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The Photochemistry of Boron Compounds

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1. Introduction

Photochemical transformations are widely employed in both organic and organometallic chemistry and have been extensively used as synthetic strategies for the formation of a variety of new compounds.[1] Light often furnishes facile pathways to species which are not accessible in other ways. In addition, photochemical pathways may proceed with high selectivity. In contrast with thermally induced reactions, photochemical processes typically possess high activation selectivities and provide firm bases for diverse synthetic applications.

Organic and organometallic reactions have been intensively investigated and a great deal is now known about the reaction profiles and mechanisms for many of these systems.[2–4] However, there has been relatively little emphasis on the photochemistry of boron compounds though the overall interest in the chemistry of boron has expanded greatly in the past 30 years.[5–8] The reason could be that in most of the photoreactions of organoboron compounds it is the organic moiety that absorbs light rather than the borane, i.e. the borane is not the primary photochemical reagent. Since the initial work of Alfred Stock[9] in 1913 on the effects of light on diborane(6) and tetraborane(10), there have been only two review articles, one mainly dealing with the inorganic photochemistry of boron compounds,[10] and the other with the thermal and photochemical redox processes of organoborates.[11] In this article, efforts have therefore been made to include all major developments in the field of boron photochemistry.

2. The Photochemistry of Boranes and Carboranes

In comparison with the extensive studies on the thermolysis of boranes, little attention has been paid to their photolysis, and there have been relatively few developments since the topic was reviewed in 1980.[10] Information on the UV spectra of binary boranes in the gas phase, which is a preliminary requirement to a quantitative study, is also very scarce.[10,12,13] Greenwood and co-workers,[14] however, have systematically recorded the UV spectra of a range of volatile boranes (Table 1).

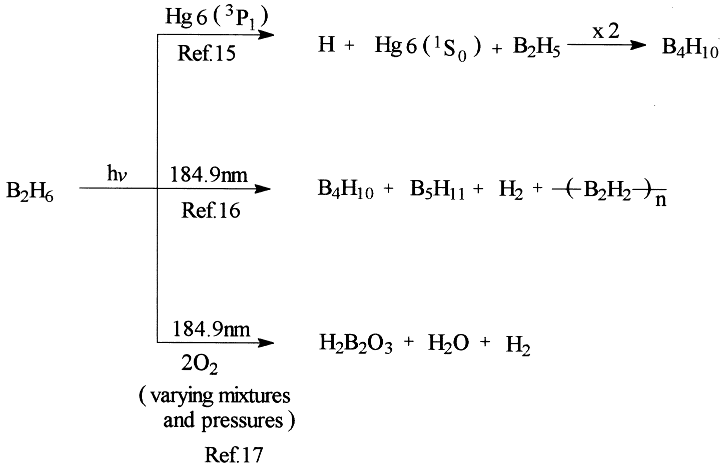
2.1. Diborane(6)

Early work on the photolysis of diborane(6) is summarised in Scheme 1.[15–17] The only report thereafter is on UV-laser photochemistry at 193.3 nm.[12] On the basis of results obtained from the exchange reaction of B_2H_6 and D_2 and measurement of the quantum yield of BH_3

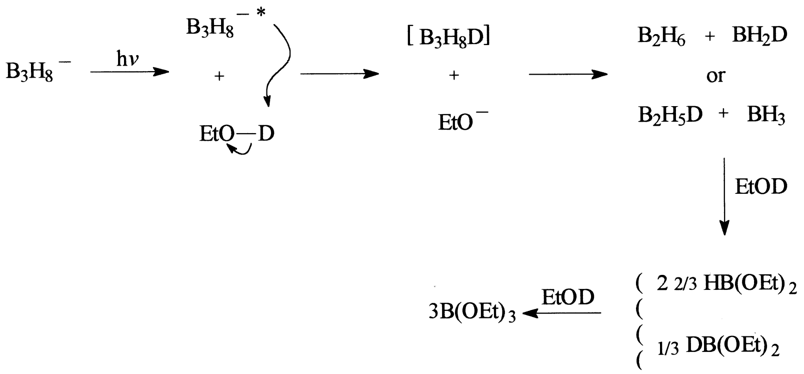
Table 1. UV parameters for binary boranes

Borane	B_2H_6	B_4H_{10}	B_5H_9	B_5H_{11}	B_6H_{10}	B_6H_{12}	n-B_9H_{15}	$B_{10}H_{14}$
λ_{max}/nm	<195	<195	<195	209	247	263	260	272
$\epsilon/m^2 mol^{-1}$	2.0[a]	0.71[a]	88[a]	82.9	165.1	278.9	~200[b]	248.6[c]

[a] Data refer to ϵ at 195 nm; λ_{max} is at shorter wavelengths
[b] Approximate value: sample decomposed during measurement
[c] In hexane solution



Scheme 1.



Scheme 2.

[$\phi(BH_3)=2.0\pm0.25$], it was concluded that the primary photochemical step is the same as that proposed in thermolysis (Eq. (1)):

$$B_2H_6 \xrightarrow{h\nu} 2(BH_3) \qquad (1)$$

2.2. Octahydrotriborate(1^-) anion

Photochemical irradiation of the octahydrotriborate(1^-) anion, $[B_3H_8]^-$ with ethanol[18] yields total ethanolysis of the boron hydride to form $HB(OEt)_2$, which ultimately forms $B(OEt)_3$. Analysis of the products of the reaction using EtOD in place of EtOH led to the proposed pathway shown in Scheme 2. The photochemical irradiation of $[B_3H_8]^-$ in a wide variety of chlorohydrocarbons has been found, however, to lead to sequential chlorination of the cluster without cage degradation.[18]

2.3. Pentaborane(9)

Apart from an early article on the irradiation of pentaborane(9) vapour[19] and some mercury sensitization work,[20,21] very little information was available in the literature until 1980. Generally, the main products of B_5H_9 photolysis are hydrogen, diborane, decaborane(14) and decaborane(16). There seemed to be agreement that the radical $B_5H_8^{\cdot}$ is the main reactive intermediate, originating from the primary step shown in Eq. (2):

$$B_5H_9 \xrightarrow{h\nu} B_5H_8^{\cdot} + H^{\cdot} \qquad (2)$$

Decaborane formation was then thought to proceed partly through recombination (Eq. (3)), or hydrogen elimination (Eq. (4)):

$$2B_5H_8^{\cdot} \rightarrow B_{10}H_{16} \qquad (3)$$

$$2B_5H_8^{\cdot} \rightarrow B_{10}H_{14} + H_2 \qquad (4)$$

However, Kline and Porter[22] disagreed with this fragmentation pattern and proposed the existence of the previously unknown neutral intermediate $[B_5H_7^*]$ generated in the primary reaction (Eq. (5)).

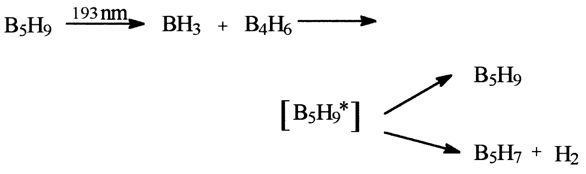
$$B_5H_9 + Hg^* \rightarrow [B_5H_7^*] + H_2 + Hg \qquad (5)$$

Collision of the intermediate $[B_5H_7^*]$ with a thermally activated B_5H_9 molecule then forms stable products (Eqs. (6) and (7)):

$$[B_5H_7^*] + B_5H_9 \rightarrow [B_{10}H_{16}^*] \xrightarrow{+M} B_{10}H_{16} \qquad (6)$$

$$[B_{10}H_{16}^*] \rightarrow B_{10}H_{14}+H_2 \qquad (7)$$

The existence of the free radical $B_5H_8^{\cdot}$ appeared doubtful.[22] Additional evidence for the reactive intermediate B_5H_7 and decaborane production has been provided[23] by direct photolysis of pentaborane in the gas phase at 193 nm using an ArF-laser. On the basis of the quantum yield of BH_3 production [ϕ_{BH3}] and B_5H_9 disappearance [ϕ_{-B5H9}], it was concluded that the primary process (Eq. (8)) is:

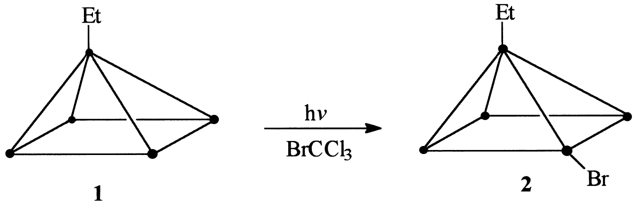


(8)

The addition of the neutral fragment B_5H_7 to a B_5H_9 molecule then leads to decaborane formation. Hexaborane(10) together with a polymer are also probably produced by decomposition of B_8H_{12} arising from the dimerisation of the B_4H_6 reactive intermediate.

The gas-phase photolytic reaction of pentaborane with hexafluoroacetone has been examined.[24] It produces *basal* and *apical* perfluoropropanol substituted compounds, 2-$[HO(CF_3)_2C]B_5H_8$ and 1-$[HO(CF_3)_2C]B_5H_8$ and the oxygen-boron bonded perfluoropinacol derivative 1-$[HO\{C(CF_3)_2\}O]B_5H_8$.

In an attempt to synthesise the 1-XB_5H_8 system, photolytic bromination of 1-ethylpentaborane(9) **1** with $BrCCl_3$ to give 2-bromo-1-ethylpentaborane **2** has been described very briefly (Eq. (9)).[25]



1 2

(9)

2.4. Hexaborane(10)

Preliminary results[14] for the photolysis of B_6H_{10} indicate that the initial step might be elimination of $\{BH_3\}$ to give B_2H_6 and B_5H_9 as the main products.

2.5. Decaborane(14)

UV irradiation[26,27] of decaborane(14) in cyclohexane for 8h produced a number of isomers of icosaborane(26), $B_{20}H_{26}$, (Eq. (10)) three of which could be separated by column chromatography in an 8:8:1 ratio (10% yield). These were characterized as 2,2′-bi(*nido*-decaboranyl), 1,2′-$(B_{10}H_{13})_2$ and 2,5′-$(B_{10}H_{13})_2$ respectively.

$$2B_{10}H_{14} \xrightarrow{h\nu} H_2 + B_{20}H_{26} \qquad (10)$$

This reaction was further explored[28] by irradiation of crystalline $B_{10}H_{14}$ with high-energy electron radiolysis from a beam of 3-MeV van der Graaf and several isomers of the conjugato-borane $(B_{10}H_{13})_2$ were separated by HPLC. Some of the products were characterized by comparison with the UV-photolysed products and identified as 1,2′-$(B_{10}H_{13})_2$, 2,5′-$(B_{10}H_{13})_2$ and 5,5′-$(B_{10}H_{13})_2$. The following mechanism was proposed[28] (Scheme 3).

$$B_{10}H_{14} \xrightarrow{h\nu} B_{10}H_{13}^{\bullet} + H^{\bullet}$$

$$H^{\bullet} + B_{10}H_{14} \longrightarrow H_2 + B_{10}H_{13}^{\bullet}$$

$$B_{10}H_{13}^{\bullet} + B_{10}H_{13}^{\bullet} \longrightarrow B_{20}H_{26}$$

Scheme 3.

2.6. Dodecaborane dianion

The photoinduced nucleophilic substitution of the perhalogenated *closo*-borane dianion $B_{12}X_{12}^{2-}$ by cyanide, cyanate and azide ions has been examined under aqueous conditions[29] (Eq. (11)):

$$B_{12}X_{12}^{2-} + nY^{-} \xrightarrow[H_2O]{h\nu} B_{12}X_{12-n}Y_n^{2-} + nX^{-} \qquad (11)$$

X=Cl, Br; Y=CN, OCN, N_3

2.7. Carboranes

Gas-phase mercury-photosensitised reactions of a variety of carboranes at 2537 Å have been investigated[20,21]and these resulted in the formation of corresponding boron–boron coupled carboranes. Thus, photolysis of 2,4-$C_2B_5H_7$ gave an 84% yield of a mixture of six isomers of the coupled cage system (Eq. (12)):

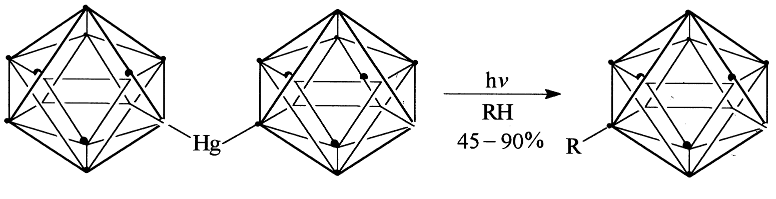
$$\begin{aligned} 2,4\text{-}C_2B_5H_7 \xrightarrow[84\%]{h\nu} & 3,3'\text{-}(C_2B_5H_6)_2 + 5,5'\text{-}(C_2B_5H_6)_2 + \\ & 1,1'\text{-}(C_2B_5H_6)_2 + 1,3'\text{-}(C_2B_5H_6)_2 + \\ & 1,5'\text{-}(C_2B_5H_6)_2 + 3,5'\text{-}(C_2B_5H_6)_2 \qquad (12) \end{aligned}$$

Cophotolysis of 1,5-$C_2B_5H_5$ and 1,6-$C_2B_4H_6$ resulted in the formation of two mixed cage coupled carboranes-2′,2-(1′,5′-$C_2B_3H_4$–1,6-$C_2B_4H_5$) and 1′,2-(1′,5′-$C_2B_3H_4$–1,6-$C_2B_4H_5$). The mercury-sensitised photolyses of 2,3-$C_2B_4H_8$ and 2,3-$Me_2C_2B_4H_6$ have also been investigated.[20] The photoreaction of 2,4- $C_2B_5H_7$ with hexafluoroacetone gave 5-[HO$(CF_3)_2$C]–2,4-$C_2B_5H_6$ and 5-[HO{C$(CF_3)_2$}O]–2,4-$C_2B_5H_6$ as the major products.[24]

For carboranes, UV irradiation has been reported to effect clean reaction between carborane clusters and inert solvents.[30] For example, alkylation of carboranes (1,7-$C_2H_2B_{10}H_9)_2$Hg and 1,7-$C_2B_{10}H_9Tl(O_2CCF_3)_2$ has been achieved by photolysis using the alkane as the solvent (Scheme 4).

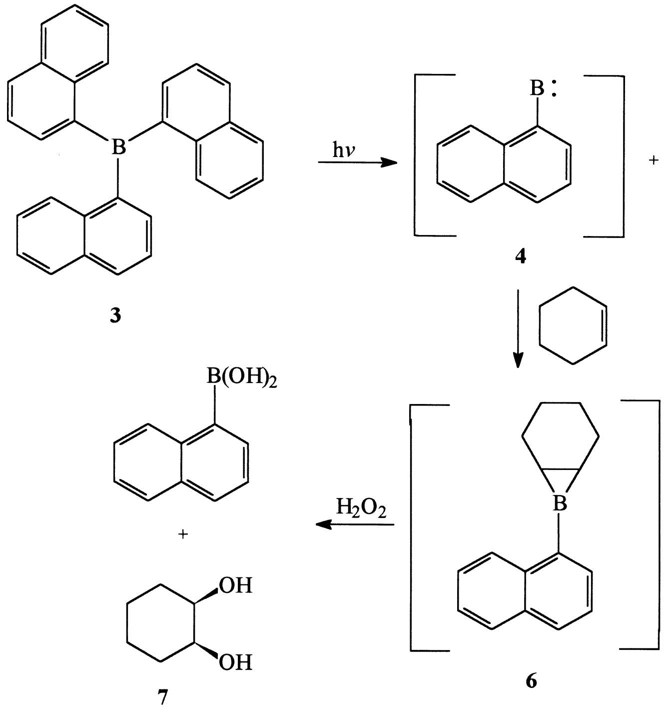
3. The Photochemistry of Triorganylboranes

Organoboranes can conceivably undergo all types of reactions photochemically that can be carried out thermally. Under appropriate conditions the organyl groups of triorganylboranes can be transferred to other atoms. If the terminus atom is carbon, new C–C bonds are formed.



R = Ph, C_6F_5, 1,4-$Me_2C_6H_3$

Scheme 4.



Scheme 5.

3.1. The photolysis of trimethylborane, triphenylborane, tribenzylborane and their adducts

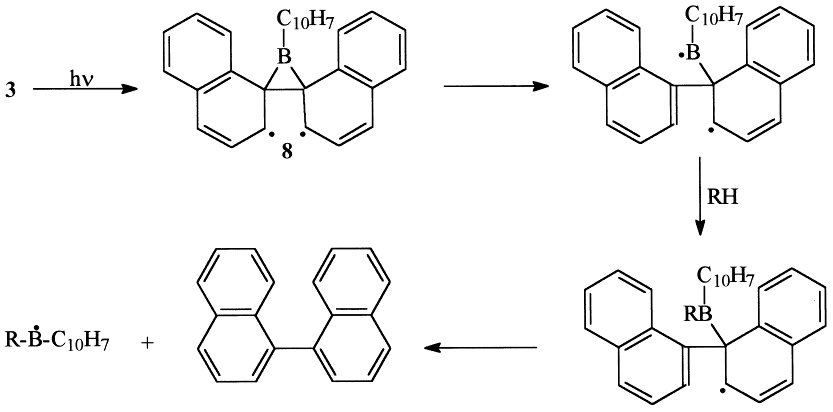
Preliminary results indicated that trimethylborane on photolysis forms methane as the major product.[31] However, γ-irradiation of trimethylborane and its ammonia adduct, has been reported to form the radicals $H_2C^{\cdot}{-}BMe_2$ and $H_2C^{\cdot}{-}BMe_2(NH_3)$ by α-hydrogen abstraction and these were characterised by ESR spectra.[32] The results suggest a π^1 structure with an estimated spin density of ~85% on carbon and ~15% on boron. It is concluded that these radicals are effectively planar at both the carbon and boron centres. On the contrary, irradiation of tribenzylborane and its ammonia complex[33] with a 500W high pressure mercury vapour lamp in a protic solvent leads to the cleavage of three boron–carbon bonds to form toluene (Eq. (13)). In an aprotic medium, however, bibenzyl is formed along with toluene.

$$\begin{array}{c} Bn_3B \\ \text{or} \\ Bn_3B:NH_3 \end{array} \xrightarrow[CH_3OD\ +\ THF]{h\nu} Bn{-}D + Ph{-}Me + Bn{-}Bn \qquad (13)$$

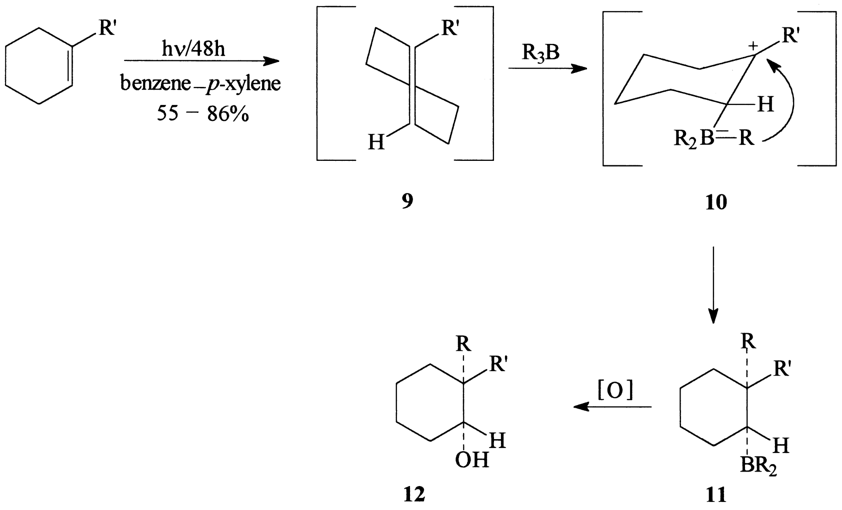
Photolysis of triphenylborane yields primarily phenol and phenylboronic acid.[34]

3.2. The photolysis of tri-1-naphthylborane

The photochemistry of tris(1-naphthyl)borane (TNB) **3** in hydrocarbon solvents has been studied.[35] Most interestingly it was claimed that there was the initial formation of 1-naphthylborene **4**, an assertion based upon the finding of



Scheme 6.



R = Et, nBu, CHOCH2CH2CH2; R' = H, Et, nBu

Scheme 7.

significant yields of 1,1-binaphthyl **5** and *cis*-1,2-cyclohexandiol **7** when the reaction was carried out in cyclohexene and then oxidized. This indicated the presence of boracyclopropane intermediate **6** (Scheme 5).

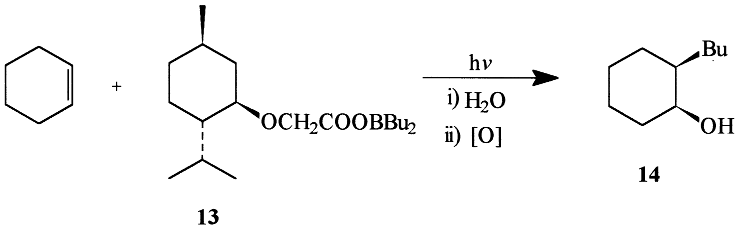
Later workers[36] were unable to reproduce these results and concluded that the production of *cis*-1,2-cyclohexanediol **7** had to be the result of over-irradiation. Instead a mechanism involving both the formation of the di-1-naphthyl-boryl radical **8** by primary B–C cleavage, and a sequence of biradical reactions was suggested as depicted in Scheme 6.

The photochemistry of TNB **3** has been also investigated by using time-resolved laser flash photolysis and matrix isolation spectroscopy.[37] The laser-flash photolysis of **3** in cyclohexane yielded a transient spectrum produced from two transient species with $\lambda_{max}=460$ nm (lifetime=10 μs) and $\lambda_{max}=640$ nm (life time=20 μs). The latter transient additionally showed some absorption at $\lambda_{max}>800$ nm arising from triplet excited states. The paradoxical situation of two long-lived triplet excited states being generated by excitation of a single compound has been explained in terms of two isomeric uncharacterised structures of starting TNB. The phosphorescence spectrum of TNB **3**, matrix isolated in Ar at 10 K, consisted of three bands, which have been attributed to two different emitting isomers. The corresponding triplet energies differ significantly and are 57.8 and ~48 kcal/mol, respectively. This laser-flash photolytic study thus gave no conclusive evidence for the formation of 1-naphthylborene **4**, or the di-1-naphthylboryl radical **8**. Since the first triplet excited states of the so called two isomers of TNB **3** are unreactive towards olefins (cyclohexene) and CCl_4, it has been concluded that it is the first excited singlet state of TNB that is responsible for most of its photochemistry.

3.3. Photochemically induced reactions of trialkylboranes

3.3.1. Photochemical reactions with cycloalkenes. Irradiation of primary trialkylboranes and cyclohexenes or cycloheptene[38] in the presence of *p*-xylene as a sensitiser proceeds by addition of the organoborane across the double bond. In the case of cyclohexenes substituted cycloalkylboranes **11** are produced which upon subsequent oxidation afford the corresponding alcohols **12**. Boranes such as **11** are difficult to access in other ways (Scheme 7).

Cyclopentene, cyclooctene and cyclododecene did not react with trialkylboranes upon irradiation. The behaviour of six- and seven-membered cyclenes[39] has been attributed to the possibility that upon irradiation they form the extremely reactive *trans*-cyclohexene **9** and *trans*-cycloheptene, with a strained double bond that adds R_3B to form ions such as **10**. Subsequent migration of the alkyl group from the boron to the positively charged carbon of the ring proceeds stereospecifically. Asymmetric photoreaction of cyclohexene has been brought about by means of

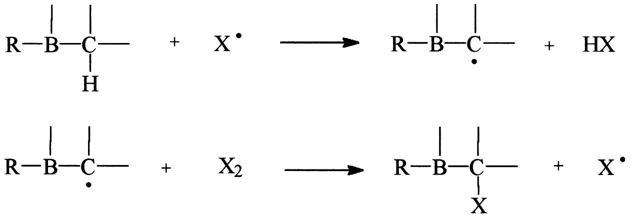


Scheme 8.

dibutylboryl-(1*S*)-menthyloxyacetate **13**.[38] Subsequent oxidation furnished an optically active alcohol **14** (Scheme 8).

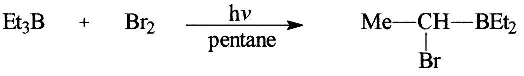
3.3.2. Photochemical reactions with halogens.

Since the first study of the bromination of organoboron compounds[40] the halogenation of organoboranes is a widely explored topic and is partially discussed in review articles[41–45] and books.[46–48] The reaction of organoboranes with halogens may proceed by a radical or ionic mechanism. In the radical mechanism, an α-hydrogen is first replaced by a halogen (Scheme 9).



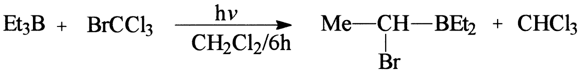
Scheme 9.

For example, Brown and co-workers[49] have reported the bromination of triethylborane in pentane with 150 W light bulbs to give α-bromoethyldiethylborane (Eq. (14)).



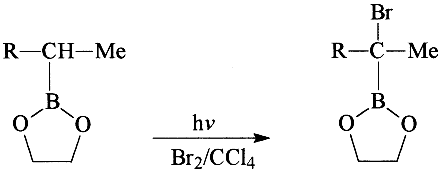
$$Et_3B + Br_2 \xrightarrow[pentane]{h\nu} Me-\underset{Br}{CH}-BEt_2 \qquad (14)$$

Instead of bromine, bromotrichloromethane has also been used as the halogenating agent[50] to give the same product (Eq. (15)).



$$Et_3B + BrCCl_3 \xrightarrow[CH_2Cl_2/6h]{h\nu} Me-\underset{Br}{CH}-BEt_2 + CHCl_3 \qquad (15)$$

Esters of *s*-alkylboronic acids are also readily photobrominated in the α-position with the formation of α-bromoalkylboranes in quantitative yields[51,52] (Eq. (16)).



(16)

This α-hydrogen abstraction upon halogenation is further supported by an investigation[53,54] of the kinetics of the photochemical iodination of triethylborane in cyclohexane (Eqs (17) and (18)). The second step (Eq. (17)), which involves the attack on triethylborane by an I˙ radical, is the rate determining step:

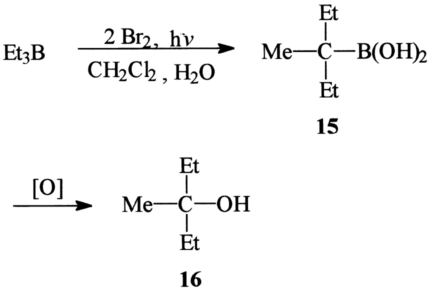
$$I_2 \leftrightharpoons 2I^{\cdot}$$

$$I^{\cdot} + Et_3B \rightarrow Et_2BI + Et^{\cdot} \qquad (17)$$

$$Et^{\cdot} + I_2 \rightarrow EtI + I^{\cdot} \qquad (18)$$

The α-haloalkylborane (Scheme 9) may either be cleaved by the HX liberated or undergo rearrangement of an alkyl group from boron to an α-carbon atom, and a halogen to a boron via a four membered transition state (Scheme 10).

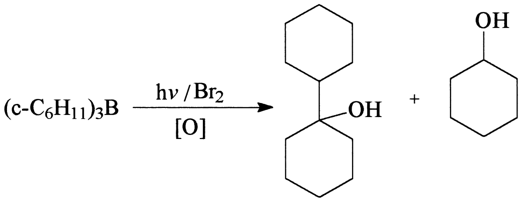
Such rearrangements[55–56] generally occur under aqueous conditions. Thus the photolysis of triethylborane and bromine in aqueous methylene chloride is accompanied by migration of two alkyl groups to produce (3-methyl-3-pentyl)boronic acid **15**, oxidation of which affords the corresponding alcohol **16**[42,57] (Eq. (19)).



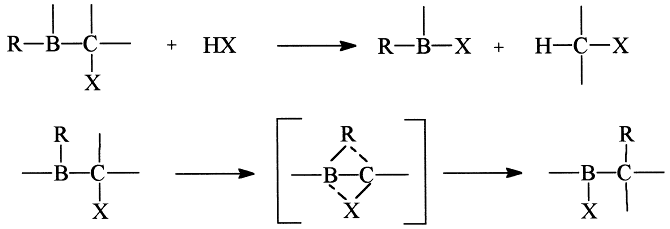
$$Et_3B \xrightarrow[CH_2Cl_2,\ H_2O]{2\,Br_2,\ h\nu} Me-\overset{Et}{\underset{Et}{C}}-B(OH)_2 \xrightarrow{[O]} Me-\overset{Et}{\underset{Et}{C}}-OH \qquad (19)$$

15 **16**

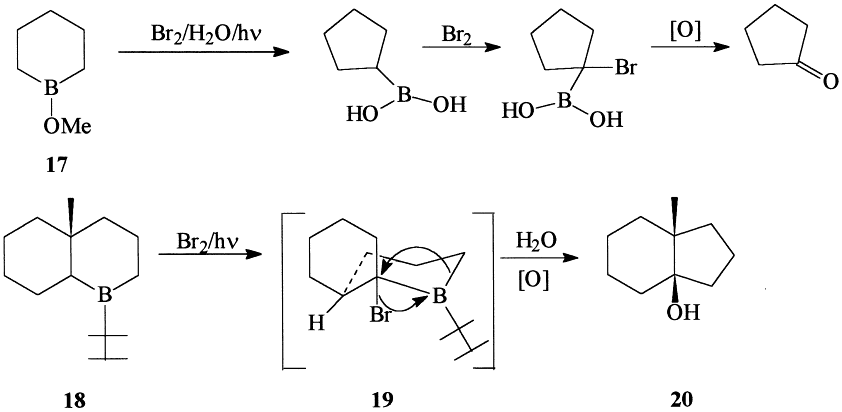
Similarly treatment of tricyclohexylborane with bromine followed by oxidation gave 89% of 1-cyclohexylcyclohexanol (Eq. (20)):



(20)

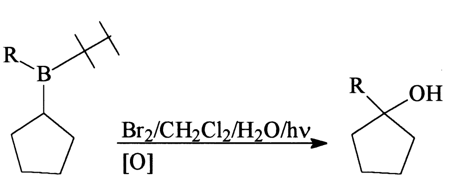


Scheme 10.



Scheme 11.

Cyclopentanols have also been prepared[58] and interestingly no migration of the bulky thexyl group took place (Eq. (21)):



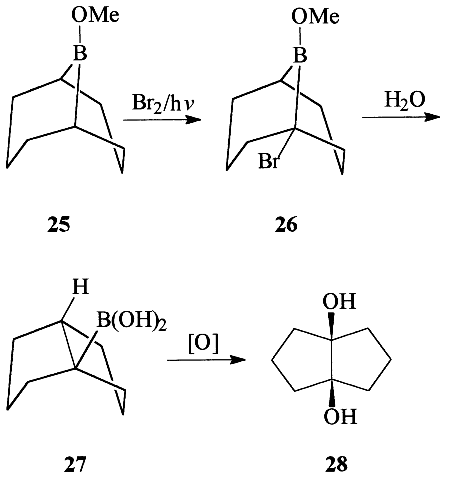
(21)

R = ^{n}Bu, ^{i}Bu, ^{n}Hex, $Cl(CH_2)_5$, $EtOCO(CH_2)_3$

Six-membered boracyclanes such as **17** and **18** undergo ring contraction to the five-membered carbocyclic compounds upon light induced bromination in the presence of water followed by oxidation[59] (Scheme 11).

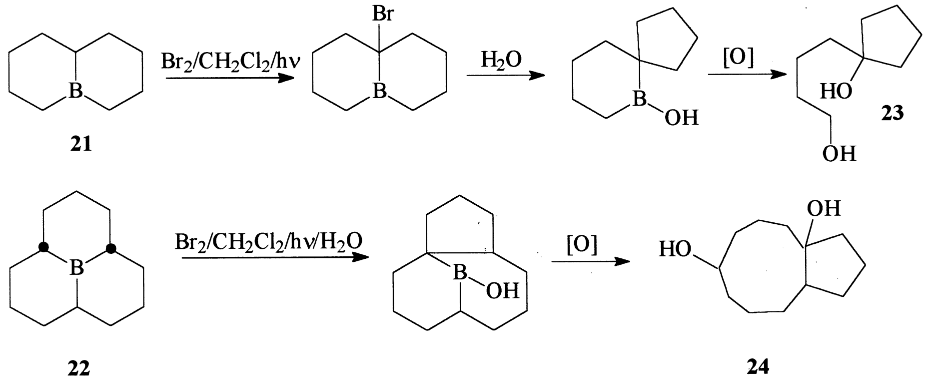
The predominant formation of the *cis*-isomer **20** in the bromination of **18** is due to the preferred formation of *cis*-9-bromo-1-thexyl-boradecalin **19** in the α-bromination stage, followed by migration of the B–C bond. Similarly light induced bromination of borapolyclanes **21** and **22** proceeds selectively at the tertiary position. Hydrolysis–oxidation then provides the diols **23** and **24** respectively[60] (Scheme 12).

However, photobromination of 9-methoxy-9-borabicyclo[3.3.1]nonane **25**, although sluggish, takes place at the bridgehead position to give **26** which rearranges to **27** and subsequently gives **28** on oxidation[60] (Eq. (22)).



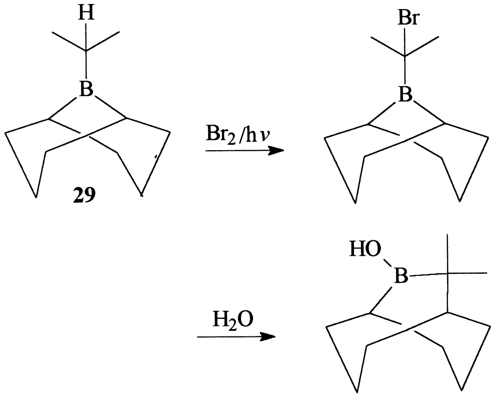
(22)

Photobromination of B-*i*-propyl-9-BBN **29** occurs almost exclusively at the α-position of the *i*-propyl group[61,62]



Scheme 12.

(Eq. (23)).



(23)

The photobromination of B-*i*-propyl-2-boraadamantane **30**[63] occurs by both radical and electrophilic mechanisms simultaneously (Scheme 13) depending on reaction conditions and affords diols **31** and **32** and oxaadamantane **33**. In the presence of water, a solvated Br$^+$ takes part in bromination and this results in the formation of hydroxy(3-noradamantyl)I-propylborane **34** which is oxidised to 3-noradamantol **35** (Scheme 14).

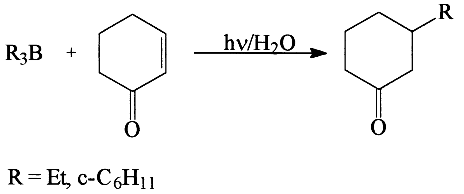
3.3.3. Photochemical reactions with ketones. Ketones in their triplet state (n,π^* or π,π^*) react with organoboranes via bimolecular homolytic substitution at boron[64,65] (Eq. (24)):

$$R_3B + [R^1R^2CO]^3 \xrightarrow{h\nu} R_2BO\underset{\mathbf{36}}{\dot{C}R^1R^2} + R^{\cdot} \qquad (24)$$

R=^{n}Bu, ^{i}Bu, ^{s}Bu; R^1, R^2=Me, Me; Me, Ph; Et, Ph; Ph, Ph

Both the alkyl radical and **36** have been observed when the ketone and borane are cophotolysed in the cavity of an ESR spectrometer. Rate constants for the S$_H$2 process have been calculated and are of the order of 10_8u l mol^{-1} s^{-1} for both $n\to\pi^*$ or $\pi\to\pi^*$ triplets. The radicals **36** have also been quenched by a conjugated diene, piperylene. It is suggested that the ketone triplets form a polar complex with the triorganylborane, which can then decompose by loss of the alkyl radical R$^{\cdot}$ or can revert to trialkylborane and a ground-state ketone.

3.3.4. Photochemical reactions with α,β-unsaturated carbonyl compounds. Trialkyl- and tricycloalkylboranes add to 3-substituted α,β-unsaturated aldehydes and ketones under UV irradiation[66,67] (Eq. (25)).



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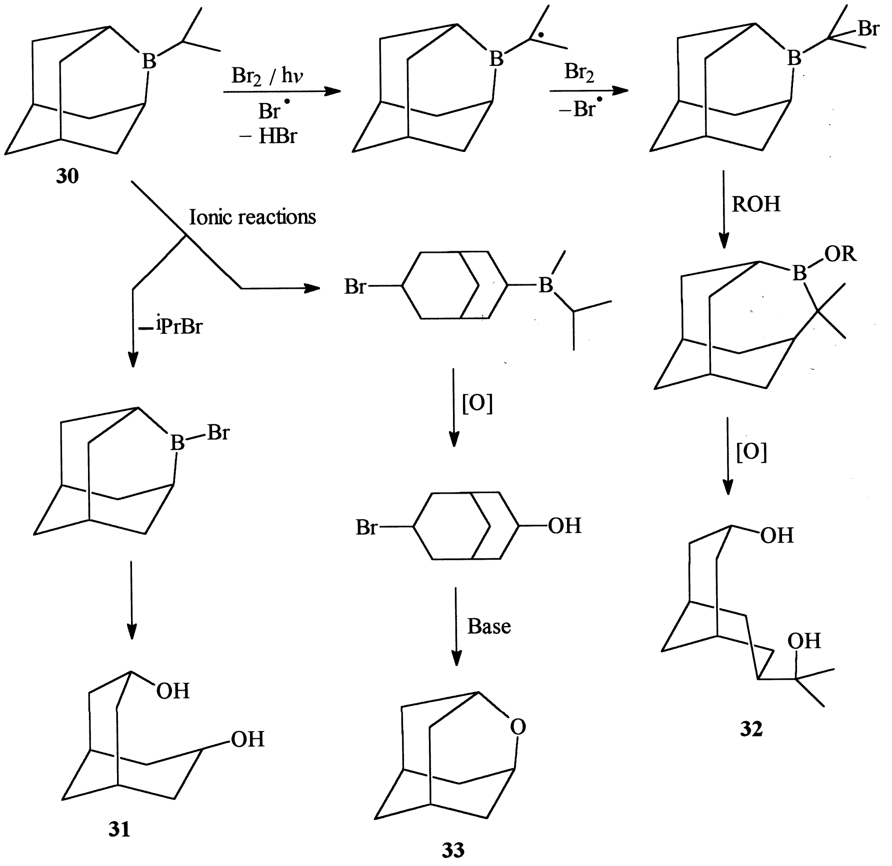
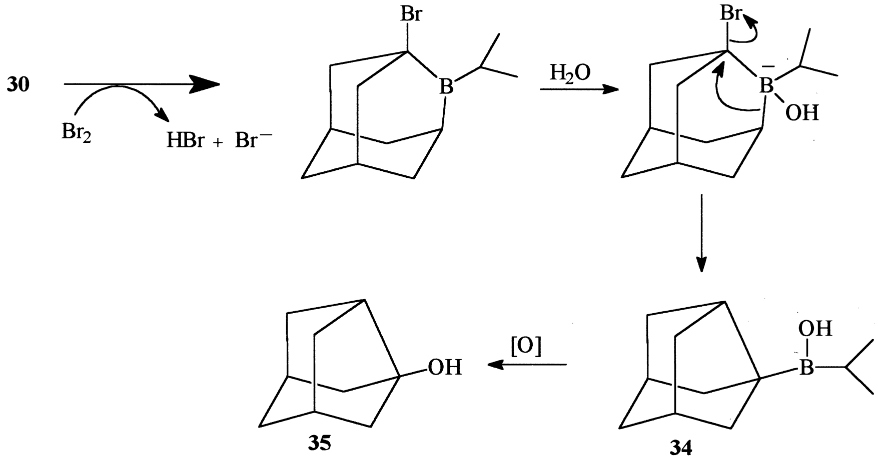


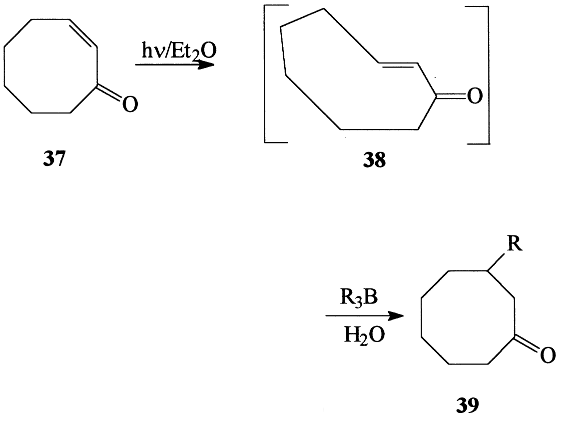
Scheme 13.



Scheme 14.

The reaction proceeds by a chain mechanism[68] as shown in Scheme 15.

Isomerisation of the *cis*-ketone **37** takes place upon mercury lamp irradiation[38] at −78°C to the *trans*-isomer **38** which readily reacts with triethyl- or tri-*i*-propylborane to form 3-alkylated cyclooctanones **39** in 70 and 83% yield, respectively, after hydrolysis (Eq. (26)).



(26)

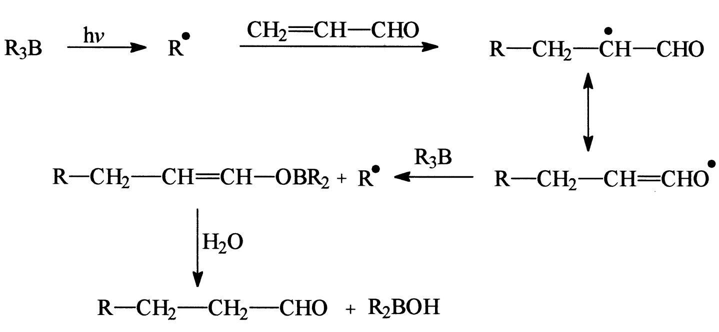
3.3.5. Photochemical reactions with β-diketones and β-ketoesters. Irradiation[69] of trialkylboranes with β-dicarbonyl compounds **40** leads to the formation of β-ketoalcohols **45** and unsaturated ketones **46** via conjugate addition of borane to the enol **41**/**42** to give **43**/**44** followed by intramolecular alcoholysis (Scheme 16).

3.3.6. Photochemical reactions with di-*t*-butylperoxide. It has been shown[70–73] that if di-*t*-butylperoxide is photolysed in the presence of alkylboranes, the *t*-butoxy radicals that are formed undergo an S_H2 reaction at boron.[64–65] The displaced alkyl radicals have been observed by ESR spectroscopy. Rate constants for the reactions were determined by allowing cyclopentane to compete with the trialkylborane for reaction with *t*-butoxy radicals (Scheme 17).

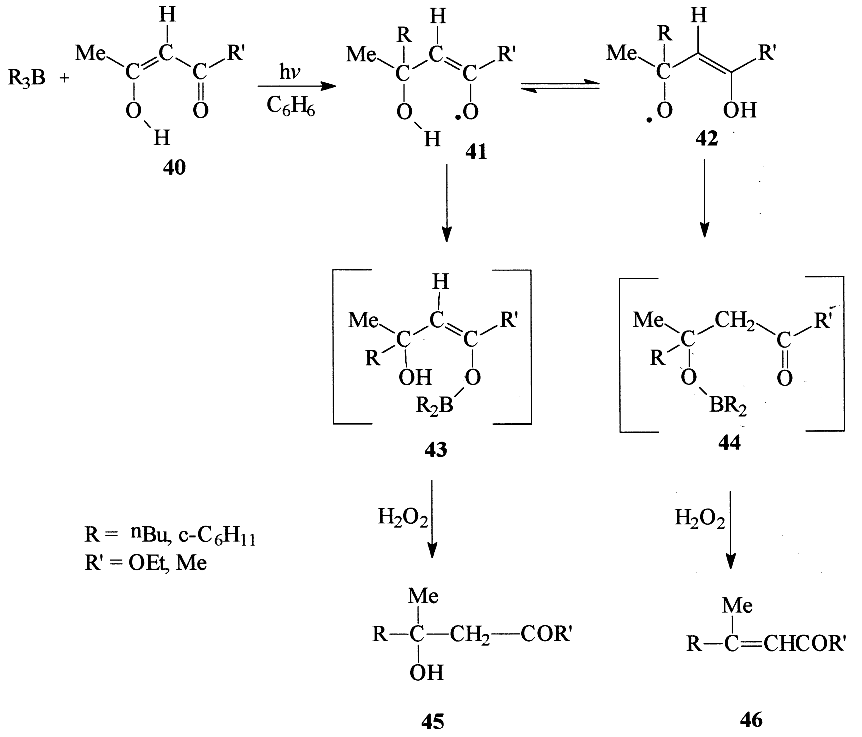
3.3.7. Photochemical reactions with amines. Reaction of tributylborane with chlorodimethylamine in the presence of galvinoxyl proceeds by path a (Scheme 18) to give dimethylbutylamine and dibutylchloroborane in quantitative yield.[74]

In the absence of galvinoxyl however, the reaction proceeds by both pathways a and b, producing equal amounts of butyl chloride and dimethylbutylamine When the reaction is initiated by UV light, the reaction follows path b by a chain radical process. Facile displacement of an alkyl radical from organoboranes by the Me_2N radical, generated photochemically from tetramethyltetrazene, has also been reported[75] (Scheme 19).

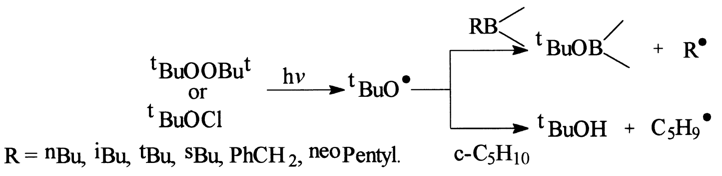
Photolysis[76] of a pentane solution of triethylborane and 2,2,4,4-tetramethylpentane-3-imine **47** in the cavity of an ESR spectrometer at below −10°C gave the radicals **48**



Scheme 15.



Scheme 16.



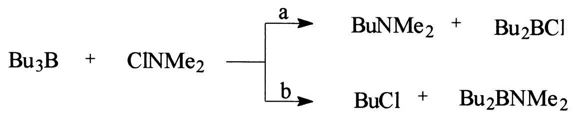
Scheme 17.

and **49** (Eq. (27)).

$$\mathrm{Et_3B} + {}^t\mathrm{Bu_2C{=}NH} \xrightarrow[\text{pentane}]{h\nu} {}^t\mathrm{Bu_2\dot{C}NHBEt_3} + \mathrm{Et}^{\cdot} \qquad (27)$$

47 **48** **49**

The formation of **48** probably involves an imine–borane complex, rather than an intramolecular S_H2 reaction.[64] The formation of the radical **48** is sensitised by the addition of conjugated dienes (butadiene and piperylene) and this is attributed to their ability to transfer singlet energy to the imine–borane complex.



Scheme 18.

$$\mathrm{Me_2N\text{-}N{=}N\text{-}NMe_2} \xrightarrow{h\nu} 2\,\mathrm{Me_2N^{\bullet}} + \mathrm{N_2}$$

$$2\,\mathrm{Me_2N^{\bullet}} + \mathrm{Bu_3B} \longrightarrow \mathrm{Bu_2BNMe_2} + \mathrm{Bu^{\bullet}}$$

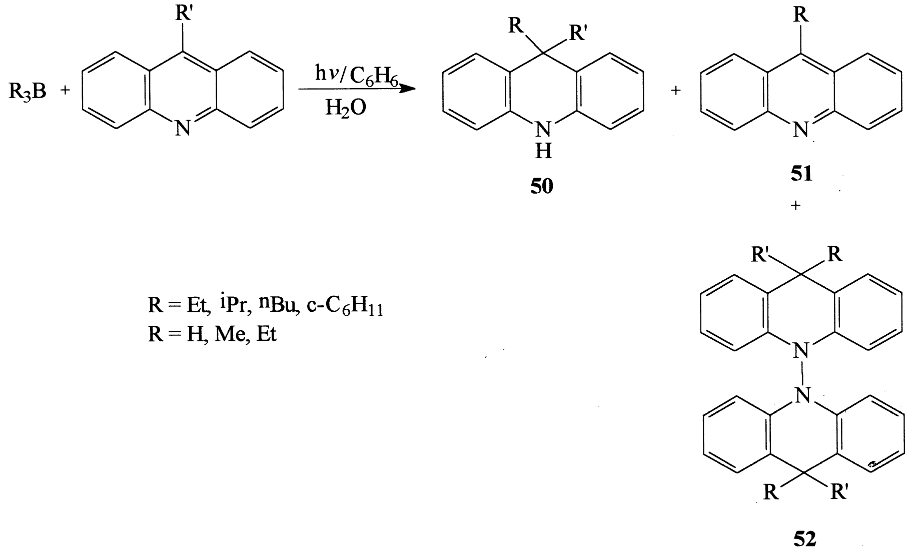
Scheme 19.

p-and *s*-Trialkylboranes add to acridine and its derivatives upon irradiation or on heating in benzene solution.[38] The main products are 9,9-dialkylacridans **50** (60–90%) with an impurity of 3–8% of the 9-alkylacridine **51** and 3–4% of the 9,9′-biacridan **52** (Scheme 20).The reaction is slow but the accelerating action of irradiation is explained by the high basicity of the acridines in the first excited singlet state.

3.3.8. Photochemical reactions with isonitriles. In an attempt to convert diboron compound **53** to 1,3-diaza-2,4-diboralidines **55** (Scheme 21), irradiation of **53** (R=R′=Et) in pentane was explored but only a 75% yield of the 2,5-diborapiperizines **54** was obtained.[77,78]

3.3.9. Photochemical reactions with mercaptans, thioketones and disulfides. Photolysis of a variety of trialkylboranes with mercaptans[79] (Eq. (28)), 4,4′-bis(dimethylamino)benzothiophenone[80] (Eq. (29)), and disulfides[81] (Eq. (30)) serves as a convenient method for the preparation of esters of dialkylthioborinic acids.

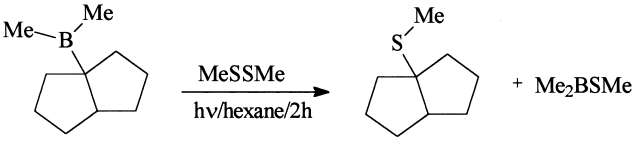
$$\mathrm{R_3B} + \mathrm{R'SH} \xrightarrow[\mathrm{ROOR}]{h\nu\text{ or}} \mathrm{R_2BSR'} + \mathrm{RH} \qquad (28)$$



Scheme 20.

$$Bu_3B + 2Ar_2C{=}S \xrightarrow[C_6H_6/3\text{–}5\ \text{days}]{h\nu} 2Bu_2BSBu + 2Ar_2C{=}CAr_2 \qquad (29)$$

$Ar{=}4\text{-}Me_2NC_6H_5$



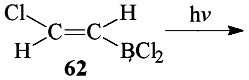
(30)

A wide range of bis(alkylthio)alkylboronate esters and organic sulfides have similarly been prepared.[82] The reactions are initiated by light or O_2 and are inhibited by iodine.

3.4. The photochemistry of alkenylboranes

3.4.1. Photocyclisations. Ultraviolet irradiation of *trans*-butadienes **56** effects their cyclization to the boracyclopent-3-ene **58**.[83,84] The transformation occurs via initial excited state *trans–cis* double bond isomerisation to the *cis*-dienylboranes **57** which then undergo cyclisation with transfer of one cycloalkyl group from boron to the adjacent carbon. Subsequent manipulation of **58** leads to a convenient stereoselective route to **59** and, via **60**, to **61** (Scheme 22).

3.4.2. Dehydrohalogenation. Light-induced dehydrohalogenation of the substituted vinylborane **62** leads to a mixture of several elimination products[85] (Eq. (31)).

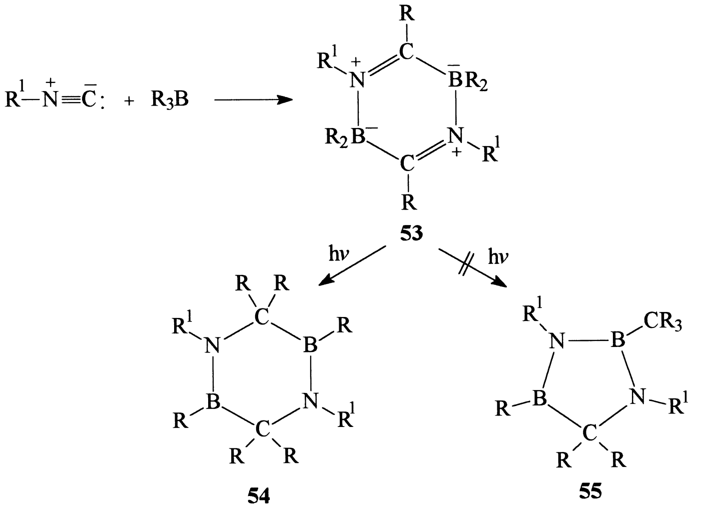


62

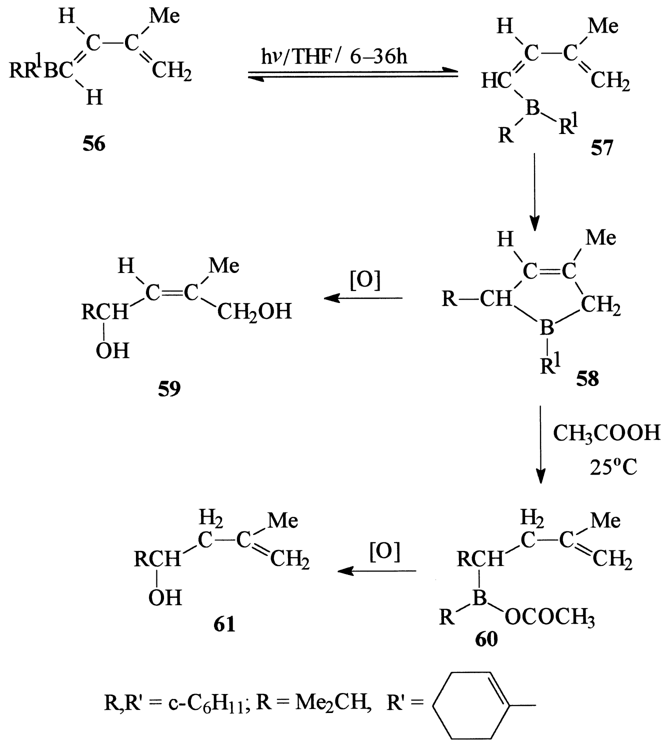
$$HC{\equiv}CBCl_2 + HC{\equiv}CH + H_2C{=}CHBCl_2 + HCl + BCl_3 \qquad (31)$$

3.5. 1,2-Photorearrangements of pyridine-alkylnyldiarylboranes to borirenes

In an earlier attempt to prepare triphenylborirene **64**, Eisch

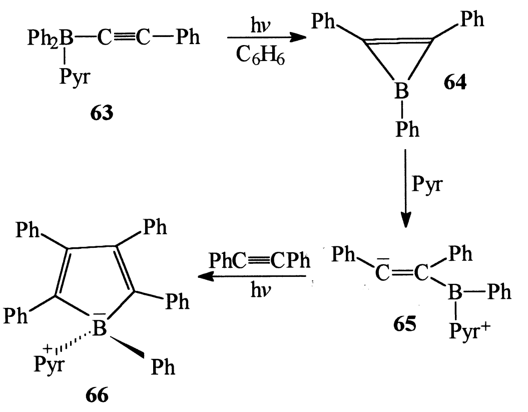


Scheme 21.

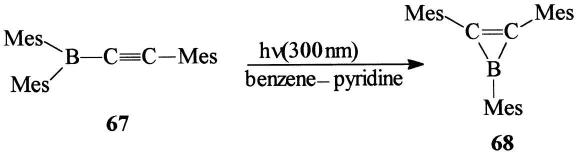


Scheme 22.

and coworkers[86] examined the photo-rearrangement of the diphenyl(phenylethynyl)borane–pyridine complex **63** (Scheme 23). Photolysis of **63** in benzene in the presence of diphenylacetylene gave pentaphenylborole–pyridine **66**, possibly via **65**, as shown in Scheme 23. Subsequently,[87] in an attempt to prepare a solid borirene, photolysis of sterically hindered dimethyl(methylethynyl)borane **67** was examined in a donor solvent. Indeed the photolysis of **67** gave the solid borirene **68** (Eq. (32)), but the high symmetry of the crystals prevented unambiguous differentiation between boron and carbon atoms in the central ring as well as the extent of any π-electron delocalisation between tricoordinate boron and sp^2-hybridised carbon in the ring.

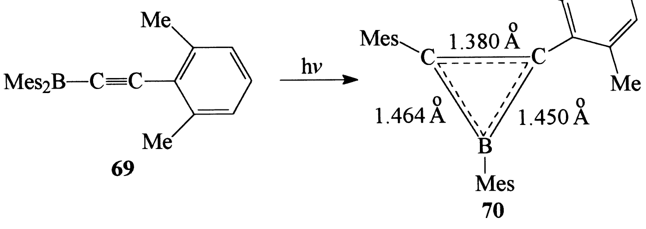


Scheme 23.



(32)

To disrupt such high symmetry, **69** was photolysed and the borirene **70** was obtained and fully characterised[88] (Eq. (33)).

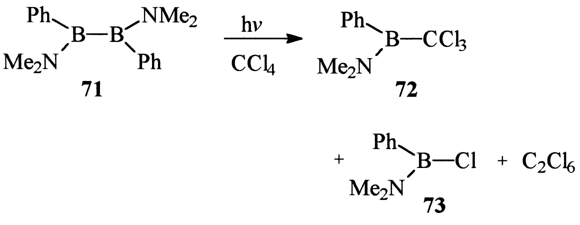


(33)

4. The Photochemistry of B–B, B–N, B–O and B–X Compounds

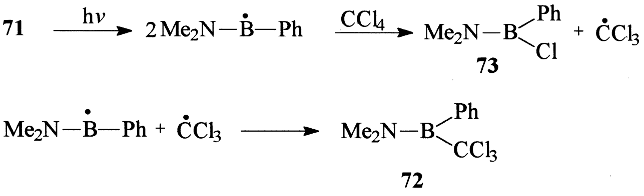
4.1. Photolytic cleavage of the B–B bond

Under photolytic conditions, the diboron(4) compound **71** underwent cleavage reactions[89] to afford two monoboron products **72** and **73** (Eq. (34)).



(34)

A free radical mechanism has been proposed for this reaction as shown in Scheme 24.



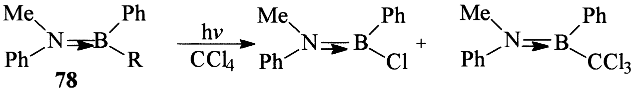
Scheme 24.

The B–B bond cleavage has been rationalised in terms of EHT-INDO theoretical calculations, which predict that σ–π^* is the lowest singlet excited state.[90]

4.2. Photochemical reactions of B–N systems

The B═N bond in aminoboranes is isoelectronic with a C═C bond. In an attempt to compare the photochemical properties of each class, Hancock and co-workers[91–93] have studied the photolysis of a series of compounds with B–N functionality. The aminoboranes, however, show different behaviour from C═C compounds. Thus it has been demonstrated that in contrast with the cleavage of only the B–B bond in the diboron compound **71**, both B–B and B–N cleavage reactions take place for tetrakis (dimethylamino)diborane(4) **74**. The reaction course was found to be solvent dependent[91] to yield **75**, **76** and **77** (Scheme 25).

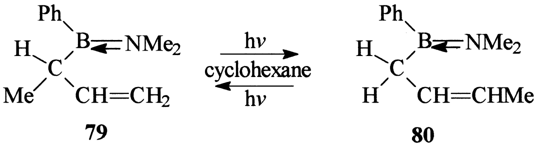
It has been postulated that charge–transfer complexation with CCl_4 and $CHCl_3$ in the excited state is responsible for the observed B–N cleavage by a free radical mechanism. The free radical cleavage of the boron–carbon bond in the photolysis of (*N*-methylanilino)phenylalkylboranes **78** has also been reported[92] (Eq. (35)).



R = Et, ^{i}Pr, Bn

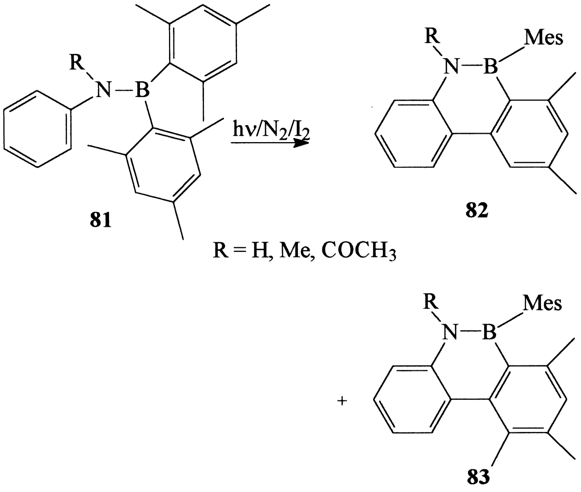
(35)

On irradiation of the allyl(amino)borane **79**, an analogue of a 1,4-diene, a 1,3-shift of an aminoboryl fragment occurs, leading to the isomeric borane **80**. The reaction is photoreversible[93] (Eq. (36)).



(36)

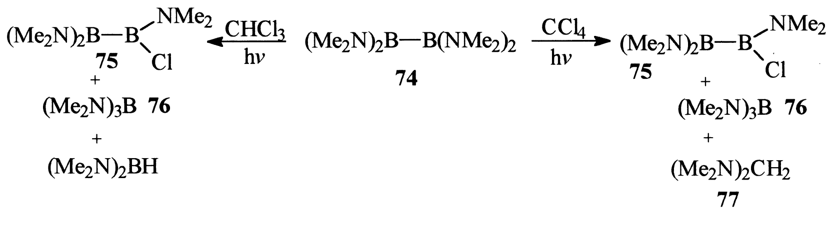
Photocyclisation of anilinodimesitylboranes **81** in the presence of iodine yields **82** and **83**[94–96] (Eq. (37)).



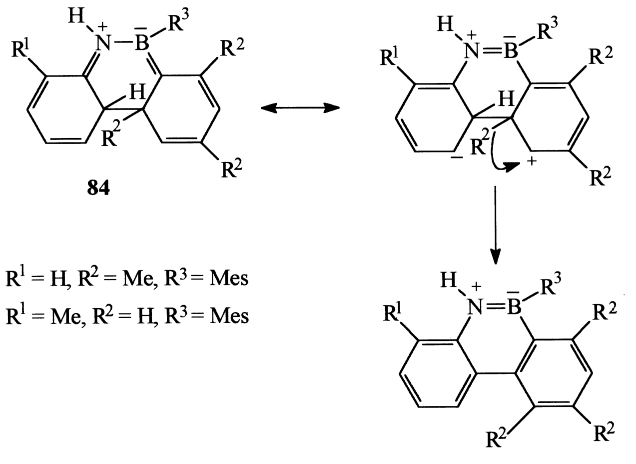
R = H, Me, $COCH_3$

(37)

It has been further shown[97] that the ratio of **83** (methyl group rearranged) to **82** (methyl group eliminated) during the photolysis of **81** is dependent upon the concentration of iodine present. At less than 10^{-3} M concentration, the major product was **82** whereas at concentrations above 5×10^{-3} M, the major product was a methyl rearranged azaborine **83**. It was postulated that during photolysis, a reduced species **84** is formed, which is then oxidised to form the aromatic system (Scheme 26). The absorption and fluorescence spectra of a series of aminoboranes have been measured



Scheme 25.



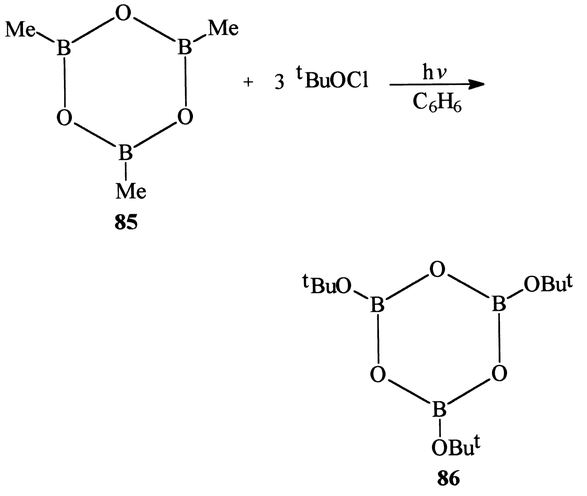
Scheme 26.

and show very large Stokes' shifts.[98] The dependence of the fluorescence wavelength on solvent polarity has been interpreted as an indication of the dipolar nature (–B–N–) of the first excited state of the borazene nucleus. Other aminoboranes, however, exhibit only slight Stokes' shifts and the emission has been characterised as that from a polar $\pi\pi^*$ excited state.[99]

The work on borazine has been previously summarised.[10]

4.3. Photochemistry of boronic acids and esters

Very little information is available on the photochemistry of compounds with B–O bonds. Nitrophenyl- and pyridylboronic acids undergo photodeboronation by methanol or alcoholic alkali under UV irradiation. The photoprotonolysis of ferrocenylboronic acid is accelerated in acid medium.[100] UV irradiation of methane boronic anhydride **85** and *t*-butyl hypochlorite in benzene resulted in the displacement of methyl radicals from boron by *t*-butoxy radicals affording tri-*t*-butoxyboroxine **86**[101] (Eq. (38)).



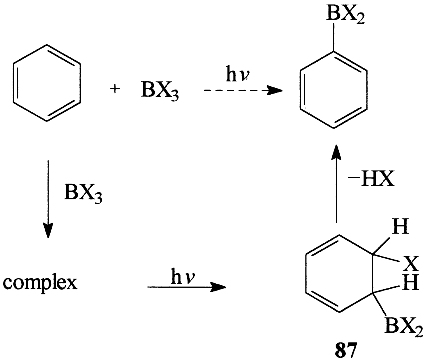
(38)

Bromine and HBr add smoothly to ethynylboronates upon UV irradiation to form 1,2-dibromovinylboronates and 1-bromovinylboronates, respectively[102] (Eq. (39)).

$$(BuO)_2B{-}C{\equiv}CH + HBr \xrightarrow[58\%]{h\nu} (BuO)_2B{-}CH{=}CHBr \qquad (39)$$

4.4. Photoreactions of trihaloboranes

Photolysis of a mixture of trihaloboranes and an arene (benzene, toluene, biphenyl and naphthalene) results in the formation of dihaloborylarenes which upon hydrolysis furnish the arylboronic acids. The reaction takes place by production of an intermediate complex which yields $^{\bullet}BX_2$ on photoactivation and this then reacts to give an addition product **87**. Subsequent elimination of hydrogen halide then affords the dihaloborylarenes[103] (Scheme 27).



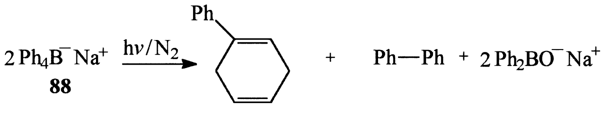
Scheme 27.

The photolysis of *cis*-1,2-bis(dichloroboryl)ethene, $Cl_2BCH{=}CHBCl_2$ gave the *trans*-isomer (50% yield).[104]

5. The Photochemistry of Alkyl(aryl)borates

5.1. Direct photolysis

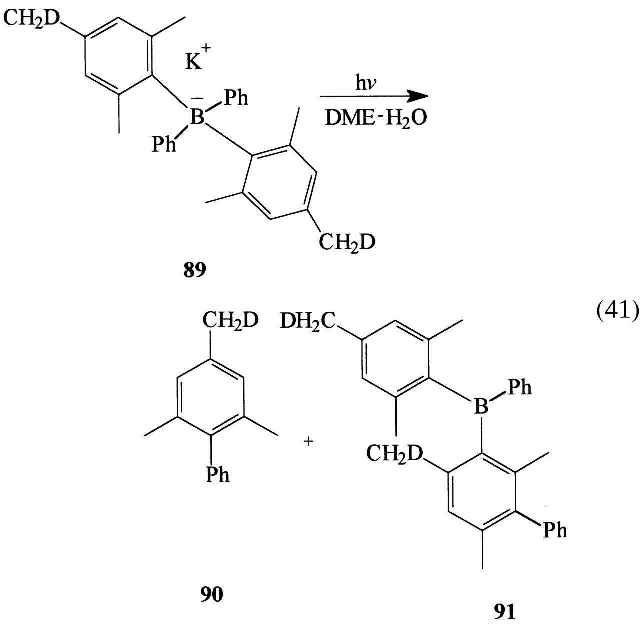
Irradiation of sodium tetraphenylborate[34,105–109] **88** in aqueous solution under a nitrogen atmosphere produces 1-phenyl-1,4-cyclohexadiene and biphenyl as the major products. Under these conditions, the ultimate boron-containing product is the sodium salt of diphenylborinic acid[105–107] (Eq. (40)).



(40)

The mechanism of this unusual rearrangement was investigated by means of labelling experiments. Thus, the photolysis of deuterium-labelled potassium dimesityldiphenylborate **89** in water containing dimethoxyethane was studied. The products were **90** and the triarylborane

91[109] (Eq. (41)).



89

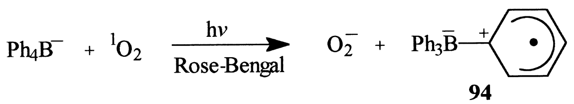
(41)

90

91

These studies showed that the new carbon–carbon bond is formed intramolecularly between carbon atoms originally bound to boron. The substitution pattern observed in the product led to the proposal that the reaction proceeds through the formation of the bicyclic bridged borate intermediate(s) **92**/**93** as shown in Scheme 28.

When the photolysis is carried out in air with Rose-Bengal as sensitizer, biphenyl is formed in up to 75% yield. These results have been interpreted as an electron transfer mechanism from the π-system of the tetraphenylborate anion to singlet oxygen[108] to initially give **94** (Eq. (42)).

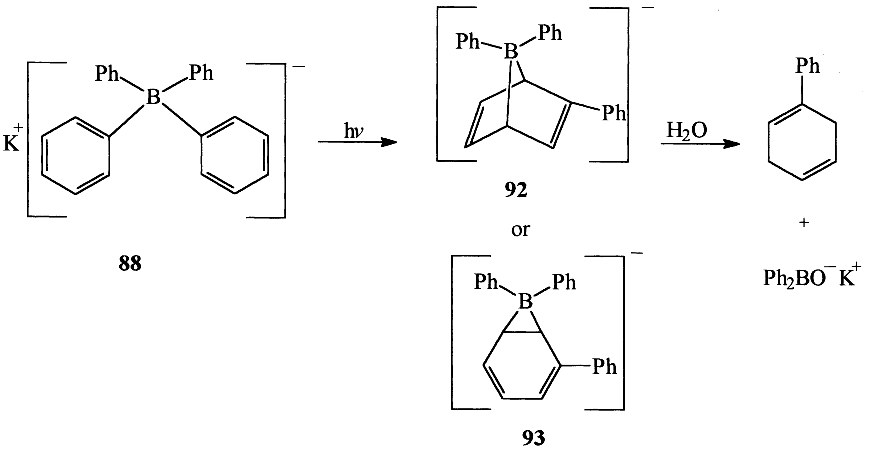


94

(42)

Photolysis of sodium tetraphenylborate in oxygen-free DME or THF solution was postulated to give the diphenylborene anion (Ph_2B^-) by loss of biphenyl (path a) in competition with the direct formation of arylborohydrides[110] (path b). The borene anion Ph_2B^- exhibits carbenoid-like activity and reacts with diphenylacetylene to give an equilibrating mixture of **95** and **96** (Scheme 29).

In contrast a subsequent study[111] of the irradiation of tetraphenylborates showed that the primary photochemical reaction is formation of one of the bridged borate intermediates **92**/**93** as originally proposed and does not result in the formation of diphenylborene anion. To substantiate this hypothesis,[112,113] the first isolation and characterization of a boratanorcaradiene anion, 2,5,7,7-tetraphenyl-7-borata-bicyclo[4.1.0] hepta-2,4-diene **98**, by X-ray crystallography was achieved by the photolysis of tetramethylammonium(4-diphenylyl)triphenylborate **97** in oxygen-

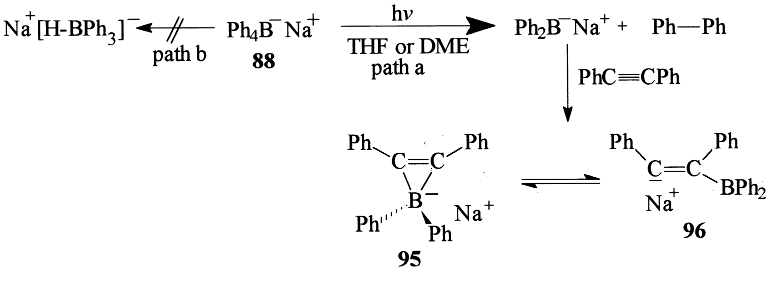


88

92

93

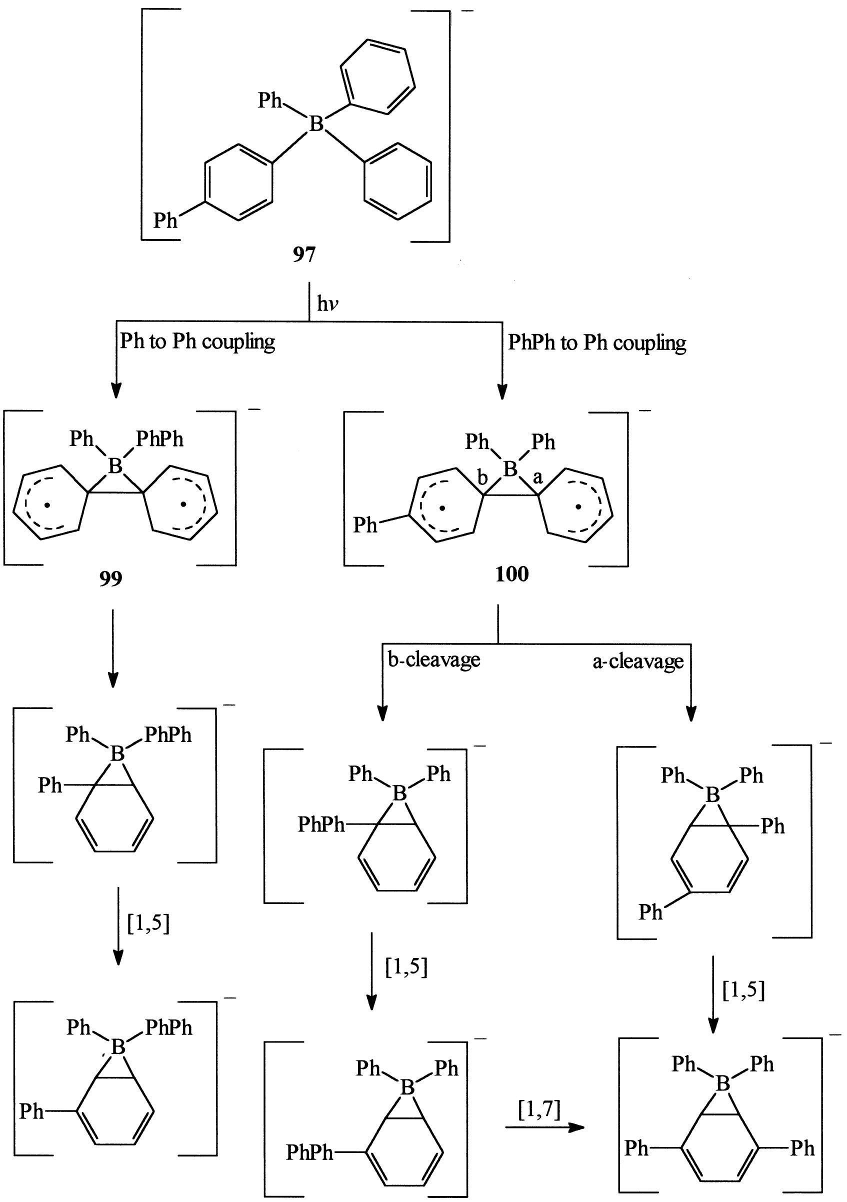
Scheme 28.



95

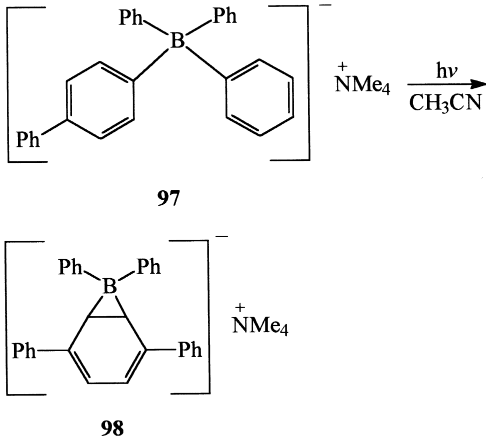
96

Scheme 29.



Scheme 30.

free acetonitrile (Eq. (43)).

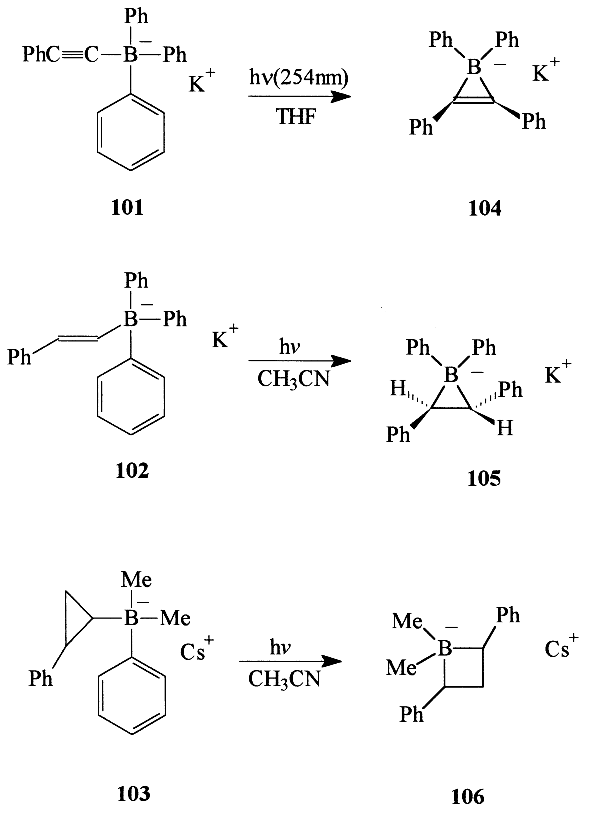


(43)

An alternative mechanism[87,88,114,115] which is analogous to a di-π-methane rearrangement,[116] and designated as a di-π-borate rearrangement has been proposed. In this proposal, reaction proceeds via the bridged biradical intermediates **99** and **100** (Scheme 30).

Evidence has been provided for the formation of borenes in the photolysis of the triarylalkynylborate **101**.[115,117,118] Thus, irradiation of potassium triphenyl(phenylethynyl)-borate **101**,[115,117] tetramethylammonium triphenyl(*trans*-β-styryl)borate **102**[117,118] and cesium phenyl(2-phenylcyclopropyl)dimethylborate **103**,[118] revealed the generation of boratirene **104**, boratirane **105**, and boratetane **106**, respectively (Scheme 31).

Scheme 32 shows the proposed mechanism for the di-π-borate rearrangement of the borate **101**. Coupling of phenylethynyl and phenyl groups leads to an intermediate



Scheme 31.

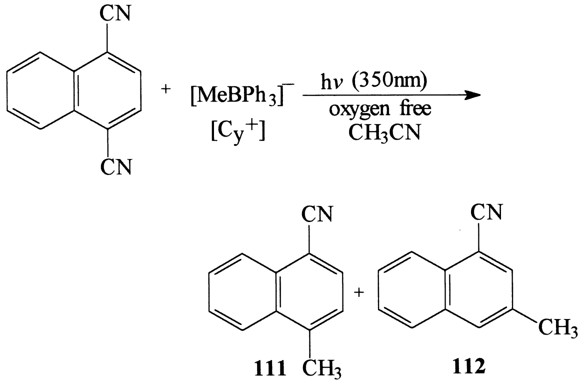
boratiranyldicarbinyl biradical anion **107** followed by a di-π-methane like path to the biradical anion **108** and ultimately to boratirene **104** as the major product.

Boratirane **105** is formed similarly. Formation of boratetane **106** may take place via a bridged biradical anion **109** followed by a cyclopropyl-π-methane like route as depicted in Scheme 33. It is interesting to note that photolysis of the borate **103** in the presence of butyl bromide and treatment with acetic acid gives amylbenzene, formation of which may take place through the boron-stabilised carbanion **110**. The chemistry of these carbanions has been extensively explored.[119]

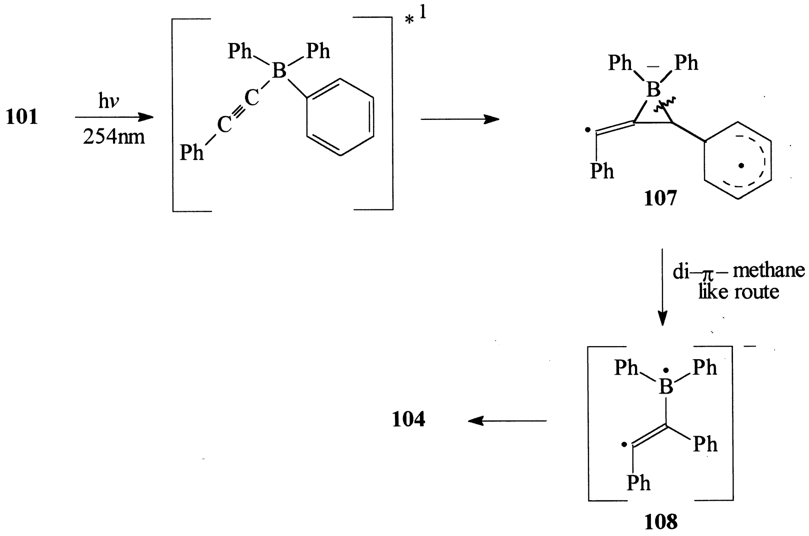
5.2. Electron-transfer reactions in charge-transfer complexes

Organometalate salts (R_nM^-) are being extensively used as nucleophilic sources of carbanionoid (R^-) ligands.[11] The metal complex is regarded as a carrier for the nucleophilic (R^-) group. Organoborate salts exemplify these reagents and the alkyltriphenylborates $R(Ph)_3B^-$ may act as sources of nucleophilic alkyl groups, just as borohydride is a source of hydride ion. As such, they represent mild and selective alternatives to Grignard and organolithium reagents in organic synthesis. Organoborates have also been identified as one-electron reducing agents (electron donors) in a variety of thermal and photochemical redox processes.[11] Thus alkyltriphenylborate salts have proven to be effective visible-light sensitive photoinitiators[120] for the photopolymerisation of acrylate systems as well as for optical memory which can be read with either absorption or emission.[121]

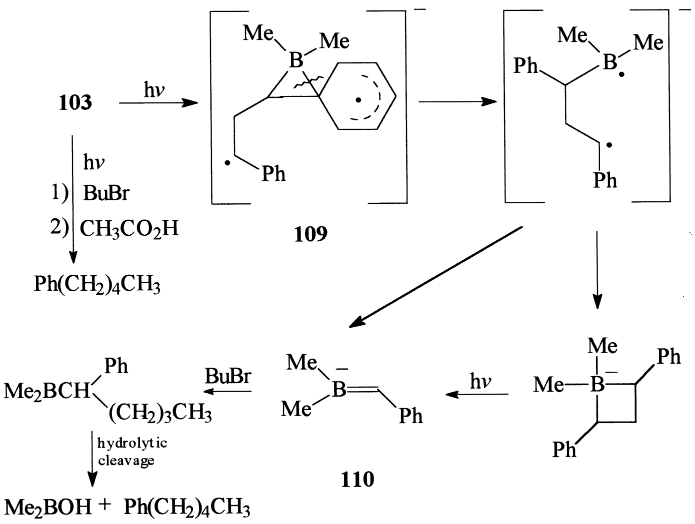
The photophysics of reactions of a wide variety of dimethylindocarbocyanine [Cy$^+$] alkyltriphenylborate salts has been studied[122] (Eq. (44)).



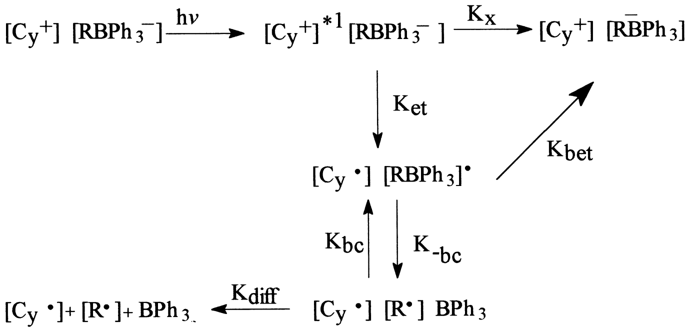
(44)



Scheme 32.



Scheme 33.



K_{et} = Rate of electron transfer

K_{bet} = Rate of back electron transfer

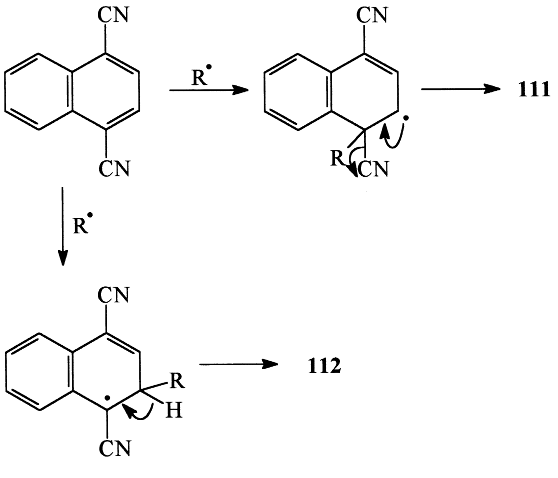
K_{bc} = Rate of boron–carbon bond cleavage

K_{diff} = Rate of cage escape

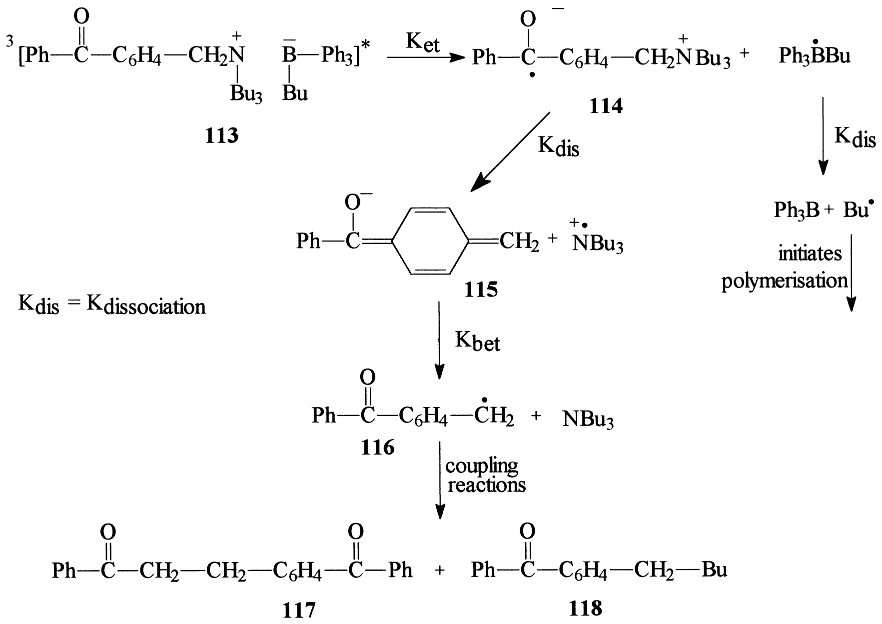
Scheme 34.

Electron transfer from the borate takes place to the singlet state of the cyanine cation (Scheme 34). According to the mechanism proposed, the radical pair formed by electron transfer from the borate to the singlet excited cyanine cation may undergo back electron transfer to regenerate the initial ion pair or it may undergo boron–carbon bond cleavage to form triphenylborane and the alkyl radical in a solvent cage with [Cy]. Since the lifetime of the cyanine singlet is short (ca picoseconds), the electron transfer is observed only in non-polar solvents in which the process may occur in the light ion-pair.[123] The products are **111** and **112** which may be formed as depicted in Scheme 35.

This type of mechanism has been well supported.[124,125] For example, in the photoreduction of ketones, the electron transfer from the borate anion **113** takes place to the triplet state of benzophenone giving **114** and boratyl radicals both of which dissociate rapidly. Radical **114** dissociates to give **115** and the amino cation radical, followed by a second electron transfer (k_{bet}) to give tributylamine and Ph–CO–C_6H_4–$\dot{C}H_2$ **116**, which is stable and couples either with a similar radical to give **117** or with the butyl radical to give **118** (Scheme 36). The butyl radical can also initiate polymerisation. The irradiation of 4-benzoylbenzyltrialkylammonium borates quantitatively gave biphenyl and a small amount of benzene in the absence of oxygen. In addition, amines and methylbenzophenone were detected by steady-state photolysis.[126]



Scheme 35.



Scheme 36.

$$[\mathrm{Py}^{+}, \mathrm{BMe}_4^{-}] \xrightarrow{h\nu_{CT}} [\mathrm{Py}^{\bullet}, \mathrm{BMe}_4^{\bullet}]$$

$$[\mathrm{Py}^{\bullet}, \mathrm{BMe}_4^{\bullet}] \xrightarrow{K_f} [\mathrm{Py}^{\bullet}, \mathrm{Me}^{\bullet}, \mathrm{BMe}_3]$$

$$[\mathrm{Py}^{\bullet}, \mathrm{Me}^{\bullet}, \mathrm{BMe}_3] \xrightarrow{K_{RR}} \mathrm{PyMe} + \mathrm{BMe}_3$$

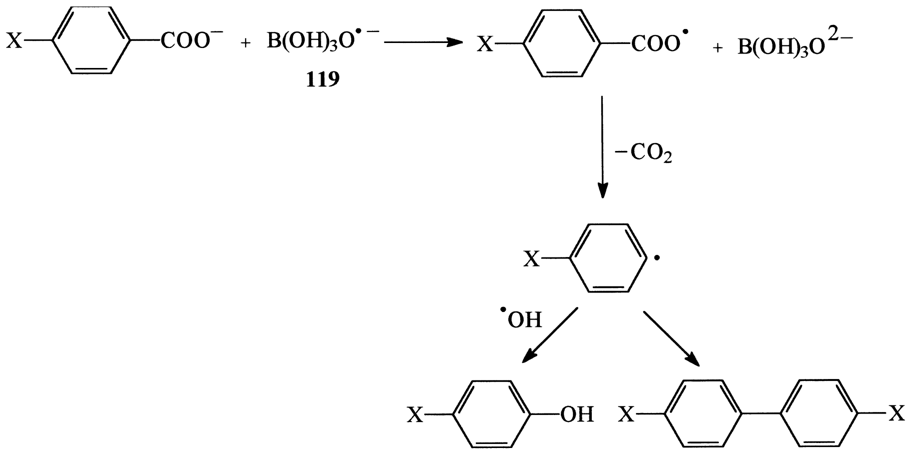
Scheme 37.

The role of the borate anion in the nucleophilic alkyl transfer has recently been examined[126] for the case of photochemical methyl transfer from tetramethylborate in pyridinium salts (Eq. (45)). Thus the borate salts which did not react spontaneously at room temperature could only be induced to react by deliberate irradiation at their charge-transfer absorption bands:

$$[\mathrm{Py}^{+}, \mathrm{BMe}_4^{-}] \xrightarrow[\text{THF/-78°C or 25°C} \atop \text{1 - 8h}]{h\nu_{CT}} \mathrm{Py{-}Me} + \mathrm{BMe}_3 \qquad (45)$$

Contact charge-transfer ion pairs have been identified as the critical intermediates in the formal nucleophilic addition and therefore play an important role in the solid-state reactivity of these salts (Scheme 37). The reaction has been carried out with substituted pyridinium salts as well as with quinolinium, azaanthracene and benzphenanthridine salts.

The actual transfer of the methyl radical to give the products occurs within a solvent cage, and free pyridinyl radicals are not involved. Spin-trapping studies have shown that tetraalkylborate anions readily yield alkyl radicals and time-resolved experiments have shown that the scission of the B-alkyl bond occurs on a picosecond or sub-picosecond time scale. Hence it is suggested that the fragmentation step is the crucial step in methyl transfer reactions. The products are formed by subsequent coupling of the methyl and pyridinyl radicals, within the solvent cage, as formulated in Scheme 37.



Scheme 38.

5.3. Miscellaneous studies

5.3.1. Heating. The reaction of the borate radical anion **119** with 4-substituted benzoic acids by flash kinetic spectrophotometry gives biphenyl and phenols. The product analysis and kinetic studies are consistent with an electron transfer mechanism followed by decarboxylation[127] (Scheme 38).

5.3.2. UV photolysis and photoreduction of hydroborates. UV photolysis of solutions containing BH_4^-, BH_3CN^- or $(t\text{-BuO})_3BH^-$ in liquid ammonia results in electron detachment from the anions to give e^-_{amm} and a borohydride which then yields a borane anion[128] (Eq. (46)).

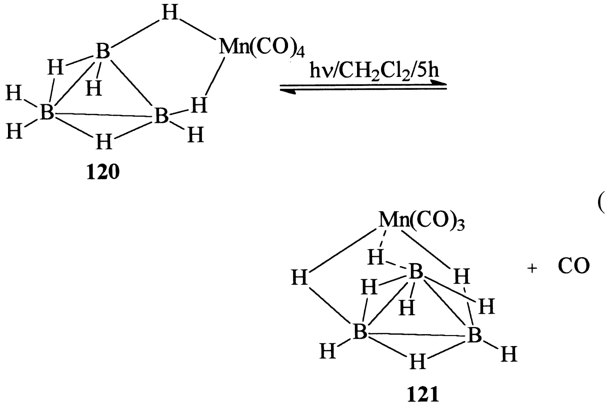
$$R_3BH^{\bullet -}\ NBu_4^+ \xrightarrow[NH_3\text{–}DME]{h\nu} [R_3BH^{\bullet}] + e^-_{amm} \xrightarrow{NH_3} R_3B^-_{amm}\,{}^+NH_4 \qquad (46)$$

The photoreduction of aromatic systems such as naphthalenes, phenols and halogenated aromatic hydrocarbons by $NaBH_4$ has been studied.[129] Based on deuterium labelling experiments, both ionic and radical mechanisms have been proposed.

6. The Photochemistry of Metalloboranes and Metallocarboranes

6.1. Photosynthesis of metalloboranes and metallocarboranes

The photochemistry of metalloboranes and metallocarboranes has received limited attention. Irradiation of the butterfly shaped manganeseborane **120**, an analogue of *arachno*-B_4H_{10}, results in the photolytic cleavage of one carbonyl-metal bond.[130] Subsequent loss of the carbonyl ligand and the formation of an M–H–B bond transform the triborane unit into a tridentate ligand **121** (Eq. (47)).



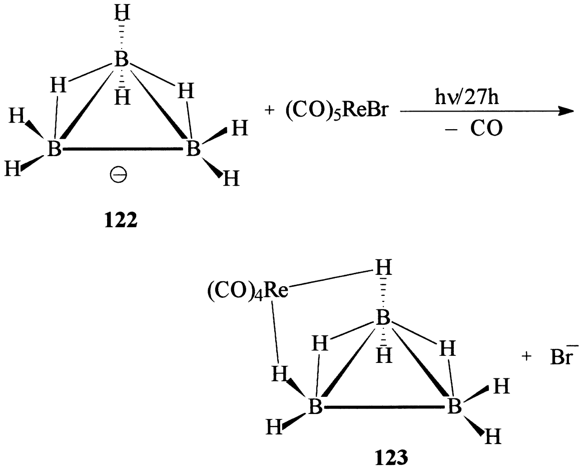
120

121

(47)

The loss of CO was found to be a reversible process with addition of CO to the solution regenerating the original bidentate triborane **120**. A similar reversible photochemical conversion of the tridentate borane $Fe(CO)_4B_3H_8$ to bidentate $Fe(CO)_3B_3H_8$ has been reported.[131]

Three examples of the photochemical synthesis of polyhedral metalloboranes have been reported by cophotolysis of organometallic compounds with octahydrotriborate (1) anion $[B_3H_8]^-$ **122**.[131] Thus photolysis of $[(CO)_5ReBr]$, $[(\eta^5\text{-}C_5H_5)(CO)_2FeI]$, and $[(\eta^5\text{-}C_5H_5)(CO)_3WCl]$ with **122** produces the complexes $[(CO)_4ReB_3H_8]$, $[(\eta^5\text{-}C_5H_5)(CO)FeB_3H_8]$ and $[(\eta^5\text{-}C_5H_5)(CO)_3WB_3H_8]$, respectively. Each metal centre loses its halide and one carbonyl ligand with the formation of two, three-centre, two electron, M–H–B bonds (Eq. (48)).



122

123

(48)

Irradiation of $NaB_{10}H_{13}$ and metal hexacarbonyls gave **124** in ca 50% yield (Eq. (49)).[132]

$$B_{10}H_{13}^- + MC(O)_6 \xrightarrow{h\nu/THF} \underset{\mathbf{124}}{[B_{10}H_{10}COH]M(CO)_4^-} \qquad (49)$$

M=Cr, Mo, W.

Similar complexes **125** have been prepared by complexation reactions (Eq. (50)).[133]

$$[Me_4N]^+[B_9H_{10}CHE]^- + M(CO)_6 \xrightarrow[THF/12\ h]{h\nu} \times \underset{\mathbf{125}}{[Me_4N]^+[B_9H_{10}CHE{\cdot}M(CO)_5]^-} \qquad (50)$$

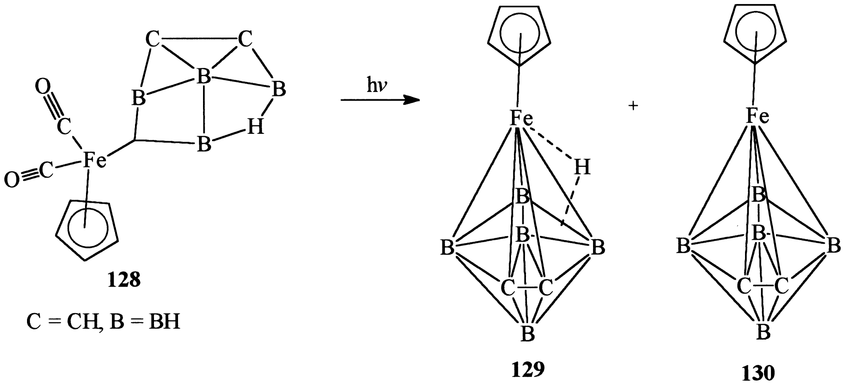
E=P or As; M=Cr, Mo, W.

Two examples are known of metallaborane isomerisation reactions initiated by light (Eqs (51) and (52)).[134]

$$\underset{\text{red}}{closo\text{-}[2\text{-}(\eta^5\text{-}C_5H_5Ni)B_9H_9]^-} \xrightarrow{h\nu} \underset{\text{yellow}}{closo\text{-}[1\text{-}(\eta^5\text{-}C_5H_5Ni)B_9H_9]^-} \qquad (51)$$

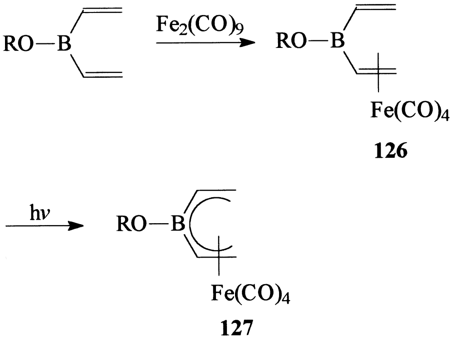
$$\underset{\text{yellow}}{closo\text{-}[1\text{-}(\eta^5\text{-}C_5H_5Ni)B_9Cl_9]^-} \xrightarrow{h\nu} \underset{\text{green}}{closo\text{-}[2\text{-}(\eta^5\text{-}C_5H_5Ni)B_9Cl_9]^-} \qquad (52)$$

The photochemical preparation of several ferra-boranes and -carboranes has been reported. Thus irradiation of the iron-organoboron complex **126**, which contains a single complexed vinyl group, produced a π-divinylborane



Scheme 39.

complex **127**[135] (Eq. (53)).



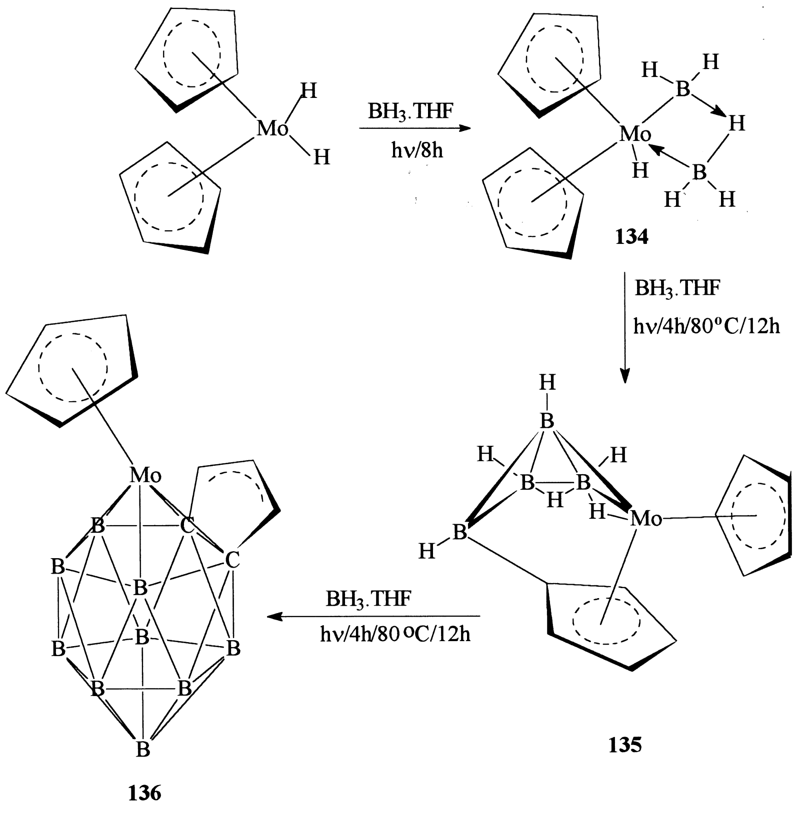
(53)

Irradiation of [Fe(η^5-C_5H_5)$(CO)_2B_{10}H_{13}$] in ether or THF produces [Fe(η^5-C_5H_5)$B_{10}H_{10}C(L)$] (where L=OEt_2 or THF) in 1–3% yield.[136] This unexpected product resulted from the insertion of both an [Fe(η^5-C_5H_5)] fragment and a carbon atom, presumably from a CO ligand, into the cage.

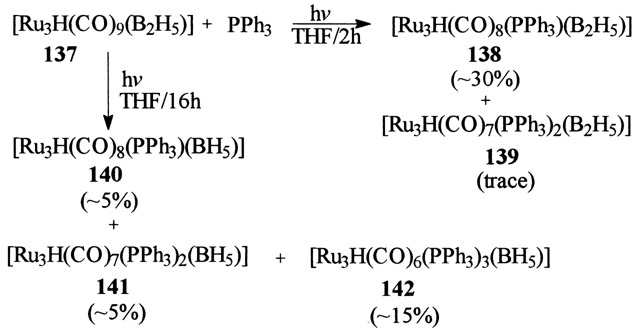
Another example[137] involved the irradiation of the complex [Fe(η^5-C_5H_5)$(CO)_2$(μ-4,5-$C_2B_4H_7$)] **128**, and this resulted in the formation of [Fe(η^5-C_5H_5)$HC_2B_4H_6$] **129** and [Fe(η^5-C_5H_5)$C_2B_4H_6$] **130** (Scheme 39).

Photo-induced cyclo-insertion addition reaction[138] of an alkyne to the ferraborane **131** yields two carboranes **132** and **133** (Eq. (54)).

$$\underset{\mathbf{131}}{B_4H_8Fe(CO)_3} + Me{-}C{\equiv}C{-}Me \xrightarrow[Et_2O/17\ h]{h\nu} \underset{\mathbf{132}}{Me_4C_4B_4H_4} + \underset{\mathbf{133}}{Me_6C_6B_4H_4} \qquad (54)$$



Scheme 40.



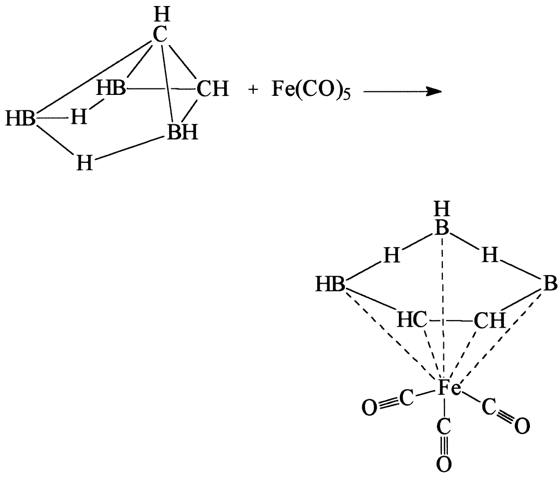
Scheme 41.

The photosynthesis of $BC_4H_5Fe(CO)_3$ has been achieved[139] by irradiation of $C_4H_4Fe(CO)_3$ in the presence of pentaborane. This demonstrates the conversion of an organometallic compound into a metallocarborane (Eq. (55)).

$$C_4H_4Fe(CO)_3 + B_5H_9 \xrightarrow[Et_2O/15\text{–}30\ \mathrm{min}]{h\nu} BC_4H_5Fe(CO)_3 \tag{55}$$

A ferraborane has also been synthesised by photolysis of a carborane with $Fe(CO)_5$ (Eq. (56)).[140]

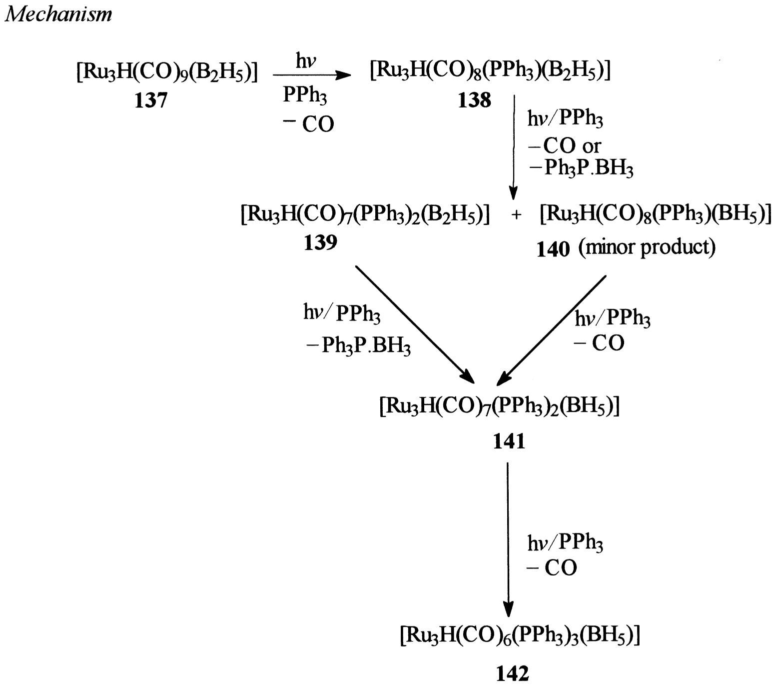
The synthesis of molybdaboranes **134**–**136** by the photolysis of $[Mo(\eta^5\text{-}C_5H_5)H_2]$ in the presence of $BH_3{\cdot}THF$ has been reported.[141–142] Initially, only the borane **134** was isolated, but prolonged photolysis and thermolysis of the reaction mixture also gave the complexes **135** and **136** which are formed via cyclopentadienyl ring activation (Scheme 40).



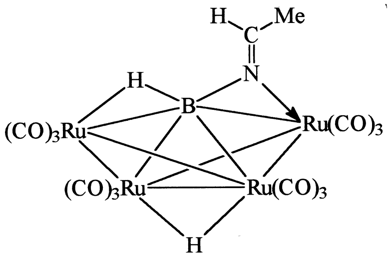
(56)

A convenient route has been described for the preparation of a series of phosphine substituted triruthenaborane clusters[143,144] of general formula $[Ru_3(CO)_{9-x}(PPh_3)_xBH_5]$ (x=1–3) (**140**–**142**) by photolysis of a mixture of $[Ru_3H(CO)_9(B_2H_5)]$ **137** with an excess of triphenylphosphine under varying conditions. The reaction proceeds via borane abstraction (Scheme 41) from **138** and **139**, the proposed pathway being illustrated in Scheme 42.

Photolysis of $[Ru_3(CO)_9BH_5]$ **143** in acetonitrile in the presence of $M(CO)_6$ (M=Cr, Mo, W) with Me_3NO for 16 h leads to the formation of boron–nitrogen coupled $[Ru_4H(CO)_{12}(\eta\text{-}NCHMe)]$ **144** (10–30%), a butterfly cluster containing a semi-interstitial boron atom.[145]



Scheme 42.



144

Photoreaction[146] of compound **143** with $[\{M(\eta^5-C_5H_5)(CO)_3\}_2]$ **145** (M=Mo) produced two products **146** and **147** (Scheme 43).

Product **146** arises by the addition of the heterometallic fragment to cluster **143** with concomitant loss of hydrogen whereas substitution of the boron vertex in **143** by a molybdenum fragment gives **147**. Reaction of **142** with **145** (M=W) gives three products **148**, **149** and **150** (Scheme 44).

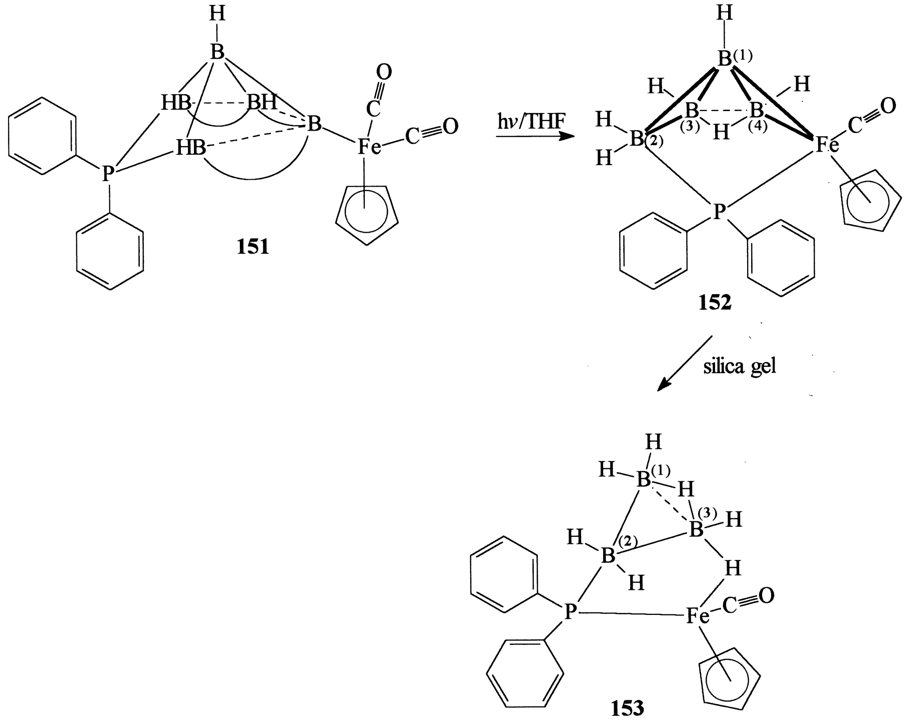
Compounds **148** and **149** are analogues of their molybdenum counterparts **146** and **147** whereas conversion to

$$\underset{\mathbf{143}}{[Ru_3(CO)_9BH_5]} + \underset{\mathbf{145}\ (M=Mo)}{[\{M(\eta^5-C_5H_5)(CO)_3\}_2]} \xrightarrow[THF/16h]{h\nu} \underset{\mathbf{146}}{[MoRu(\eta^5-C_5H_5)H(CO)_{11}(BH)]} + \underset{\mathbf{147}}{[MoRu_3(\eta^5-C_5H_5)H_3(CO)_{11}]}$$

Scheme 43.

$$\underset{\mathbf{143}}{[Ru_3(CO)_9BH_5]} + \underset{\mathbf{145}\ (M=W)}{[\{M(\eta^5-C_5H_5)(CO)_3\}_2]} \xrightarrow[THF/16h]{h\nu} \underset{\mathbf{148}}{[WRu_3(\eta^5-C_5H_5)H(CO)_{11}(BH)]} + \underset{\mathbf{149}}{[WRu_3(\eta^5-C_5H_5)H_3(CO)_{11}]} + \underset{\mathbf{150}}{[W_2Ru_3(\eta^5-C_5H_5)_2(CO)_{13}]}$$

Scheme 44.



Scheme 45.

150 has been described[146] as a combination of a W-for-B substitution followed by a tungsten–trapping reaction.

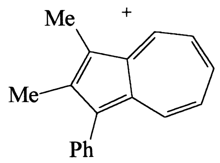
In contrast, photoreaction of **137** with **145** (M=Mo) produced only **146** by replacement of one $\{BH_2\}$ fragment by a $[(\eta^5\text{-}C_5H_5)Mo(CO)_2]$ fragment with subsequent hydrogen loss. However, reaction with **145** (M=W) produced **148–150**[141] (Eq. (57)).

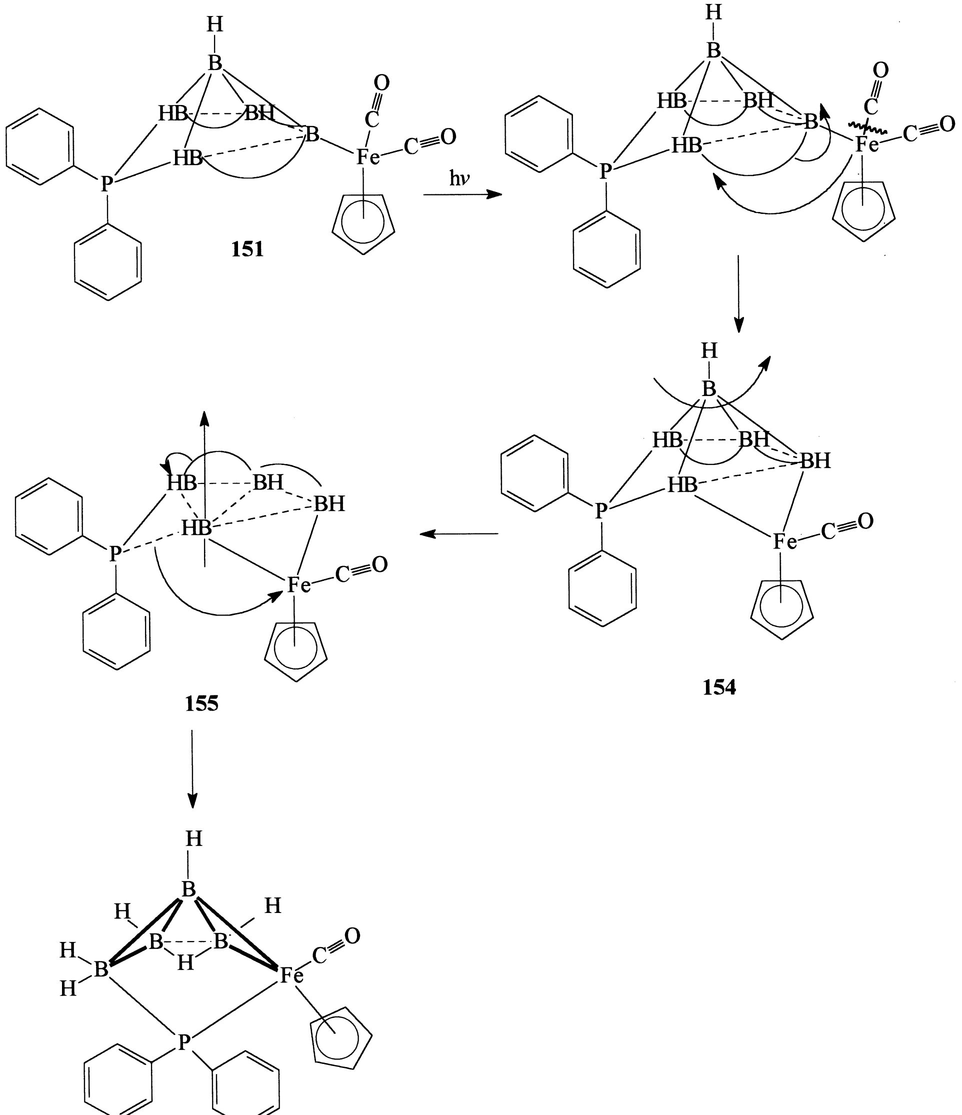
$$\underset{(30\%)}{\mathbf{148}} + \underset{(10\%)}{\mathbf{149}} + \underset{(25\%)}{\mathbf{150}} \xleftarrow[h\nu/\mathrm{THF}/16\mathrm{h}]{\mathbf{145}\ (\mathrm{M=W})} \mathbf{137} \xrightarrow[h\nu/\mathrm{THF}/16\mathrm{h}]{\mathbf{145}\ (\mathrm{M=Mo})} \mathbf{146}\ \text{(trace)} \qquad (57)$$

Photoreactions of ruthenaborane clusters with diphenylacetylene have also been investigated.[147] For example upon photolysis, the clusters $[HRu_4(CO)_{12}BH_2]$ and $[H(\eta^5\text{-}C_5H_5)WRu_3(CO)_{11}BH]$ undergo alkyne addition to produce $[HRu_4(CO)_{12}B(H)C(Ph)PhH]$ and $[H(\eta^5\text{-}C_5H_5)WRu_3(CO)_{11}BC(Ph)CPhH]$ in 60 and 75% yield, respectively. The insertion of the alkyne into the cluster is accompanied by: (i) B–H bond activation, (ii) B–C bond formation, and (iii) Ru–Ru bond cleavage.

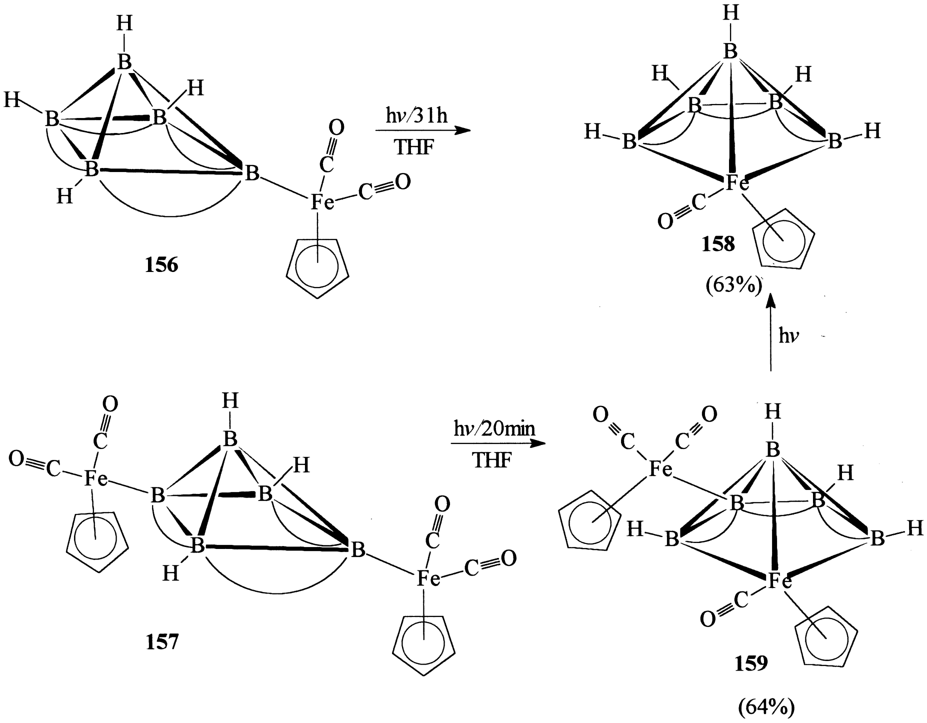
This work was further extended to the reaction of the tetraruthenaborane cluster $[HRu_4(CO)_{12}BH_2]$ with 1-phenyl-1-propyne.[148] In addition to the expected product $HRu_4(CO)_{12}B(H)C(Ph)CMeH$, 1-phenyl-2,3-dimethylazulene was also obtained (Eq. (58)).

$$HRu_4(CO)_{12}BH_2 + PhC{\equiv}CMe \xrightarrow[h\nu/15\mathrm{h}]{CH_2Cl_2/CD_2Cl_2} \underset{(10\%)}{HRu_4(CO)_{12}B(H)C(Ph)C} \qquad (58)$$





Scheme 46.



Scheme 47.

6.2. Photorearrangements of borane cluster compounds

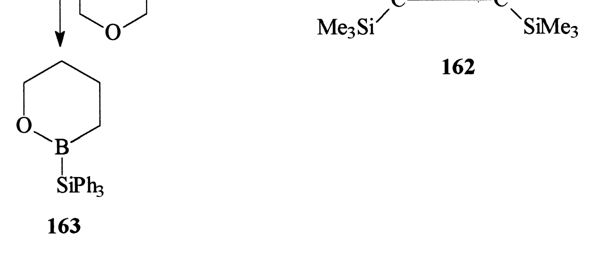
The photochemistry of small borane cluster compounds σ bonded to a metal has been examined.[18,149–152] Photolysis of the phosphinopentaborane cluster [Fe(η^5-C_5H_5)$(CO)_2$-B_5H_8(μ-PPh_2)] **151** yields tetraborane [Fe(η^5-C_5H_5)-(CO)B_4H_6(PPh_2)] **152** which on passage down a silica column, gives the triborane [Fe(η^5-C_5H_5)(CO)B_3H_7(PPh_2)] complex **153** (Scheme 45).

It was proposed that the conversion of **151** to **152** was accompanied by loss of a carbonyl ligand from the iron fragment to give **154**, which can lose a boron vertex from the cage to give **155,** from which a structural rearrangement yields **152** (Scheme 46).

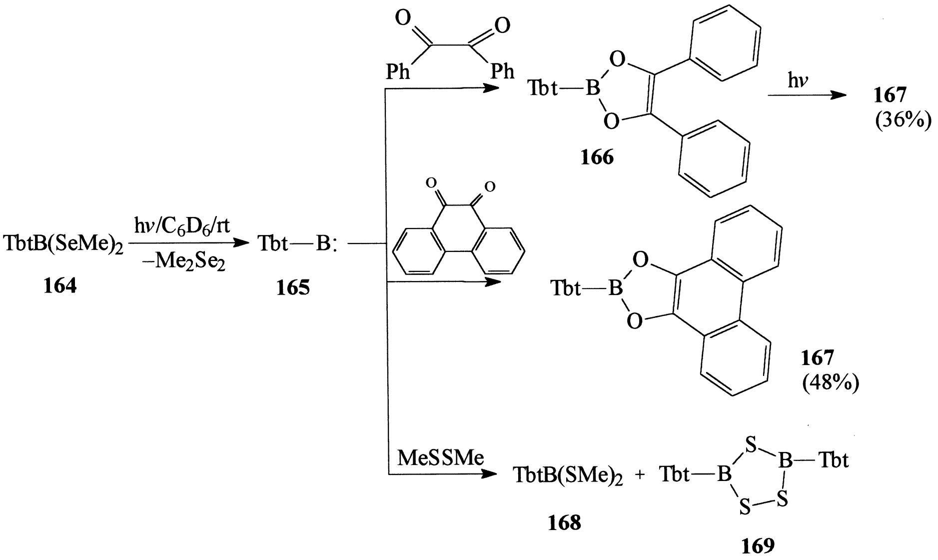
The photochemical decarbonylation and rearrangement chemistry of the σ-metalated pentaborane cluster [2-Fe(η^5-C_5H_5)$(CO)_2B_5H_8$] **156** and the disubstituted complex [2,4-{Fe(η^5-C_5H_5)$(CO)_2B_5H_7$] **157** has been investigated. The photoirradiation of **157** yielded the cage-inserted [2-(η^5-C_5H_5)(CO)-2-FeB_5H_8] complex **158** in 63% yield,[150–152] while **157** gave **159** (Scheme 47) in 64% yield. The high yield preparation of **158** and **159** is in sharp contrast to the observed very low yield (1–3%) of the only product isolated from irradiation of the decarborane(14) cluster [Fe(η^5-C_5H_5)$(CO)_2B_{10}H_{13}$].[152]

6.3. Photochemical generation of borylene

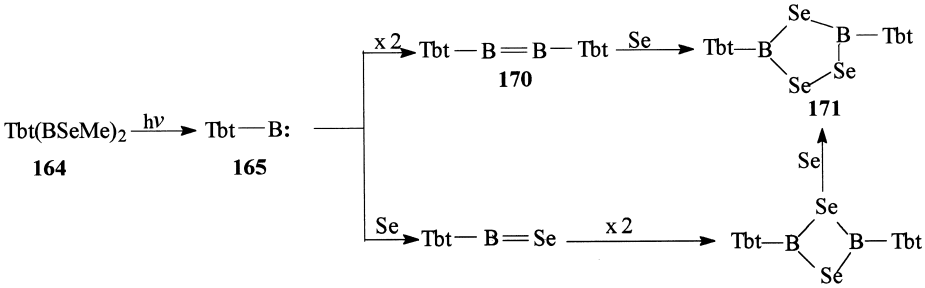
Borylenes have been generated by photolytic cleavage of boron-metal bonds. Thus photolysis of silyl- and more recently methylseleno-substituted boranes have been found to yield borylenes. The formation of triphenylsilylborylene **161** by photolysis of tris(triphenylsilyl)borane **160** in a 3-methylpentane matrix at −196°C has been reported.[153] Cophotolysis of **160** with bis(trimethylsilyl)-acetylene gave 1-triphenylsilyl-2,3-bis(trimethylsilyl)-borirene **162** whereas cophotolysis with THF produced the 1,2-oxaborinane **163** (Scheme 48).



Scheme 48.



Scheme 49.



Scheme 50.

The formation of a borylene **165** bearing a bulky aryl group, 2,4,6-tri[{bis(trimethylsilyl)methyl}]phenyl (Tbt), by photolysis of bis(methylseleno)borane **164** yields the borylene **165**. This has been trapped with benzil, phenanthrenequinone and dimethyl sulfide to give **166**, **167** and **168** and **169,** respectively (Scheme 49).[154]

The photolysis of **164** without a trapping agent did not yield the diborane **170** but instead produced the 1,2,4,3,5-triselenodiborolane **171**. Possible pathways for the formation of **171** are shown in Scheme 50.

Acknowledgements

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References

1. *Photochemistry*, Ramamurthy, V., Turro, N. J., Eds. *Chem. Rev.* **1993**, *93*, 1–723.
2. Turro, N. J. *Modern Molecular Photochemistry*, Benzamin/Cummings: Menlo Park, 1978.
3. Ferraudi, G. *Elements of Inorganic Photochemistry*, Wiley Interscience: New York, 1988.
4. Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*, Academic: New York, 1979.
5. Brown, H. C.; Kramer, G. W.; Levy, M. B.; Midland, M. M. *Organic Synthesis via Boranes*, Wiley Interscience: New York, 1973.
6. Pelter, A.; Smith, K. Chemistry of Organoboron Compounds; In *Comprehensive Organic Chemistry*, Jones, N., Ed.; Pergamon: Oxford, 1979; Vol. 3, pp 689–940 (Section 4).
7. Pelter, A.; Smith, K.; Brown, H. C. *Borane Reagents*, Academic: New York, 1988.
8. Mikhailov, B. M.; Bubnov, Y. *Organoboron Compounds in Organic Synthesis*, Harwood Academic Science: Amsterdam, 1984.
9. Stock, A.; Friederici, K.; Press, O. *Chem. Ber.* **1913**, *46*, 3353.
10. Porter, R. F.; Turbini, L. P. *Top. Curr. Chem.* **1980**, *96*, 1.
11. Billing, R.; Rohorek, D.; Hennig, H. *Top. Curr. Chem.* **1990**, *158*, 151.
12. Irion, M. P.; Kompa, K. L. *J. Chem. Phys.* **1982**, *76*, 2338; Irion, M. P.; Kompa, K. L. *J. Photochem.* **1986**, *32*, 139.
13. Irion, M. P.; Seitz, M.; Kompa, K. L. *J. Mol. Spectrosc.* **1986**, *118*, 64.
14. Greenwood, N. N.; Greatrex, R. *Pure Appl. Chem.* **1987**, *59*, 857.

15. Hirata, T.; Gunning, J. E. *J. Chem. Phys.* **1957**, *27*, 477.
16. Kreye, W. C.; Marcus, R. A. *J. Chem. Phys.* **1962**, *37*, 419.
17. Grimm, F. A.; Porter, R. F. *Inorg. Chem.* **1968**, *1*, 706.
18. Davies, C. M.; Spencer, J. T. *Inorg. Chim. Acta* **1993**, *212*, 317.
19. Burwassar, H.; Pease, R. N. *J. Chem. Phys.* **1956**, *60*, 1589.
20. Plotkin, J. S.; Astheimer, R. J.; Sneddon, L. G. *J. Am. Chem. Soc.* **1979**, *101*, 4155.
21. Plotkin, J. S.; Sneddon, L. G. *J. Chem. Soc., Chem. Commun.* **1976**, 95.
22. Kline, G. A.; Porter, R. F. *Inorg. Chem.* **1980**, *19*, 447.
23. Irion, M. P.; Kompa, K. L. *J. Photochem.* **1987**, *37*, 233.
24. Astheirmer, R. J.; Sneddon, L. G. *Inorg. Chem.* **1984**, *23*, 3207.
25. Lowman, D. W.; Ellis, P. D.; Odom, J. D. *Inorg. Chem.* **1973**, *12*, 681.
26. Greenwood, N. N.; Kennedy, J. D.; Spalding, T. R.; Taylorson, D. *J. Chem. Soc., Dalton Trans.* **1979**, 840.
27. Boocock, S. K.; Greenwood, N. N.; Kennedy, J. D.; McDonald, W. S.; Staver, J. *J. Chem. Soc., Dalton Trans.* **1980**, 790.
28. Boocock, S. K.; Cheek, Y. M.; Greenwood, N. N.; Kennedy, J. D. *J. Chem. Soc., Dalton. Trans.* **1981**, 1430.
29. Trofimenko, S. *J. Am. Chem. Soc.* **1966**, *88*, 1899; Trofimenko, S.; Cripps, H. N. *J. Am. Chem. Soc.* **1965**, *87*, 653.
30. Usiatinskii, A. Y.; Kampel, V. T.; Shcherbina, T. M.; Antonovich, V. A.; Bregadze, V. I.; Godovikov, N. N. *Organomet. Chem. USSR* **1988**, *1*, 1420.
31. Buchanan, A. S.; Creutzberg, F. *Aust. J. Chem.* **1962**, *15*, 744.
32. Lyons, A. R.; Symons, M. C. R. *J. Chem. Soc., Faraday Trans. 2* **1972**, 502.
33. Chung, V. V.; Inagaki, K.; Tokuda, M.; Itoh, M. *Chem. Lett.* **1976**, 209.
34. Williams, J. L. R.; Grisdale, P. J.; Doty, J. C. *J. Am. Chem. Soc.* **1967**, *89*, 4538.
35. Ramsey, B. G.; Anjo, D. *J. Am. Chem. Soc.* **1977**, *99*, 3182.
36. Calhoun, G. C.; Schuster, G. B. *J. Org. Chem.* **1984**, *49*, 1925.
37. Buchner, G. *Liebigs Ann. Org. Bioorg. Chem.* **1997**, 1415.
38. Miyamoto, N.; Isiyama, S.; Utimoto, K.; Nozaki, H. *Tetrahedron Lett.* **1971**, 4597; Miyamoto, N.; Isiyama, S.; Utimoto, K.; Nozaki, H. *Tetrahedron* **1973**, *29*, 2365.
39. Marshall, J. A. *Acc. Chem. Res.* **1969**, *2*, 33; Marshall, J. A. *Science* **1970**, *170*, 137.
40. Johnson, J. R.; Snyder, H. R.; van Campen, M. G. *J. Am. Chem. Soc.* **1938**, *60*, 115.
41. Brown, H. C.; Negishi, E. *Synthesis* **1974**, 77.
42. Lane, C. F. *Intra-Sci. Chem. Rep.* **1973**, *7*, 133.
43. Lane, C. F. *Aldrichim. Acta* **1973**, *6*, 21.
44. Paetzold, P. I.; Grundke, H. *Synthesis* **1973**, 635.
45. Suzuki, A. *Kagaku No Ryoiki, Zokan* **1970**, *89*, 213; *Chem. Abstr.* **1970**, *73*, 14886n.
46. Brown, H. C. *Boranes in Organic Chemistry*, Cornell University: Ithaca, New York, 1972.
47. Reutov, O. A.; Belletskaya, I. P.; Sokolov, V. I. *Mechanisms of Reactions of Organometallic Compounds*, Khimiya: Moscow, 1972.
48. Lappert, M. F. *The Chemistry of Boron and its Compounds*; Muetterties, E. L., Ed.; Wiley: New York, 1967.
49. Brown, H. C.; Yamamoto, Y. *J. Am. Chem. Soc.* **1971**, *93*, 2796.
50. Brown, H. C.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1971**, 1535.
51. Pasto, D. J.; McReynolds, K. *Tetrahedron Lett.* **1971**, 801.
52. Pasto, D. J.; Chow, J.; Arora, S. K. *Tetrahedron* **1969**, *25*, 1557.
53. Lissi, E.; Sanhueza, E. *J. Organomet. Chem.* **1971**, *26*, C59.
54. Abufhele, A.; Andersen, C.; Lissi, E.; Sanhueza, E. *J. Organomet. Chem.* **1972**, *42*, 19.
55. Pasto, D. J.; Hickman, J. *J. Am. Chem. Soc.* **1967**, *89*, 5608.
56. Matteson, D. S.; Mah, R. *Chem. Rev.* **1966**, *1*, 1.
57. Brown, H. C.; Lane, C. F. *J. Am. Chem. Soc.* **1971**, *93*, 1025.
58. Brown, H. C.; Yamamoto, Y.; Lane, C. F. *Synthesis* **1972**, 304.
59. Brown, H. C.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1973**, 801.
60. Brown, H. C.; Yamamoto, Y. *J. Org. Chem.* **1974**, *39*, 861.
61. Brown, H. C.; DeLue, N. R. *Tetrahedron Lett.* **1977**, 3007.
62. Brown, H. C.; DeLue, N. R. *J. Am. Chem. Soc.* **1974**, *96*, 311.
63. Mikhailov, B. M.; Shchegoleva, T. A.; Shashkova, E. M.; Kiselev, V. G. *J. Organomet. Chem.* **1983**, *250*, 23.
64. Davies, A. G.; Scaiano, J. C. *J. Chem. Soc., Perkin Trans. 2* **1972**, 2234.
65. Davies, A. G.; Scaiano, J. C.; Roberts, B. P. *J. Chem. Soc. Chem. Commun.* **1971**, 196; Davies, A. G.; Scaiano, J. C.; Roberts, B. P. *J. Chem. Soc. (B)* **1971**, 2171.
66. Kabalka, G. W. *Intra-Sci. Chem. Rep.* **1973**, *7*, 57.
67. Brown, H. C.; Kabalka, G. W. *J. Am. Chem. Soc.* **1970**, *92*, 712.
68. Brown, H. C.; Kabalka, G. W.; Suzuki, A.; Honma, S.; Arase, A.; Itoh, M. *J. Am. Chem. Soc.* **1970**, *92*, 710.
69. Utimoto, K.; Tanaka, T.; Nozaki, H. *Tetrahedron Lett.* **1972**, 1167.
70. Krusic, P. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1969**, *91*, 3942.
71. Davies, A. G.; Roberts, B. P. *J. Chem. Soc., Chem. Commun.* **1969**, 699.
72. Davies, A. G.; Griller, D.; Roberts, B. P. *J. Chem. Soc. (B)* **1971**, 1823.
73. Davies, A. G.; Maki, T.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1972**, 744.
74. Davies, A. G.; Hook, S. C. W.; Roberts, B. P. *J. Organomet. Chem.* **1970**, *23*, C11.
75. Davies, A. G.; Hook, S. C. W.; Roberts, B. P. *J. Organomet. Chem.* **1970**, *22*, C37.
76. Scaiano, J. C.; Ingold, K. U. *J. Chem. Soc., Chem. Commun.* **1975**, 878.
77. Haag, A.; Hesse, G. *Intra-Sci. Chem. Rep.* **1973**, *7*, 105.
78. Casanova, J., Jr.; Kiefer, H. R. *J. Org. Chem.* **1969**, *34*, 2579.
79. Mikhailov, B. M.; Bubnov, Yu. N. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1964**, 2248.
80. Inatome, M.; Kuhn, L. *Tetrahedron Lett.* **1965**, 73.
81. Kramer, G. W.; Brown, H. C. *J. Org. Chem.* **1977**, *42*, 2832.
82. Brown, H. C.; Midland, M. *J. Am. Chem. Soc.* **1971**, *93*, 3291.
83. Clark, G. M.; Hancock, K. G.; Zweifel, G. *J. Am. Chem. Soc.* **1971**, *93*, 1308.
84. Zweifel, G.; Backlund, S. J.; Leung, T. *J. Am. Chem. Soc.* **1977**, *99*, 5192.
85. Onak, T. *Organoborane Chemistry*; Academic: New York, 1975, p 221.
86. Eisch, J. J.; Shen, F.; Tamao, K. *Heterocycles* **1982**, *18*, 245; Eisch, J. J. *Adv. Organomet. Chem.* **1977**, *16*, 67; Eisch, J. J. *Adv. Organomet. Chem.* **1996**, *39*, 375.
87. Eisch, J. J.; Shaffi, B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 2526; Eisch, J. J.; Shaffi, B.; Boleslavski, M. P. *Pure Appl. Chem.* **1991**, *63*, 365.
88. Eisch, J. J.; Shaffi, B.; Odom, J. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 1847.

89. Hancock, K. G.; Uriarte, A. K. *J. Am. Chem. Soc.* **1970**, *92*, 6374.
90. Uriarte, A. K.; Hancock, K. G. *Inorg. Chem.* **1973**, *12*, 1428.
91. Hancock, K. G.; Uriarte, A. K.; Dickinson, D. A. *J. Am. Chem. Soc.* **1973**, *95*, 6980.
92. Hancock, K. G.; Dickinson, D. A. *J. Am. Chem. Soc.* **1973**, *95*, 280.
93. Hancock, K. G.; Kramer, J. D. *J. Am. Chem. Soc.* **1973**, *95*, 3425.
94. Glogowski, M. E.; Grisdale, P. J.; Williams, J. L. R.; Regan, T. H. *J. Organomet. Chem.* **1973**, *54*, 51.
95. Grisdale, P. J.; Glogowski, M. E.; Williams, J. L. R. *J. Org. Chem.* **1971**, *36*, 3821.
96. Grisdale, P. J.; Williams, J. L. R. *J. Org. Chem.* **1969**, *34*, 1675.
97. Glogowski, M. E.; Williams, J. L. R. *J. Organomet. Chem.* **1980**, *195*, 123.
98. Glogowski, M. E.; Grisdale, P. J.; Williams, J. L. R.; Costa, L. *J. Organomet. Chem.* **1974**, *74*, 175.
99. Hancock, K. G.; Ko, Y.; Dickinson, D. A.; Kramer, J. D. *J. Organomet. Chem.* **1975**, *90*, 23.
100. van Riel, H. C. H. A.; Fischer, F. G.; Lugtenburg, J.; Havinga, E. *Tetrahedron Lett.* **1969**, 3085.
101. Matteson, D. S. *J. Org. Chem.* **1964**, *29*, 3399.
102. Matteson, D. S.; Peacock, K. *J. Org. Chem.* **1963**, *28*, 369.
103. Bowie, R. A.; Musgrave, O. C. *Proc. Chem. Soc., London* **1964**, 15; Bowie, R. A.; Musgrave, O. C. *J. Chem. Soc. (C)* **1970**, 485.
104. Coyle, T. D.; Ritter, J. J. *J. Am. Chem. Soc.* **1967**, *89*, 5739.
105. Williams, J. L. R.; Doty, J. C.; Grisdale, P. J.; Regan, T. H.; Borden, D. G. *J. Chem. Soc. Chem. Commun.* **1967**, 109.
106. Williams, J. L. R.; Doty, J. C.; Grisdale, P. J.; Searle, R.; Regan, T. H.; Happ, G. P.; Maier, D. P. *J. Am. Chem. Soc.* **1967**, *89*, 5153.
107. Williams, J. L. R.; Doty, J. C.; Grisdale, P. J.; Regan, T. H.; Happ, G. P.; Maier, D. P. *J. Am. Chem. Soc.* **1968**, *90*, 53.
108. Doty, J. C.; Grisdale, P. J.; Evans, T. R.; Williams, J. L. R. *J. Organomet. Chem.* **1971**, *32*, C35.
109. Grisdale, P. J.; Williams, J. L. R.; Glogowski, M. E.; Babb, B. E., *J. Org. Chem.* **1971**, *36*, 544; Grisdale, P. J.; Babb, B. E.; Doty, J. C.; Regan, T. H.; Maier, D. P.; Williams, J. L. R. *J. Organomet. Chem.* **1968**, *14*, 63.
110. Eisch, J. J.; Tamao, K.; Wilcsek, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 895.
111. Wilkey, J. D.; Schuster, G. B. *J. Org. Chem.* **1987**, *52*, 2117.
112. Wilkey, J. D.; Schuster, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 7569.
113. Wilkey, J. D.; Schuster, G. B. *J. Am. Chem. Soc.* **1991**, *113*, 2149.
114. Kropp, M.; Bhamidapaty, K.; Schuster, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 6252.
115. Kropp, M.; Schuster, G. B. *J. Am. Chem. Soc.* **1989**, *111*, 2316.
116. Zimmerman, H. E. In *Rearrangements in Ground and Excited States*, de Mayo, P. D., Ed.; Academic: New York, 1980; Vol. 3.
117. Kropp, M.; Baillargeon, M.; Park, K. M.; Bhamidapaty, K.; Schuster, G. B. *J. Am. Chem. Soc.* **1991**, *113*, 2155.
118. Kropp, M.; Bhamidapaty, K.; Schuster, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 6252.
119. Pelter, A.; Singaram, B.; Warren, L.; Wilson, J. W. *Tetrahedron* **1993**, *49*, 2965; Wilson, J. W.; Pelter, A.; Garad, M. V.; Pardasani, R. *Tetrahedron* **1993**, *49*, 2979; Pelter, A.; Bugden, G.; Rosser, R. *Tetrahedron Lett.* **1985**, *26*, 5097.
120. Eaton, D. F. *Pure Appl. Chem.* **1984**, *56*, 1191; Gottschalk, P.; Neckers, D. C.; Schuster, G. B. Eur. Pat. EP 223,587, 1987; *Chem. Abstr.* **1987**, *107*, 187434n; Farid, S. Y.; Moody, R. E.; US Patent 4,859, 572, 1989 (*Chem. Abstr.* **1990**, *112*, 88310r); Koike, M.; Kita, N.; US Patent 4,950,581, 1990 (*Chem. Abstr.* **1989**, *110*, 183030s); Shanklin, M. S.; Gottschalk, P.; Adair, P. C.; US Patent 5,055,372, 1991 (*Chem. Abstr.* **1992**, *116*, 265621y); Neckers, D. C.; Sarker, A. M.; Hassoon, S. A.; Polykarpov, A. Y.; DeRaaff, A. M.; Marino, T. L. *Chem. Abstr.* **1997**, *127*, 122109d.
121. Sakai, K.; Muta, S.; Nagamura, T. *J. Photochem. Photobiol. A.: Chem.* **1995**, *87*, 151.
122. Chatterjee, S.; Davis, P. D.; Gottschalk, P.; Kurz, M. E.; Sauerwein, B.; Yang, X.; Schuster, G. B. *J. Am. Chem. Soc.* **1990**, *112*, 6329; Schuster, G. B. *Pure Appl. Chem.* **1990**, *62*, 1565., Chrisope, D. R.; Schuster, G. B. *Organometallics* **1989**, *8*, 2737; Chatterjee, S.; Davis, P. D.; Schuster, G. B.; Gottschalk, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 2326.
123. Schuster, G. B.; Yang, X.; Zou, C.; Sauerwein, B. *J. Photochem. Photobiol. A.: Chem.* **1992**, *65*, 191.
124. Hassoon, S.; Sarkar, A.; Polykarpov, A. Y.; Rodgers, M. A. J.; Neckers, D.C. *J. Phys. Chem.* **1996**, *100*, 12386; Hassoon, S.; Sarkar, A.; Rodgers, M. A. J.; Neckers, D. C. *J. Am. Chem. Soc.* **1995**, *117*, 11369; Hassoon, S.; Neckers, D. C., *J. Phys. Chem.* **1995**, *99*, 9416; Feng, K.; Zang, H.; Martin, D.; Marino, T. L.; Neckers, D. C., *J. Poly. Chem.* **1998**, *36*, 1667.
125. Etter, M. C.; Holmes, B. N.; Kress, R. B.; Filipovich, G. *Isr. J. Chem.* **1985**, *25*, 264.
126. Zhu, D.; Kochi, J. K. *Organometallics* **1999**, *18*, 161.
127. Padmaja, S.; Rajaram, J.; Ramakrishnan, V.; Kuriacose, J. C. *J. Photochem. Photobiol. A.: Chem.* **1990**, *52*, 451.
128. Baban, J. A.; Brand, J. C.; Roberts, B. P. *J. Chem. Soc., Chem. Commun.* **1983**, 315.
129. Barltrop, J. A.; Bradbury, D. *J. Chem. Soc., Chem. Commun.* **1975**, 842; Barltrop, J. A.; Bradbury, D. *J. Am. Chem. Soc.*, **1973**, *95*, 5085; Barltrop, J. A.; Owers, R. J. *J. Chem. Soc., Chem. Commun.* **1972**, 592.
130. Gains, D. F.; Hildebrandt, S. J. *J. Am. Chem. Soc.* **1974**, *96*, 5574.
131. Gains, D. F.; Hildebrandt, S. J. *Inorg. Chem.* **1978**, *17*, 794.
132. Wegner, P. A.; Guggenberg, L. J.; Muetterties, E. L. *J. Am. Chem. Soc.* **1970**, *92*, 3473.
133. Silverstein, H. T.; Beer, D. C.; Todd, L. J. *J. Organomet. Chem.* **1970**, *21*, 139.
134. Leyden, R. N.; Sullivan, B. P.; Baker, R. T.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1978**, *100*, 3758.
135. Herberich, G. E.; Muller, H. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 937.
136. Schultz, R. V.; Sato, F.; Todd, L. J. *J. Organomet. Chem.* **1977**, *125*, 115.
137. Sneddon, L. G.; Beer, D. C.; Grimes, R. N. *J. Am. Chem. Soc.* **1973**, *95*, 6623.
138. Fehlner, T. P. *J. Am. Chem. Soc.* **1977**, *99*, 8355.
139. Fehlner, T. P. *J. Am. Chem. Soc.* **1978**, *100*, 3250.
140. Franz, D. A.; Mitler, V. R.; Grimes, R. N. *J. Am. Chem. Soc.* **1972**, *94*, 412.
141. Grebenik, P. D.; Green, M. L. H.; Kelland, M. A.; Leach, J. B.; Mountford, P.; Stringer, G.; Walker, N. M.; Wong, L. L. *J. Chem. Soc., Chem. Commun.* **1988**, 799.
142. Grebenik, P. D.; Green, M. L. H.; Kelland, M. A.; Leach, J. B.; Mountford, P. *J. Chem. Soc., Chem. Commun.* **1989**, 1397.
143. Housecroft, C. E.; Mathews, D. M.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1992**, 323.

144. Housecroft, C. E.; Mathews, D. M.; Edwards, A. J.; Rheingold, A. L. *J. Chem. Soc., Dalton Trans.* **1993**, 2727.

145. Galsworthy, J. R.; Housecroft, C. E.; Humphrey, J. S.; Song, X.; Edwards, A. J.; Rheingold, A. L. *J. Chem. Soc., Dalton Trans.* **1994**, 3273.

146. Housecroft, C. E.; Mathews, D. M.; Rheingold, A. L.; Song, X. *J. Chem. Soc., Dalton Trans.* **1992**, 2855.

147. Housecroft, C. E.; Humphrey, J. S.; Keep, A. K.; Mathews, D. M.; Seed, N. J.; Haggerty, B. S., Rheingold, A. L. *Organometallics* **1992**, *11*, 4048; Chipperfield, A. K.; Haggerty, B. S.; Housecroft, C. E.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1990**, 1174.

148. Draper, S. M.; Housecroft, C. E.; Keep, A. K.; Mathews, D. M.; Haggerty, B. S.; Rheingold, A. L. *J. Organomet. Chem.* **1991**, *410*, C44.

149. Goodreau, B. H.; Orlando, L. R.; Spencer, J. T. *J. Am. Chem. Soc.* **1992**, *114*, 3827.

150. Goodreau, B. H.; Orlando, L. R.; Spencer, J. T. *Inorg. Chem.* **1992**, *31*, 1731.

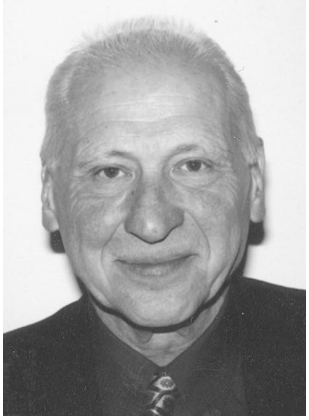
151. Goodreau, B. H.; Orlando, L. R.; Spencer, J. T. *J. Am. Chem. Soc.* **1995**, *117*, 11754.

152. Davies, C. M.; Goodreau, B. H.; Nardone, R. A.; Orlando, L. R.; Spencer, J. T. *Current Topics in the Chemistry of Boron*; Kabalka, G. W., Ed.; Royal Society of Chemistry: Cambridge, 1994, p 322.

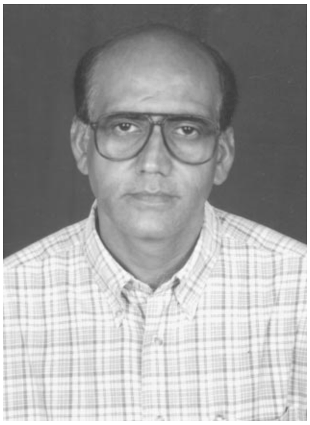
153. Pachaly, B.; West, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 454.

154. Ito, M.; Tokitoh, N.; Kawashima, T.; Okazaki, R. *Tetrahedron Lett.* **1999**, *40*, 5557.

Biographical sketch



Andrew Pelter received his B.Sc and Ph.D degrees from Bristol University where he studied under Professors Wilson Baker and David Ollis. Later he was awarded a D.Sc from the same University. After his Ph.D he moved to ICI Pharmaceuticals where he worked for one year under Professor F. L. Rose and then spent five years at the NIMR at Mill Hill with Nobel Laureate, Professor John Cornforth. With Prof. Cornforth he unravelled the vexed problem of the methyl shifts in cholesterol biosynthesis and worked on the synthesis of vitamin B_{12}. In 1962, he was appointed as Lecturer at Manchester University with Professor Arthur Birch and in 1967 was promoted to Senior Lecturer. In 1972 he was appointed as founder Professor of Organic Chemistry at the University of Wales Swansea, the position he currently holds. Andrew Pelter was awarded the Tilden Medal of the Royal Society of Chemistry in 1981 and gave the R.S.C. sponsored Warren Lecture in South Africa in 1993. He is the author of more than 300 articles about 100 of which are on organoboron chemistry. His current interests are centred on: (i) organoboron chemistry; (ii) two electron oxidation of phenols; (iii) the use of chiral [2:2] paracyclophane derivatives as reagents, catalysts and chiral auxiliaries.



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