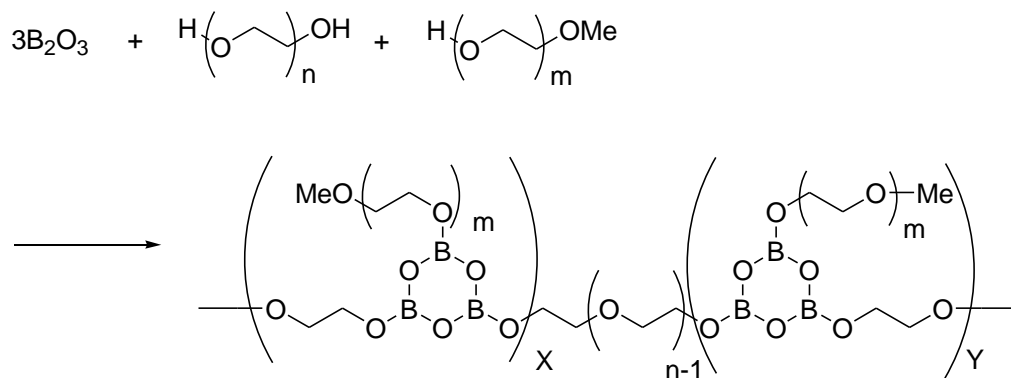
Novel stable blue-light-emitting oligofluorene networks were immobilised via a boroxine formation reaction. D'iorio *et al.* selected oligofluorene as a blue-light emitter because of its high photoluminescence efficiency and excellent chemical and thermal stabilities and prepared three diboronic acids **61** ($n = 2, 3, 4$), which partially included their boroxines **62** (Scheme 22).⁷⁷ Under mild reaction conditions, these oligomers underwent cross-linking reactions through the dehydration of boronic acid, as indicated by IR spectroscopy and DSC/TG experiments. The resulting three boroxine networks showed thermal and morphological stability, although their spectra differed somewhat. Compounds **62** emitted bright violet–blue ($n = 2$) and blue ($n = 3$ and 4) light both in solution and in the solid state under UV irradiation.



Scheme 22

6-3. Boroxine as an Electrolyte Material

Fujinami *et al.* presented a new series of polymer electrolytes that incorporate boroxine rings with pendant oligoether side chains.^{11,78,79} For example, a polymer electrolyte was prepared through the boroxine formation reaction of boric oxide, poly(ethylene glycol) and poly(ethylene glycol) monomethyl ether (Scheme 23). High ionic conductivity and a high lithium transference number were observed when the polymer (boroxine ring:lithium salt = 2:1) was used as an electrolyte. The effectiveness of the boroxine might be based on its Lewis acidity. The authors concluded that an interaction between the anion of the lithium salt and boroxine caused a reduction in ion pairing and that the enhancement of the lithium-ion transference was greater than those commonly observed in polyether systems.⁸⁰



Scheme 23

Forsyth focused on the enhancement of ion dissociation in a boroxine–polymer electrolyte.⁸¹ ^{11}B and ^7Li NMR experiments showed that boroxine interacted with the anionic species on the polymer backbone (poly(lithium-2-acrylamido-2-methyl-1-propanesulfonate-*co*-dimethylacrylamide)), and hence produced some mobile lithium ions for conduction when boroxine was added to a polymer electrolyte gel. Recently, the effects of perfluorophenylboroxines were investigated for potential applications in lithium-ion batteries.⁸²

6-4. Two-Dimensional and Three-Dimensional Molecular Architectures Based on Boroxine in the Solid State

Irie *et al.* reported the fabrication of thin films of triphenylboroxine **1a** on inorganic substrates via vacuum deposition.⁸³ Interestingly, the films were found to evaporate comparatively quickly in air, whereas evaporation was not observed under an Ar atmosphere. These results suggest that triphenylboroxine in the thin films hydrolyses to phenylboronic acid in the presence of water in air and then evaporates. These results agree well with those observed during the construction of highly ordered surface covalent organic frameworks in the presence of a small amount of water (as described in Section 5: construction of covalent organic frameworks).

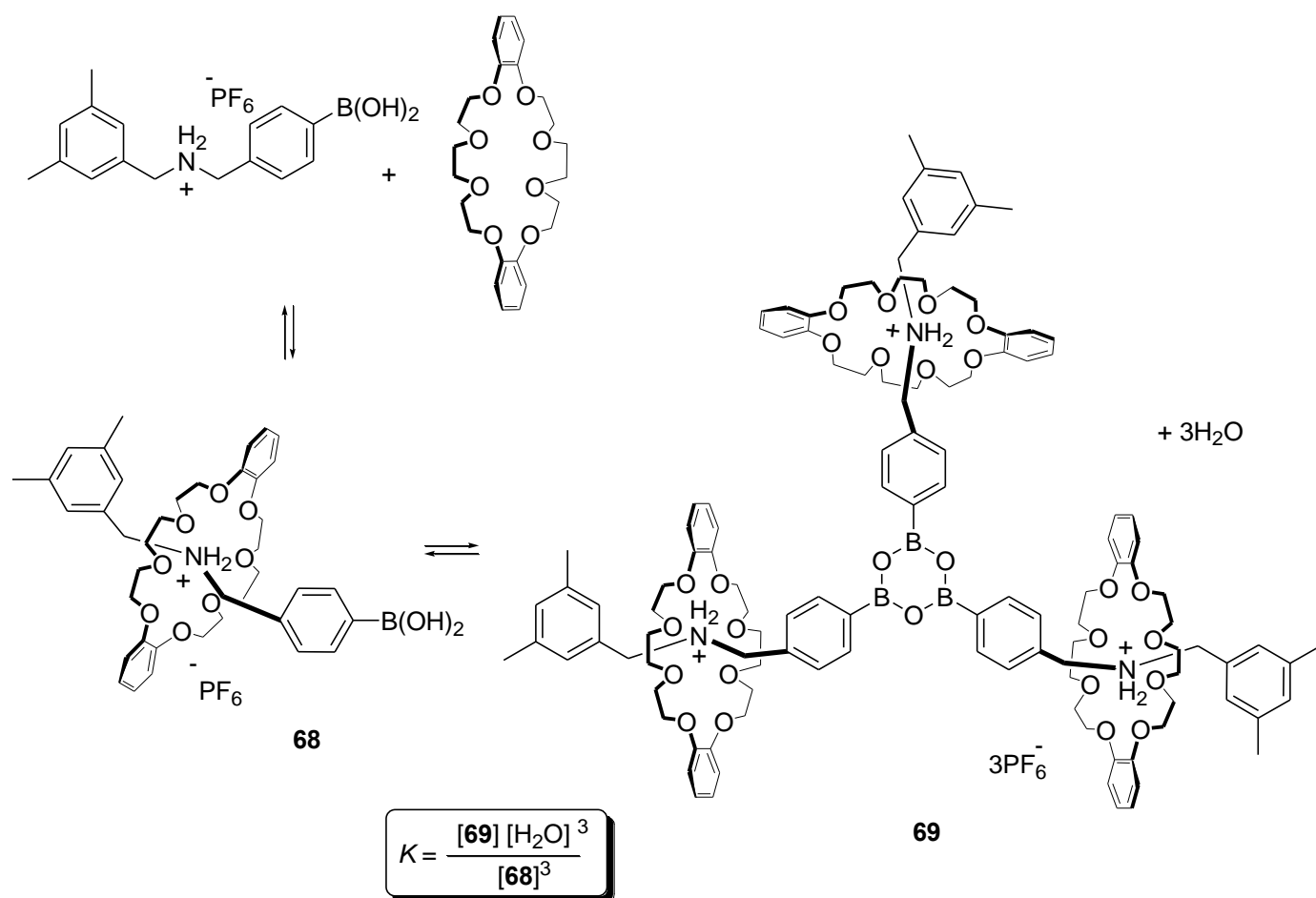
The Lackinger group constructed covalent two-dimensional phenylene–boroxine hybrid networks through surface-mediated polymerisation (Scheme 24).⁸⁴ The thermal condensation of dibromophenylboronic acid **63** and subsequent sublimation afforded deposition of corresponding boroxine **64** on graphite as well as on Ag(111). On the graphite substrates, well-ordered self-assembled trigonal monolayers were observed in STM topographs. Threefold symmetric molecular entities were identified, and their size and symmetry were consistent with intact boroxine molecules. In addition, cyclic halogen–halogen–halogen bonds among three bromine substituents stabilised the self-assembled monolayer. The thermal dehalogenation reaction was aided by the catalytic properties of the Ag(111) surface, and polymerisation of the generated radical resulted in the construction of two-dimensional phenylene–boroxine networks **65**, which were identified via STM experiments.

A three-dimensional network based on pyridine–boroxine complexation was reported by the Höpfl group (Scheme 25).⁸⁵ The complex was prepared in a one-pot reaction from a total of 15 molecules of 3-pyridineboronic acid **66**; dehydration of the boronic acid and the consequent boron–nitrogen coordination gave boroxine-pentamer **67** in high yield. Single-crystal X-ray diffraction analysis revealed that five boroxine molecules were linked through a total of ten N–B bonds to a pentadecanuclear boron cage with pseudo C_2 -symmetry (Figure 10). ^1H and ^{11}B NMR spectra obtained using nonpolar solvents showed single sets of resonances that were in agreement with the boroxine-pentamer structure observed in the solid state.

Concentrated borate solutions contain significant amounts of polyborate anions as well as $B(OH)_3$ and $B(OH)_4^-$, most notably $B_5O_6(OH)_4^-$, $B_3O_3(OH)_4^-$, $B_4O_5(OH)_4^{2-}$ and so on.⁸⁶ These anions are listed in the order of increasing basicity, and their distributions depend on the boron concentration, pH and temperature. Recently, complexes that contain six-membered borate anions (boroxinate anions) and polyborate anions have been synthesised.⁸⁷ These reports indicate that supramolecular structures were templated by cations and involved efficient hydrogen bonds and coordination bonds in the solid state.⁸⁸

6-5. Construction of Interlocked Molecule by the Boroxine Formation Reaction in Solution

Dynamic covalent chemistry is a powerful tool for the selective synthesis of thermodynamically stable products from a series of potential products in solution.⁸⁹ In particular, it is very effective for the construction and functionalisation of mechanically interlocked molecules, such as catenanes and rotaxanes. We reported an efficient method for the construction of a C_3 -symmetric [4]rotaxane through two reversible bond-forming reactions: hydrogen-bond-guided self-assembly (i.e. formation of pseudorotaxane **68** from ammonium ion and crown ether) and boroxine formation (Scheme 26).⁹⁰



Scheme 26

The reactions proceed under mild conditions in solution, and entropically driven forces promote the formation of [4]rotaxane **69**. VT NMR spectroscopy experiments provided unusual thermodynamic parameters for the boroxine formation process compared to those for typical arylboroxine formation processes. It was likely that the structure of the C_3 -symmetric [4]rotaxane stabilised the boroxine core both electronically and sterically against hydrolysis.

7. SUMMARY AND OUTLOOK

This review mainly highlights the broad array of boroxine chemistry that has been developed in recent years, and it clarifies the key challenges that lie ahead. Fundamental research on boroxine largely reflects the emphasis of the previously discussed content on the construction of molecular architectures. For example, understanding of the stabilities and adducts of boroxines has enabled the selective formation of hetero-boroxine,³⁷ stabilisation of vinylboroxine as a vinylation reagent,⁴⁰ functionalisation of polymer chains⁷³ and formation of three-dimensional supramolecular structures.⁸⁵ In addition, understanding of the Lewis acidity of boroxine has enabled it to be used in the development of high-performance polymer electrolytes.^{11,78-80}

The construction of high levels of molecular architecture is enabled by the reversible process of boroxine formation, which facilitates thermodynamic self-control and self-correction. The development of accurate covalent organic frameworks¹² and the selective formation of thermodynamically stable higher-ordered rotaxane⁹⁰ were realised through attractive dynamic covalent chemistry with precise molecular design. Boroxine has other fascinating properties based on its Lewis acidity. In particular, structural changes in the boroxine core (i.e. the C–B bond distance and C–B–O bond angle) and weakening of the C–B bonds are induced by coordination of a Lewis base on a boron atom, which has led to Lewis-base-controllable molecular systems⁷² and to other activating reactivities of boroxine as a reagent.⁴¹

As boroxine chemistry expands, the design of building blocks for the construction of highly complex and functional architectures using dynamic covalent chemistry will become important. The appropriate choice of building blocks and functionalities and/or template-directed synthesis methods can be effective in this regard. Moreover, modulation of the process, which consists of two reversible reactions (i.e. the boroxine formation reaction and the complexation of boroxine and amine), produces a multi-state-switchable and stimuli-responsive self-assembled system that may be useful in materials science.

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