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Chapter 3

ELEMENTS OF GROUP 3

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3.1 BORON

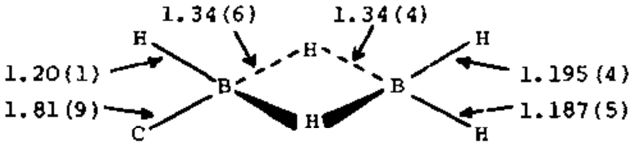
3.1.1 Boranes

Bands of the $A^2\pi$-$X^2\Sigma^+$ transition of BH^+ have been analysed. These yielded a value for the B-H distance of $^{11}BH^+$ of 1.24397(5)Å in the $A^2\pi$ state and 1.20292(5)Å in the $X^2\Sigma^+$ state.[1] MO-SCF calculations have been carried out on BH^+ and AlH^+ ions, for the $X^2\Sigma^+$, $A^2\pi$ and $B'^2\Sigma^+$ states. It was possible to predict the so-far-unobserved part of the B^1-X emission system for BH^+.[2]

A new model for the structure and bonding in boron hydrides has been proposed, based on the tensor surface harmonic theory. The model produces the characteristic structural and electron-counting rules for closo-, nido- and arachno-boranes in a simple and direct manner. Nido- and arachno-boranes have pairs of high-energy occupied orbitals localised around the open (non-triangular) face. These are similar in form to those found in cyclic planar hydrocarbons.[3]

Heats of formation of some boron hydrides (BH_3, B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, $B_{10}H_{14}$) have been calculated by the molecular orbital bond index method. This gives a satisfactory correlation with known data and hence has some predictive value for molecules where such data are not experimentally determined.[4]

Analysis of the microwave spectra of 10 isotopic variants of methyldiborane, $B_2H_5CH_3$, gave the structural parameters summarised in (1) (all bond distances in Å). The B---B distance of 1.82(2)Å is longer than in related molecules.[5]



(1)

Treatment of the borane anions BH_4^-, $B_3H_8^-$, $B_4H_9^-$, $B_9H_{14}^-$ with one molar equivalent of the Lewis acid BX_3 (X=F, Cl or Br) leads to hydride ion abstraction. This gives good yields of B_2H_6, B_4H_{10}, B_5H_{11} and $B_{10}H_{14}$ respectively. A high-yield conversion of B_5H_9 to $B_9H_{14}^-$ is the first step in an overall 50% conversion of B_5H_9 to $B_{10}H_{14}$. The hydride abstraction by BCl_3 and BBr_3 produces the new anions HBX_3^- (X=Cl or Br).[6]

Ab initio m.o. calculations have been performed on the transient boron hydrides B_3H_7, B_3H_9, B_4H_8, B_4H_{12}, and the fluxional $B_3H_8^-$ ion, with optimisation at the 3-21G level. At each minimum for a given symmetry, the 6-31G level is extended by polarisation on boron (6-31G*) and by correlation at the MP3/6-31G level. The most stable structures predicted are: C_s 2102 for B_3H_7, D_{3h} 3003 for B_3H_9, C_1 3111 for B_4H_8, D_{4h} 4004 for B_4H_{12} and C_{2v} 2102 for $B_3H_8^-$. For B_3H_7 C_{2v} 1103ST is only 4 kcal mol^{-1} less stable, for B_4H_8 the C_s 2112 and C_{2v} 4200 forms are less stable by 4, 6 kcal mol^{-1} respectively. For $B_3H_8^-$ the C_s 1104 form is less stable by only 1 kcal mol^{-1}.[7]

The adduct $B_2H_4.2PMe_3$ induces unsymmetrical cleavage of B_2H_6 or B_4H_{10}. Extension to B_5H_{11} shows that such a reaction does not take place in this case. The final reaction products were $Me_3P.BH_3$, $Me_3P.B_5H_9$, B_5H_9 and B_2H_6. The 1:1 adduct $Me_3P.B_5H_9$ cannot be made directly from its constituents. N.m.r. spectra of this adduct showed that 4 of the 9 borane hydrogen atoms form rigid terminal B-H bonds at the four basal positions of the square pyramidal B_5 framework. The other 5 hydrogen atoms undergo rapid tautomeric motion below the four basal edges of the pyramid.[8]

Fenske-Hall LCAO-MO-SCF calculations have been performed on B_5H_9, 1-$Fe(CO)_3B_4H_8$, 2-$Fe(CO)_3B_4H_8$ and 1,2-$[Fe(CO)_3]_2B_3H_7$. The orbital contour diagrams for the a_1 and e cluster molecular orbitals for B_5H_9 and 1-$Fe(CO)_3B_4H_8$ are consistent with the isolobal principle. The apical and basal BH units of B_5H_9 have almost identical Mulliken overlap populations for framework cluster-type interaction. In all the ferraboranes the 1-$Fe(CO)_3$ (apical) units have larger cluster-type Mulliken overlap than do the 2-$Fe(CO)_3$ (basal) units.[9]

Air-stable adducts $B_5H_9.L$ (L= bis(diphenylphosphino)methane, dppm; 1,2-bis(diphenylphosphino)ethane, dppe; or *NNN'N'*-tetramethylethylenediamine, tmen) and B_4H_8.tmen are formed by the action of the ligand on the borane at room temperature. No cleavage of the B_5 unit occurs even with excess ligand. The B_5H_9 complexes (derivatives of the *hypho*-$B_5H_{11}^{2-}$ ion) were fully characterised by X-ray diffraction. In the dppm and dppe adducts, the phosphorus atoms bridge apical and basal atoms of a flattened pyramidal B_5 skeleton. The tmen adducts are very different, as the ligand chelates one of the original basal boron atoms, which is then singly-bonded to the apical boron, and separated from the remaining basal atoms by typical non-bonding distances.[10]

(μ-Dichloroboryl)pentaborane (9) is prepared by reaction (1) in dichloromethane solution. The product is an extremely air-

$$KB_5H_8 + BCl_3 \longrightarrow KCl + (\mu\text{-}Cl_2B)B_5H_8 \qquad ...(1)$$

sensitive liquid (spontaneously inflammable in air). It was characterised by i.r., ^{11}B and ^1H n.m.r.[11]

The reactions of BCl_3 with B_5H_9 or 2-Cl-B_5H_8 give 1-$(Cl_2B)B_5H_8$, 1-(Cl_2B)-2-ClB_5H_7 respectively, in the presence of Friedel-Crafts catalysts. These are the first examples of σ-bonding between borane cluster atoms and external trigonal boron atoms. The B-B bonds are cleaved at high temperature in the presence of Et_2O, and insert ethene at ambient temperature to form 1-[2-(dichlorboryl)-ethyl]pentaborane (9).[12]

2-Aryl substituted derivatives of B_5H_9 can be prepared by $AlCl_3$-catalysed electrophilic substitution of 2-ClB_5H_8 by various alkylbenzenes. ^1H n.m.r. data indicate that the site of attack of the B_5H_8 group is sterically controlled.[13]

Crystals of bis(dimethylsulphide)-*closo*-nonaborane (7), $B_9H_7(SMe_2)_2$, are orthorhombic, belonging to the space group $P2_12_12_1$. The boron cage is a tricapped trigonal prism with one Me_2S bonding to a capping B aton, and one to a trigonal prismatic B atom.[14]

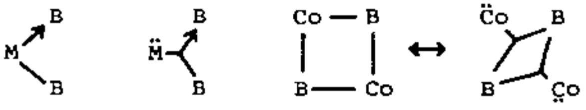
The structure and bonding in 1,10-$B_{10}H_8(N_2)_2$ have been elucidated by HeI and HeII photoelectron spectroscopy, X-ray crystallography and m.o. calculations. The structure is based on a *closo*-B_{10} bicapped square antiprism cage. The photoelectron spectra were assigned using m.o. calculations on this compound and on *closo*-$B_{10}H_{10}^{2-}$. The $B(N_2)$ unit is electronically very similar to BH^-.[15]

3.1.2 Borane Anions and their Metallo-Derivatives.

Both m.o. and localised bond considerations were used to rationalise the structures of *closo*-clusters with unusual electron numbers. The arguments show that the degeneracies of the HOMO and LUMO of *closo*-, *n*-atom, (*n*+1) bond pair clusters provide a better guide to the possible shapes of related clusters with 2 more or 2 fewer electrons than do localised bond schemes. The latter do have some value in deducing the electron distribution and approximate bond orders in clusters of known structure. The calculations particularly concentrated on $B_nH_n^{2-}$ and $Cp_4M_4B_4H_4$ (M = Co,Ni).[16]

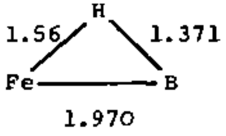
A new theoretical approach has been proposed for bonding in closo-boron hydrides $B_nH_n^{2-}$, in which each boron atom is considered to bond directly to all other boron atoms. A simple relationship was found between the energy and internuclear distance, which allowed the assessment of a large number of complex molecular polyhedra.[17]

A description has been given of some sample bonding schemes for some eight-vertex, D_{2d}, dodecahedral cluster compounds which violate Wade's rules, e.g. $Cp_4M_4B_4H_4$, where M = Ni or Co. The bonding requires the arrangements (2a) and (2b) for both M, and (2c) for Co only.[18]



(a) (b) (c)

(2)



(3)

Electrochemical data have been given on nonaqueous solutions of cobaltaboranes or -carbaboranes in which one or two boron atoms have been replaced by phosphorus or arsenic. One or more reversible electron-transfer reactions were found for each compound. Oxidation states from zero to +4 were all detected; the preferred oxidation state was determined largely by the formal charge on the borane ligand.[19]

$HFe(BH_2)(CO)_{12}$ has been prepared from $B_2H_6Fe(CO)_6$ and excess $Fe_2(CO)_9$. Spectroscopic and X-ray diffraction experiments show that the structure contains an $HFe_4(CO)_{12}$ "butterfly" with a BH_2 fragment bridging the wing tips. The Fe-H-B interaction is as shown in (<u>3</u>).[20]

The crystal structure of $NEt_4^+[Mo(CO)_3\{HB(3,5\text{-}Me_2pz)_3\}]^-$, where $HB(Me_2pz)_3^-$ is hydridotris(3,5-trimethylpyrazolyl), shows that the boron ligand is tridentate, coordinated to facial octahedral sites about the molybdenum.[21]

In strongly acid media, the hydrolysis of hydro(pyrrolyl-1)-borates ($[BH_n(NC_4H_4)_{4-n}]^-$, n = 1-3) takes place in a stepwise manner. Neutral or mildly alkaline media cause a general acid-catalysed hydrolysis.[22]

The Raman spectra of the ^{10}B and ^{11}B isotopic forms of BH_4^- and BD_4^- isolated in alkali halide matrices have been reported. The effects of Fermi resonance are significant.[23] Further studies of the vibrational spectra of BH_4^- and BD_4^- isolated in alkali halide matrices showed that if the lattice has the NaCl structure, then the anion preserves T_d symmetry. For the CsCl structure, the anion symmetry is reduced to C_{3v}.[24]

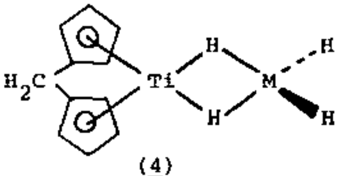
The minimum energy path and geometry of the transition state for the first stage of the reduction of R_2CO (where R = H or Me) by $LiBH_4$ have been determined by <u>ab initio</u> SCF calculations using a small basis set. These were confirmed by further calculations using a larger basis set with configuration interaction.[25]

$Mg(BH_4)_2.3THF$ can be prepared from MgH_2 and B_2H_6 in THF. It forms monoclinic crystals (space group C2/c), and the BH_4 is coordinated in bidentate fashion to the magnesium.[26]

Electron diffraction results on $Ti(BH_4)_3$ have been reported. I.r., u.v. and photoelectron spectra have suggested terdentate coordination, and it was possible to analyse the data on this model, i.e. $Ti[(\mu\text{-}H)_3BH]_3$, i.e. nine-fold coordination of the titanium. The TiB_3 skeleton is <u>non</u>-planar (with ∠BTiB approximately 116°), and vibrational data also were consistent with approximately C_{3v} symmetry for the TiB_3 skeleton.[27]

$[CH_2(C_5H_4)_2]TiMH_4$, where M = B or Al, contain bidentate MH_4 groups, (<u>4</u>). The boron compound is prepared from $CH_2(C_5H_4)_2TiCl_2$ and $LiBH_4$; the aluminium compound from the boron compound with $LiAlH_4$ in ether.[28]

$[Ti(salen)Cl_2]$, where salen = <u>NN</u>'-ethylenebis(salicylidene-iminato), reacts with $LiBH_4$ in Et_2O to form $[\{Ti(salen)(BH_4)_2\}_2].2THF$. The i.r. spectrum shows that νC=N has disappeared, but that strong νTiH and νBH bands are present. The crystal structure shows that the dimeric units contain seven



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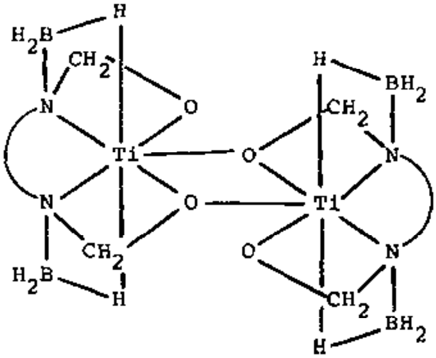


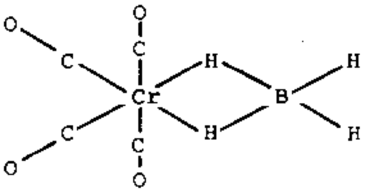
(5)

coordinate titanium, (5).[29]

The final product of the reaction of BH_3.THF with Cp_2ZrMe_2 is $Cp_2Zr(BH_4)_2$. ^{11}B n.m.r. spectra show that the reaction proceeds via intermediates containing coordinated BH_3Me^- and $BH_2Me_2^-$ ligands. Hence this reaction is a formal insertion of BH_3 into a $Zr-CH_3$ bond. The intermediates react further with borane to give a complex equilibrium mixture of alkyldiboranes, $B_2Me_nH_{6-n}$, and $Zr(BH_4)$ groups.[30]

The HeI u.v.-photoelectron spectra of $M(BH_4)_4$, where M = Zr or Hf, have been analysed with help from LCAO-HFS(Xα) calculations on the zirconium compound. The proposed assignments differ somewhat from those in earlier work.[31]

$(\mu-H)_2BH_2Cr(CO)_4^-$ is a by-product of the reaction of BH_3.THF with $HCr(CO)_5^-$. The crystal structure shows the presence of the unit (6).[32]



(6)

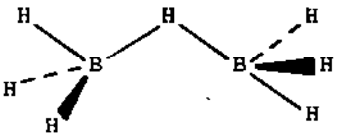
(Triphos)Cu(BH_4), where triphos = 1,1,1-tris[(diphenylphosphino)-methyl]ethane, $CH_3C(CH_2PPh_2)_3$, has been shown to involve unidentate attachment of the BH_4 ligand. The Cu-H-B unit is bent, with an angle of about 121°.[33] Reactions between chlorotris(methyldiphenylphosphine)copper(I) and several hydroborates containing a B-O bond have been studied. The new complex $(Ph_2MeP)_3CuH_3B(O_2CCH_3)$ was isolated.[34]

Solubility was studied at 25°C in the system $NaBH_4$-$La(BH_4)_3$-THF. There is a mutual increase in solubility of both tetrahydroborates.[35] In the $La(BH_4)_3$-$Mg(BH_4)_2$-THF system the lanthanum tetrahydroborate solubility increases to 6 mass % in the presence of $Mg(BH_4)_2$.[36]

$[Bu_4N][BH_4]$ reacts with $Ln(BH_4)_3.2THF$, where Ln = La, Pr or Nd, in benzene at 20°C to form $[Bu_4N][Ln(BH_4)_4(THF)]$ at a 1:1 ratio, or $[Bu_4N]_2[Ln(BH_4)_5]$ at 2:1 or 3:1 ratios. I.r., and ^1H n.m.r. data were recorded, but no structural conclusions were drawn.[37] The following complexes have been obtained in crystalline form: $NaLn(BH_4)_4.4DME$, where Ln = La, Ce, Pr, Nd, Sm or Eu; DME = dimethoxyethane.[38]

The crystal structure of $[(Ph_3P)_2N]^+[B_2H_7]^-.CH_2Cl_2$ reveals the structure of the $B_2H_7^-$ ion. The key result is that the B-H-B bridge is bent, (7), with ∠BHB = 136(4)°. The staggered conformation gives C_s symmetry, and the B----B distance is quite short (2.107(7)Å). The results are in conflict with _ab initio_ m.o. calculations, which suggest that the B-H-B bridge should be linear, at least in the gas-phase.[39]

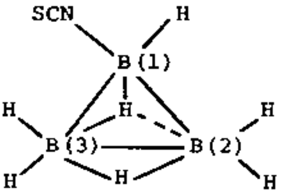
$B_3H_8^-$ reacts with mercury(I) halides to form the substituted anions $B_3H_7Cl^-$, $B_3H_6Cl_2^-$ and $B_3H_7Br^-$. Treatment of $B_3H_7Cl^-$ with CN^-, SCN^-, BH_3CN^- yields $B_3H_7X^-$, where X = CN, NCS or CNB_3H_7. There was some evidence for the formation of $B_3H_7F^-$ from $B_3H_8^-$ and Hg_2F_2.[40]



(7)

The electrochemical oxidation, in acetonitrile solutions, of $B_3H_8^-$ and $[B_3H_7L]^-$ (where L = Cl, NCS or $NCBH_3$) was studied by cyclic voltammetry and controlled potential coulometry. Some new complexes were prepared, e.g. $[Cu(H_3BCNB_3H_7)(PPh_3)_2]$: the first example of a substituted tetrahydroborate complexed to a metal.[41]

The crystal structure of $[(Ph_3P)_2N]^+[B_3H_7NCS]^-$ shows that the anion contains an unusual asymmetric face-bridging mode for one hydrogen atom, (8).[42]



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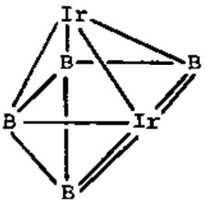


(9)

Metal-boron bonding in 3 metalloboranes has been studied: $(Me_2PPh)_2PtB_3H_7$ ("borallyl" form), $(OC)_4MnB_3H_8$, and the ferraborane $(OC)_6Fe_2B_3H_7$ (formally a dimetallapentaborane). The extended Hückel technique was used. Important aspects of the structures can be rationalised in terms of the frontier-orbital behaviour of the triborane fragments, as a function of the triborane geometry.[43]

Reaction of *closo*-$B_{10}H_{10}^{2-}$ with *trans*-$[Ir(CO)Cl(PPh_3)_2]$ in methanol gives as one product $[1,1,2-(CO)_3-1-(PPh_3)-2,2-(Ph_2P-$*ortho*-$C_6H_4)_2$-*closo*-$(1,2-Ir_2B_4H_2)]$. The structure of this is based on a closed octahedral Ir_2B_4 cluster, with metal atoms at adjacent vertices, (9).[44]

Nido-$B_9H_{12}^-$ reacts with *trans*-$[Ir(CO)Cl(PMe_3)_2]$ giving several new compounds, including the *arachno*-1-metallapentaborane $[1,1,1-(CO)(PMe_3)_2(1-IrB_4H_9)]$. This has the same relationship to *arachno*-B_5H_{11} as does *nido*-[1,1,1-$(CO)_3(1\text{-}FeB_4H_8)$] to *nido*-$B_5H_9$. The new compound is fluxional, and its n.m.r. (^1H, ^{11}B, ^{31}P) spectra were described.[45]

The two anions $B_5H_8^-$ and $B_9H_{14}^-$ react with $CoCl_2$ and LiC_5Me_5 in THF in quite different ways. $B_5H_8^-$ gives a large, structurally diverse range of products, none in greater than 5% yield. The main ones are 2-$(C_5Me_5)CoB_4H_8$, 1,2-$(C_5Me_5)_2Co_2B_4H_6$, 1,2,3-$(C_5Me_5)_3Co_3B_4H_4$, with others which do not have C_5H_5-analogues, e.g. 1,2-$(C_5Me_5)_2Co_2B_5H_7$. Thermolysis of this leads to loss of hydrogen and formation of $(C_5Me_5)_2Co_2B_5H_5$, a 2n-electron cage system with a capped-octahedral geometry. $B_9H_{14}^-$, on the other hand, gives only 4 reaction products, and all have 10-vertex cages, either CoB_9 or Co_2B_8, analogous to $B_{10}H_{14}$: 6-$(C_5Me_5)CoB_9H_{13}$, 6,9-$(C_5Me_5)_2Co_2B_6H_{12}$, 5,7-$(C_5Me_5)_2Co_2$-B_8H_{12} and the 6-chloro derivative of the last.[46]

X-ray diffraction of $(\eta^5\text{-}C_5Me_5)_3Co_3B_4H_4$ confirms the structure as a *closo*-Co_3B_3 octahedral unit, with the Co_3 face-capped by BH - as in the C_5H_5 analogue. There is severe steric crowding of C_5Me_5 ligands, leading to distortions of the ligands, and lengthening of the Co-Co bonds. The structure is as expected from the electron-counting rules.[47]

$NaCo(CO)_4$ and 2-XB_5H_8 (where X = Cl or Br) react by equation (2).

$$2XB_5H_8 + NaCo(CO)_4 \rightarrow 2\text{-}[Co(CO)_4]B_5H_8 + NaX \qquad \ldots(2)$$

The product is, however, only stable for a very brief period. LiB_5H_8 and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2I]$, on the other hand, give the reasonably stable 2-$[\eta^5\text{-}C_5H_5Fe(CO)_2]B_5H_8$.[48]

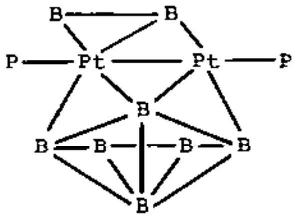
A detailed vibrational assignment has been made for the $B_6H_6^{2-}$ ion, from the i.r. and Raman spectra of the Cs^+ and NMe_4^+ salts, and for the isoelectronic 1,6-$C_2B_4H_6$. The latter appears to have stronger B-H and B-B bonds.[49]

SCF-type Hückel m.o. calculations on $B_6H_6^{2-}$, 1,6-$C_2B_4H_6$, 1,2,4-$[C_2B_3H_5Fe(CO)_3]$, $[B_5(CO)_2H_3Fe(CO)_3]$, $[B_4H_6\{Fe(CO)_3\}_2]$, $[B_3H_5\{Fe(CO)_3\}_3]$ and the hypothetical $[B_5H_5Fe(CO)_3]^{2-}$, $[B_5H_7Fe(CO)_3]$ and $[B_4H_4\{Fe(CO)_3\}_2]^{2-}$ have been carried out. The overlap populations bonding the BH, CH and B(CO) groups into the clusters show that all have about two electrons associated with them. The 'extra' electron from CH or B(CO) has become delocalised into the cluster bonding.[50]

E.H.M.O. calculations were reported for sandwich complexes derived from nido-pentagonal bipyramidal $B_6H_6^{4-}$ and $C_2B_4H_6^{2-}$ ligands, and compared to those for cyclopentadienyl analogues. Examples were $Fe(B_6H_6)_2^{6-}$ and $[FeH_2(B_6H_6)_2]^{4-}$. The calculations can explain the electronic factors which prevent the formation of stable 'bent sandwich' compounds derived from pentagonal borane ligands.[51]

Other extended Hückel m.o. calculations have been carried out on the related closo-platinaboranes $[(H_3P)_2Pt(B_6H_6)]^{2-}$ and $[(H_3P)_2Pt(B_{11}H_{11})]^{2-}$ and the closo-carbaplatinaboranes $[(H_3P)_2Pt(C_2B_4H_6)]$ and $[(H_3P)_2Pt(C_2B_9H_{11})]$. These suggest that the larger "slip" distortions in the pentagonal bipyramidal derivatives are largely due to the different metal-ligand interactions induced by different elevation angles of the substituents on the pentagonal faces of the ligands.[52]

$[(PMe_2Ph)_2(Pt_2B_8H_{14})]$ contains four-vertex and eight-vertex subclusters $\{Pt_2B_2\}$ and $\{Pt_2B_6\}$, linked via a common Pt-Pt edge. It may be regarded as an iso-arachno-diplatinadecaborane, (10).[53]



(10)

Direct electrophilic substitutions can be carried out on $B_9H_9^{2-}$ in non-aqueous solvents in the absence of oxygen. The products include $[B_9H_8NR_3]^-$, where R = H or Me. $B_{11}H_{11}^{2-}$ with acetic anhydride in DMSO produces a dimethyl sulphido derivative; this is fluxional in solution. These were the first examples of non-halogenated derivatives of the B_9 and B_{11} polyhedral boranes.[54]

$B_9H_9^{2-}$ reacts similarly with acetic anhydride/DMSO, giving two isomers of $B_9H_8SMe_2^-$. Variable temperature ^1H and ^{13}C n.m.r. spectra showed that these provide the first examples of intramolecular rearrangement of a 9-boron cluster. The activation barrier to this dynamic process is 22 kcal.mole^{-1}. Prolonged reaction gave di-substitution, but only one isomer, 1,5-$B_9H_7(SMe_2)_2$. This showed dynamic behaviour at or above ambient temperature, probably involving equilibration with 4,5- and 1-8(9) isomers.[55]

Crystal and molecular structures have been determined for 6-$[\eta^5\text{-}C_5Me_5]CoB_9H_{13}$, 6,9-$[\eta^5\text{-}C_5Me_5]_2Co_2B_8H_{12}$, 5,7-$[\eta^5\text{-}C_5Me_5]_2Co_2B_8H_{12}$ and 6-Cl-5,7-$[\eta^5\text{-}C_5Me_5]_2Co_2B_8H_{11}$. All have 10-vertex *nido*-cage structures, similar to $B_{10}H_{14}$, with one or two borons replaced by $Co(C_5Me_5)$. The bridging hydrogens were situated as in $B_{10}H_{14}$ itself.[56]

Iridanona- and iridadecaboranes which have adjacent open-face bridging hydrogen atoms and terminal Ir-H bonds can easily lose H_2 in formal cluster oxidations which involve stable, isolable Ir($\overline{\mathrm{V}}$) species such as *closo*-$[H(PMe_3)_2(IrB_9H_9)]$.[57]

Ortho-cycloboronation reactions of *P*-phenyl groups on phosphine ligands in iridadecaboranes accompany both *nido* cluster expansion and *nido* → *closo* cluster closing processes associated with changes in formal oxidation state of the metal. One product has a new cluster structure - an *iso*-*closo* ten-vertex Ir($\overline{\mathrm{V}}$) unit ($IrB_3B_3B_3$) of idealised C_{3v} symmetry, i.e. $[1,1,1\text{-}H(PPh_3)(Ph_2P\text{-}\textit{ortho}\text{-}C_6H_4)\text{-}\textit{iso}\text{-}\textit{closo}\text{-}(1\text{-}IrB_9H_8\text{-}2\text{-})]$.[58]

Arachno-$B_9H_{14}^-$ reacts with *trans*-$[Ir(CO)Cl(PR_3)_2]$, where R = Ph or Me, or $[\{M(cod)Cl\}_2]$, where M = Ir or Rh, to give low yields of *nido*-6-metalladecaboranes: $[6\text{-}H\text{-}6,6\text{-}(PR_3)_2\text{-}\textit{nido}\text{-}6\text{-}IrB_9H_{13}]$, where R = Me or Ph, or $[6\text{-}(\eta^2\text{:}\eta^2\text{-}cod)\text{-}6\text{-}Cl\text{-}\textit{nido}\text{-}6\text{-}MB_9H_{13}]$, where M = Ir or Rh. They were characterised by single- and multiple-resonance n.m.r. and by single-crystal X-ray analysis of $[6\text{-}H\text{-}6,6\text{-}(PPh_3)_2\text{-}\textit{nido}\text{-}6\text{-}IrB_9H_{13}]$.[59]

$B_{10}H_{14}$ reacts with slurries of elemental Ni, Zn or Co (formed by the potassium reduction of MCl_2 in ether solutions) to give the corresponding $M(B_{10}H_{12})_2^{2-}$ complexes, with M in the +2 oxidation state. The yields were better than for other preparative methods. Other boranes may undergo similar reactions.[60]

An improved method has been reported for the synthesis of $B_{12}H_{11}NEt_3^-$, from $B_{10}H_{14}$ and $NMe_3.BH_3$. The crystal structure of $KB_{12}H_{11}NEt_3$ was determined, showing that the unit cell dimensions are considerably greater than in $M_2B_{12}H_{12}$.[61]

The vibrational spectra have been reported for $M_2B_{12}X_{12}$ (X = H, D, Cl, Br or I; M = K or Cs) and assigned, using data on solid-phase and solutions. All of the anions follow the selection rules expected for the I_h point group in the solution spectra.

Changes in the spectra of the solids due to crystal field effects were discussed.[62]

The adducts $UO_2B_{12}H_{12}.nL$ (where L = urea, n = 3,5-8) have been made for the first time. Chemical analysis and X-ray diffraction show that they are definite compounds.[63]

$[7-(PMe_2Ph)\{7-PtB_{16}H_{18}-9'-(PMe_2Ph)\}]$ is a complex of a macropolyhedral, 16-vertex borane ligand. The latter is based on the structure of a so far unknown B_6-B_{10} conjuncto-borane. The complex is the first example of a contiguous 17-vertex cluster species.[64]

Reaction of the deprotonated anti-isomer of $B_{18}H_{22}$ and cis-$[PtCl_2(PMe_2Ph)_2]$ produces the expected $[(Pt-\eta^4$-anti-$B_{18}H_{20})$-$(PMe_2Ph)_2]$, and also a novel μ-η^1, η^2-isomer, with the $Pt(PMe_2Ph)_2$ group bridging the two edge-linked B_{10} clusters, as well as a more compact diplatina-derivative, $[(Pt_2B_{18}H_{16})(PMe_2Ph)_4]$. In the last, the new confacial conjuncto-borane unit $B_{18}H_{16}$ is η^4-bonded to one $Pt(PMe_2Ph)_2$, and $(\eta^4 + \eta^2)$-bonded to the other. If syn-$B_{18}H_{22}$ is used, a third isomer of $[(PtB_{18}H_{20})(PMe_2Ph)_2]$ is formed.[65]

3.1.3 Carba- and other Non-metal Heteroboranes.

Closo-carbaboranes that can be formally divided into rings and caps follow a six-electron rule. The relative stability of isomers for a given carbaborane depends on the size of the ring on which the polyhedral structure is based. In 3- and 4-membered rings the CH group fits in as the best cap. Thus the stability of $1,5-C_2B_3H_5$ is greater than that of $1,2-C_2B_3H_5$. The BH group,with more diffuse orbitals, overlaps better with orbitals of a 5-membered ring: hence the stability sequence $2,4-C_2B_5H_7 >$ $1,2-C_2B_5H_7 > 1,7-C_2B_5H_7$. The orbitals of BH are not diffuse enough to overlap favourably with the orbitals of a 6-membered ring. Hence $C_2B_6H_8$ prefers a dodecahedron to a hexagonal bipyramid configuration.[66]

^{11}B and ^{13}C n.m.r. data have been reported on peralkylated nido-2,3,4,5-tetracarbahexaboranes (6). Selective heteronuclear triple resonance experiments $^{13}C\{^1H,^{11}B\}$ enabled various isomers to be characterised.[67]

M.o. and bond energy calculations were used to probe changes that occur when B_4H_{10} reacts with C_2H_4 or C_2H_2 to give H_2 and closo-carbaboranes 1,2- and $1,6-C_2B_4H_6$, via arachno- and nido-precursors.

The driving force for stepwise cluster oxidation is provided by progressive increases in B-C bonding, accompanied by transfer of electronic charge to the carbon atoms. The system can be used as a model for the behaviour of unsaturated hydrocarbons on surfaces.[68]

A technique has been reported for revealing the spin-spin coupling (and hence direct bonding) interactions in borane or heteroborane frameworks - this involves two-dimensional, J-correlated ^{11}B-^{11}B F.T. n.m.r. Results were quoted for 2,3-$Et_2C_2B_4H_6$ and 6-$(C_5Me_5)CoB_9H_{13}$ but the technique is believed to be of widespread application.[69]

The complexes $(RC_2R')Co_2(CO)_6$, where R,R' = H,Me or Et, catalyse the reaction of alkynes (acetylene, 1- or 2-butyne) with small carbaboranes (1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$, 2,4-$C_2B_5H_7$ or 2,3-$C_2B_4H_6$). The reaction products are the corresponding B-substituted alkenylcarbaboranes: $(RHC{=}CR)_nC_2B_3H_{5-n}$, $(RHC{=}CR')_nC_2B_4H_{6-n}$, $(RHC{=}CR')_nC_2B_5H_{7-n}$ and $(RHC{=}CR')_nC_2B_4H_{8-n}$. The degree of carbaborane substitution is varied by altering the reaction conditions, and all degrees of substitution, up to complete replacement of B-H units, could be achieved.[70]

The rates of rearrangement of 5- and 3-CH_3-*closo*-2,4-$C_2B_5H_6$, at 295°C, to give *B*-CH_3-*closo*-2,4-$C_2B_5H_6$ have been measured. The data could be rationalised much better by the diamond-square-diamond mechanistic route than by the triangle face rotation.[71]

Both 3-Cl- and 5-Cl-*closo*-2,4-$C_2B_5H_6$ react readily with Me_3E (where E = N or P) to form 1:1 adducts. BCl_3 removes chloride ion from these adducts to give the novel cations $[3\text{-}Me_3E\text{-}closo\text{-}2,4\text{-}C_2B_5H_6]^+$ or $[5\text{-}Me_3E\text{-}closo\text{-}2,4\text{-}C_2B_5H_6]^+$. Trimethylamine reacts with 1-Cl-*closo*-2,4-$C_2B_5H_6$ with greater difficulty, but the 1:1 adduct combines with BCl_3 to yield a rearrangment product: $[3\text{-}Me_3N\text{-}closo\text{-}2,4\text{-}C_2B_5H_6]^+[BCl_4]^-$.[72]

The complete assignment of the ^{11}B n.m.r. spectrum of 5,6-dicarba-*nido*-decaborane (12), 5,6-$C_2B_8H_{12}$, has been achieved by examining the spectra of a number of substituted derivatives.[73]

A variety of experimental evidence suggests that the electron donor abilities and steric requirements are very similar for the $B_9C_2H_{11}^{2-}$ carbaborane cluster and the η^5-C_5Me_5 ligand.[74]

The crystal structure of the tetramethylammonium salt of 7-phenyl-7,8-dicarba-*nido*-undecaborane, $[PhC_2B_9H_{11}]^-$, shows that one of the hydrogen atoms of the anion is centred above a pentagonal open face of the carbaborane polyhedron, at a distance of 0.81(5)Å from the average plane of this face.[75]

Base degradation of p-carbaborane is promoted by the crown ether 18-crown-6 in KOH. Thus, 1,12-$C_2B_{10}H_{12}$ gives [K(18-crown-6)][nido-2,9-$C_2B_9H_{12}$], from which a number of metallocarbaboranes can be prepared.[76]

Racemic (±)-5,6-dicarba-nido-decaborane (12) can be converted into its laevorotatory enantiomer by means of (+)-N-methylcamphidine.[77]

The molecular structure of 1,12-$C_2Me_2B_{10}H_{10}$ has been determined by gas-phase electron diffraction. The following bond lengths were found: B-C, 1.716(13)Å; B_2-B_3, 1.777(7)Å; B_2-B_7, 1.766(20)Å; C-C, 1.533(19)Å; B-H, 1.216(19)Å and C-H, 1.088(33)Å.[78]

Phenyl-9-m-carbaboranyliodonium tetrafluoroborate, $[C_2H_2B_{10}H_9IPh]^+BF_4^-$, proves to be a general "carbaboranylation" reagent, with, for example, RCOONa (R = Me or Ph) producing 9-m-$C_2H_2B_{10}H_9OCOR$.[79]

9-Organo-substituted o- and m-carbaboranes and 2-organo-substituted p-carbaboranes can be prepared by the substitution of iodine in 9-iodo-o-, 9-iodo-m- and 2-iodo-p-carbaboranes, using an organomagnesium compound with catalytic amounts of palladium phosphine complexes.[80]

The first preparation of a series of compounds of I(III) with a carbaborane unit has been announced. All contain B-I bonds: 9-$C_2H_2B_{10}H_9IX_2$, where X = Cl or $OCOCF_3$.[81]

Molecular motion in o-carbaborane has been studied by determining the proton second moments and spin-lattice relaxation times T_1 and $T_{1\rho}$ in the temperature range 77-320K.[82]

B-mercurated and B-thalliated carbaboranes react with Se or Te

$$(C_2B_{10}H_{11})_2Hg + E \xrightarrow[300^{\circ}C]{270-} (C_2B_{10}H_{11})_2E_n \qquad ...(3)$$

(E = Se, n = 2; E = Te, n = 1).

to form carbaboranyl derivatives with B-Se or B-Te bonds, e.g. as in equation (3).[83]

3.1.4 Metallo-heteroboranes.

The reaction of $Co(PEt_3)_4$ with closo-2,4-Me_2-2,4-$C_2B_5H_5$ produces a novel dicobalthydrido-complex containing a phosphido-bridge: 4-(Et_3P)-1,7-Me_2-$\mu_{4,8}$-{Co(H)(PEt_3)$_2$-μ(H)-μ(PEt_2)}-1,4,7-$CCoCB_5H_4$.

$Fe(CNBu^t)_5$, on the other hand, forms a mononuclear eight-atom cage, in which the iron atom has a cluster convectivity of 5: 4,4,4-$(Bu^tNC)_3$-1,7-Me_2-1,4,7-$CFeCB_5H_5$.[84]

The crystal structure of 6:4',5'-$[(\eta\text{-}C_5H_5)Co\text{-}2,3\text{-}Me_2C_2B_4H_3]$-$[2',3'\text{-}Me_2C_2B_4H_5]$ shows it to be a coupled cage cobaltacarbaborane. The two cages are linked by a three-centred B-B-B bond.[85]

The first known examples of borane-metal-carbaborane sandwich complexes have been prepared - from $B_5H_8^-$ or $B_9H_{14}^-$ and $CoCl_2$/THF, followed by the addition of $R_2C_2B_4H_5^-$ (where R = Me or Et). Thus, from $B_5H_8^-$ and $Et_2C_2B_4H_5^-$ are prepared $[2,3\text{-}Et_2C_2B_4H_4]\text{-}2\text{-}Co[B_5H_{10}]$; $[2,3\text{-}Et_2C_2B_4H_4]\text{-}5\text{-}Co[B_9H_{12}\text{-}1\text{-}O(CH_2)_4]$ and $[2,3\text{-}Et_2C_2B_3H_5]\text{-}5\text{-}Co[B_9H_{12}\text{-}1\text{-}O(CH_2)_4]$. The reaction conditions must be controlled very carefully to give these products, which were characterised by n.m.r. (^1H, ^{11}B), i.r. and mass spectra, and (in some cases) by X-ray diffraction.[86] These were reported in detail for $[2,3\text{-}Et_2C_2B_4H_4]\text{-}5\text{-}Co[B_9H_{12}\text{-}1\text{-}O(CH_2)_4]$, $[2,3\text{-}Et_2C_2B_3H_5]\text{-}5\text{-}Co[B_9H_{12}\text{-}1\text{-}O(CH_2)_4]$ and $[1,2\text{-}Et_2C_2B_7H_7]\text{-}6\text{-}Co[B_9H_{12}\text{-}2\text{-}O(CH_2)_4]$. The borane and carbaborane are bonding simultaneously to Co, and the CoB_9 unit is similar to the B_{10} cage in $B_{10}H_{14}$. The carbaborane units are (respectively) a 7-vertex *closo*-CoC_2B_4, a 6-vertex *nido*-CoC_2B_3 and a 10-vertex *closo*-CoC_2B_7 framework.[87]

Electrochemical data have been presented for 6 iron or cobalt metallacarbaboranes with 5-7 vertices. Cobalt compounds such as $CpCo(C_2B_4H_6)$ can undergo one oxidation and two reductions, all one-electron. Only the first reduction (CoII to CoI) is fully reversible. The *nido*-cobaltaborane 2-$CpCoB_4H_8$ undergoes reversible reduction to a Co(II) monoanion. Compared to larger clusters, the small clusters stabilise high metal oxidation states.[88]

The conversion of the red, diamagnetic sandwich complexes $(R_2C_2B_4H_4)_2FeH_2$ or $(R_2C_2B_4H_4)_2CoH$ (where R = alkyl) to the corresponding $R_4C_4B_8H_8$ carbaborane *via* oxidative fusion of the formal $R_2C_2B_4H_4^{2-}$ ligands has been considered in detail. The reaction is intramolecular with respect to the ligands, as no alkyl exchange occurs in reactions of mixtures of $(R_2C_2B_4H_4)_2FeH_2$ and $(R'_2C_2B_4H_4)_2FeH_2$. THF solutions of the iron complexes produce purple, paramagnetic di-iron complexes $(R_2C_2B_4H_4)_2Fe_2(THF)_2$. In the presence of O_2 this gives $R_4C_4B_8H_8$ and hence it is an intermediate in the oxidative fusion of the mono-iron system.[89]

X-ray diffraction studies on the paramagnetic di-iron complex with R = Me, and a related one containing $(OMe)_2C_2H_4$ instead of THF, showed that they can be formulated as $[Me_2C_2B_4H_4]_2[Fe^{II}(\text{low-spin})][Fe^{II}(\text{high-spin})]L_2$ (where L_2 = 2THF or $(OMe)_2C_2H_4$). One iron atom is sandwiched between two $Me_2C_2B_4H_4^{2-}$ ligands, with a second iron in a 'wedging" position, coordinated to the rest of the complex by four Fe-B interactions. The 'outer' iron is the high-spin one.[90]

Closo-2,4-R_2-2,4-$C_2B_5H_5$ (where R = H or Me) and $[Pt_2(\eta\text{-COD})(PEt_3)_4]$ react to give the carbaplatinaboranes 4,4-$(Et_3P)_2$-1,7-R_2-1,4,7-$CPtCB_5H_5$ and 1,1-$(Et_3P)_2$-6,6-$(Et_3P)_2$-4,5-R_2-1,4,5,6-$PtC_2PtB_5H_5$. X-ray diffraction was used to establish the structures of these derivatives.[91]

It has been possible to produce the 10-vertex closo-metallacarbaboranes 10-η^5-C_5H_5Ni-η^4-1-CB_8H_9, 6-η^5-C_5H_5Ni-η^5-1-CB_8H_9, $(\eta^5\text{-}C_5H_5Ni)_2$-1-$CB_7H_8$ and $[2\text{-}\eta^5\text{-}C_5H_5Co\text{-}\eta^5\text{-}1\text{-}CB_8H_9]^-$ from 4-CB_8H_{14}, e.g. by treatment with NaOH and $NiCp_2$.[92]

Polynuclear Co(III) π-complexes of the bidentate $(\pi\text{-}B_8C_2H_{10}\text{-}\pi)^{4-}$ ligand have been prepared, with more than 3 cobalt atoms present. It was possible to isolate and identify $Cs_4[B_9C_2H_{11})_2\text{-}Co_4(B_8C_2H_{10})_3]$, but no structure was indicated.[93]

The synthesis of 1-substituted functional derivatives 3-π-$CpFe^{III}$-π-$C_2B_9H_{10}$-1-R (where R = CH_2OH, CHO, COOH, COMe, CH_2COOH etc) has been reported. The group 3-π-$CpFe^{III}$-π-1,2-$C_2B_9H_{10}$-1 was shown to be strongly electron-withdrawing.[94]

Bis(arene)iron(II) salts (where arene = mesitylene or hexamethylbenzene) or the benzenedichlororuthenium(II) dimer react with $Tl[3,1,2\text{-}TlC_2B_9H_{11}]$ in THF to produce neutral, air-stable π-(arene)$MC_2B_9H_{11}$ (M = Fe or Ru). These are formal analogues of $[\pi\text{-}(arene)M^{n+}(C_5H_5)]$. Single-crystal X-ray diffraction for 3,1,2-$(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)FeC_2B_9H_{11}$ confirmed the closo- sandwich structure expected from the electron-counting rules.[95]

The crystal and molecular structures of the triethylammonium salt of $[Co(C_2B_9H_{11})_2]^-$ show that in the sandwich structure the C_2B_3 faces interacting with the cobalt are almost parallel (dihedral angle of 3.7°). The two $C_2B_9H_{11}^{2-}$ ligands are mutually rotated by 37°. There were no significant distortions from twelve-vertex closo geometry.[96]

Halogenation of $Cs^+[Co(C_2B_9H_{11})_2]^-$ by elemental halogens in alcohol, and γ-irradiation-induced halogenation by $CHBr_3$, $CHCl_3$ or CCl_4 in polar solvents proceeds alternately in both ligands.

The successive series of products is 8-, 8,8'-, 8,9,8'-, 8,9,8',9'-, 8,9,12,8',9'- and 8,9,12,8',9',12'. Thirteen different halogen derivatives were produced and characterised.[97]

Sulphuric acid nitric acids convert [*closo*-3,3-(PPh$_3$)$_2$-3-H-3,1,2-RhC$_2$B$_9$H$_{11}$] to [*closo*-3,3-(PPh$_3$)$_2$-3-HSO$_4$-3,1,2-RhC$_2$B$_9$H$_{11}$] and [*closo*-3-PPh$_3$-3,3-(NO$_3$)$_2$-3,1,2-RhC$_2$B$_9$H$_{11}$] respectively (the latter was also produced by the reaction of the hydrido complex with NO$_2$/N$_2$O$_4$). These products were then used to prepare other new metallacarbaboranes, e.g. [*closo*-3-PPh$_3$-3,3-{C(Ph)-C(PPh$_3$)-C(H)-C(Ph)}-3,1,2-RhC$_2$B$_9$H$_{11}$] and [{*closo*-3-PPh$_3$-3-(μ-CN)-3,1,2-RhC$_2$B$_9$H$_{11}$}$_4$]. Both of these were subjected to X-ray single-crystal diffraction, and their molecular structures determined.[98]

[FeH$_2$(2,3-Me$_2$-2,3-C$_2$B$_4$H$_4$)$_2$] reacts with [Co(PEt$_3$)$_4$], [Pt$_2$(μ-COD)(PEt$_3$)$_4$] or [Fe(COD)(η-C$_5$H$_5$)] to give (respectively) the dimetallic species: [CoFe(Me$_4$C$_4$B$_8$H$_8$)(PEt$_3$)$_2$], [FePt(Me$_4$C$_4$B$_8$H$_8$)(PEt$_3$)$_2$],[Fe$_2$(Me$_4$C$_4$B$_8$H$_8$)(η-C$_5$H$_5$)]. Each contains a direct metal-metal bond. The FeCo compound belongs to the structural family involving two pentagonal bipyramids fused about a common iron apical vertex, and sharing a double-capping BH group.[99]

C- and *B*-mercuricarbaboranes react with lanthanides (La,Tm,Yb) in THF at 200°C to form carbaboranyl derivatives of the lanthanides with either C-Ln or B-Ln bonds.[100]

[Ir(σ-carb)(CO)(PhCN)(PPh$_3$)], where carb = -7-C$_6$H$_5$-1,2-C$_2$B$_{10}$H$_{10}$, is an effective catalyst for the homogeneous hydrogenation of terminal olefins and acetylenes at room temperature and H$_2$ pressures below atmospheric.[101]

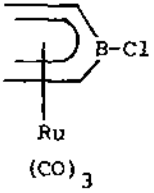
3.1.5 Compounds containing B-C or B-Si Bonds.

A detailed i.r. and Raman spectroscopic study has been made of CH$_3$NC·BH$_3$, for several isotopic species. All fundamental vibrations were assigned, except for the internal torsion, on the basis of C_{3v} symmetry. The νN≡C mode increased by about 150cm^{-1} on complex formation. The B-C stretching force constant was calculated to be 2.90mdyn.Å^{-1}, compared to the N-B value of 2.45 mdyn.Å^{-1} in CH$_3$CN·BH$_3$.[102]

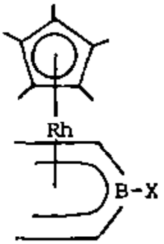
The i.r. and Raman spectra of K[CH$_3{}^{10}$BF$_3$], K[CH$_3{}^{11}$BF$_3$] and K[CD$_3{}^{11}$BF$_3$] have been reported and assigned, and a normal coordinate analysis carried out on the anion. The crystal structure shows that in the solid state the symmetry of

$[CH_3CF_3]^-$ deviates only slightly from C_{3v}. The B-C distance (1.575(3)Å) is the shortest, and the mean B-F distance (1.424(5)Å) is the longest yet found in organoborate compounds.[103a]

Ab initio m.o. calculations on vinyldifluoroborane, $(H_2C{=}CH)BF_2$, show that there is a π-contribution of 23 kJ.mol^{-1} to the B-C bond energy, mainly due to the interaction with the C=C bond.[103b] A general synthesis has been developed for dialkylvinylboranes, by the monohydroboration of alkynes by R_2BH.[104]



(11)



(12)

Several new (η^5-divinylborane)metal complexes have been prepared, e.g. (11), from $(CH_2{=}CH)_2BCl$ and $^1/3Ru_3(CO)_{12}$, and (12, where X = OMe, Me or Ph). All were characterised by C and H analysis, n.m.r. and mass spectra.[105]

MNDO m.o. calculations, using UHF functions, have been carried out for BMe_3, $AlMe_3$, for their molecular cations, and for all the fragment ions in their mass spectra, together with the corresponding neutral fragments.[106]

Me_2B^+ and Me_2Al^+ are the principal ions produced by electron impact on Me_3B, Me_3Al respectively. Measurements of halide affinities show that the aluminium ion is ca. 9 kcal.mol^{-1} more stable than Me_2B^+, and also a softer acid.[107]

Published enthalpy data for simple (trigonally coordinated) boron compounds have been used to calculate bond enthalpy terms E(B-X) for their B-X bonds, where X = N,O,F,Cl or Br. These vary with bond order, n(B-X), as follows:

$$E(B\text{-}X) = A[n(B\text{-}X)]^m$$

where A depends on X, and m varies between 0.20 and 0.65. It was possible to estimate enthalpies of atomisation and standard heats of formation of gaseous mixed boranes, e.g. $BR^1R^2R^3$ (containing H, alkyls and/or halogens) which have not been measured experimentally.[108]

A detailed study of the infrared and Raman spectra of cyclopropyldimethylborane shows that only one conformer is present in the gaseous, liquid and solid states. This is the 'bisected' structure of C_s symmetry. A complete vibrational assignment was proposed, except for the BC_2 and two methyl torsional modes.[109]

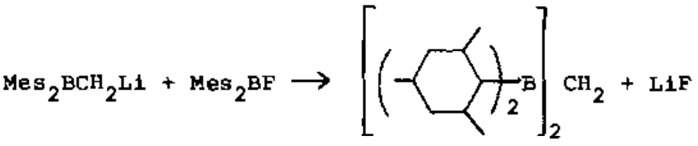
Exchange reactions between triorganylboranes, R_3B, where R = Me, Et, nPr, iPr, nBu, iBu, sBu, tBu, C_6H_{11} or Ph, and borane, BH_3, in THF or dimethylsulphide were followed by ^{11}B n.m.r. A number of mixed species were identified. The reactivity of the organyl boranes RBH_2 and R_2BH depends on both steric and electronic effects, and on the donor strength of the solvent.[110]

Boron 1s binding energies have been determined by X-ray photoelectron spectroscopy for the tetraphenylborates $MBPh_4$, where M = Na, K, Rb, Cs or NH_4.[111]

^{13}C n.m.r. parameters for phenylethynyl borane, e.g. $B(C{\equiv}CPh)_3$ and $B(C{\equiv}CPh)_4^-$, provide some evidence for $B{-}C{\equiv}$ (p-p)π-bonding. It is, however, weak compared with the $C{-}C{\equiv}$ (p-p)π-bonding in phenylethynyl carbocations.[112]

Tris(1-norbornyl)-, tris(2-norbornyl)- and tris(7-norbornyl)-borane can be prepared from $BF_3.OEt_2$ and 1-norbornyl-lithium, 2- or 7-norbornylmagnesium halides respectively. The products were characterised by i.r., ^{13}C and ^{11}B n.m.r. spectra.[113]

Bis(dimesitylboryl)methane can be prepared according to equation



...(4)

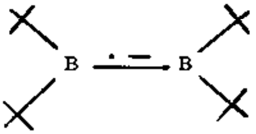
(4), where Mes = mesityl. The solid is air-stable, but solutions are rapidly oxidised.[114]

If isonitriles are treated successively with organolithium

$$tBuNC + RLi \rightarrow tBuN{=}C(R)Li \xrightarrow[-LiX]{+XBR^1R^2} tBuN{=}C(R)BR^1R^2 \qquad ...(5)$$

compounds and aminohaloboranes, the products are monomeric carbiminoboranes, equation (5), where $R = nBu$, $R^1 = NMe_2$, $R^2 = NMe_2$, Me or Ph, X = halide.[115]

The reaction of $(Me_3Si)_3CLi$ with BF_3 in Et_2O/THF produces $(Me_3Si)_3CB(F)[O(CH_2)_4C(SiMe_3)_3]$. This, on oxidation of phenyllithium, forms the phenyl compound $(Me_3Si)_3CB(Ph)[O(CH_2)_4C(SiMe_3)_3]$. In the latter the three bonds to boron are coplanar, and lie approximately perpendicular to the plane of the phenyl group.[116]



(13)

The radical anion from tetra-*t*-butyldiborane (4), (13), is generated from di-*t*-butylchloro- or di-*t*-butylbromoborane by reduction with Na/K alloy. It was identified by e.s.r.[117] It can also be made by treating the parent diborane(4) with Na/K alloy. The reductive dimerisation of di-*t*-butyldichlorodiborane (4) produces tBu_4B_4, which was identified by ^{11}B n.m.r.[118]

The silylborates $Li\{R_{3-n}B[SiMe_3]_{n+1}\}$ are prepared by the reaction of $LiSiMe_3$ and methoxyboranes $R_{3-n}B(OCH_3)_n$ (where n = 1-3). Two isomers were found for $LiB(SiMe_3)_4$, but only one could be isolated. Trimethylsilylboranes are stronger Lewis acids than the corresponding t-butylboranes.[119]

3.1.6 Compounds containing B-N or B-P Bonds.

Microwave spectra of 8 isotopic species of boranediamine, $BH(NH_2)_2$, can be interpreted in terms of planar, C_{2v} geometry. The following bond lengths were obtained: B-H, 1.193±0.001Å; B-N, 1.418±0.001Å; $N\text{-}H_{cis}$, 1.005±0.005Å; $N\text{-}H_{trans}$, 1.000±0.003Å (*cis* and *trans* relative to the B-bonded hydrogen), as well as the bond angles: NBN, 122.0±0.3°; BNH_{cis}, 121.1±0.1°; BNH_{trans} 123.7±0.6°.[120]

F.T.I.R. and Raman spectra were obtained for $^{11}BH(NH_2)_2$, $^{10}BH(NH_2)_2$, $^{11}BH(ND_2)_2$ and $^{10}BH(ND_2)_2$; these gave detailed vibrational assignments for the ^{11}B, and partial ones for the ^{10}B species. A normal coordinate analysis yielded a B-N stretching force constant of 6.0 mdyn.$Å^{-1}$, consistent with partial B-N double bonding.[121]

The nuclear quadrupole double-resonance spectrum of $H_3B.NH_3$ has been investigated at room temperature. The ^{14}N line, the ^{11}B line and most of the ^{10}B lines were found.[122]

The kinetics and mechanism of the hypochlorite oxidation of morpholine-borane, $O(CH_2)_4NH.BH_3$, have been studied.[123]

Ab initio m.o. calculations have been performed on the isolated molecule and on the dimer of the boron analogue of glycine, $NH_3.BH_2CO_2H$. The optimum geometry, dipole moments, orbital energies, electronic configuration, charge distribution and electrostatic molecular potentials were reported. These differ in many ways from the values for glycine itself.[124] pK_a values were determined for amine.BH_2CO_2H, where amine = NH_3 (8.33), $MeNH_2$ (8.23), Me_2NH (8.14) or Me_3N (8.38). These compounds, unlike their glycine analogues, do not chelate Zn^{2+} or Cu^{2+}. Coordination only occurs via the carboxylato group.[125]

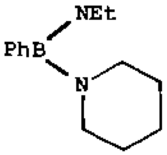
The ^{19}F chemical shifts of mixed boron trihalide adducts of tertiary amines, $D.BF_{3-n}X_n$, where X = Cl, Br, I; n = 0, 1 or 2; D = NMe_3, NEt_3, NEt^iPr_2, NMeEtPh, quinuclidine, 4-methylpyridine etc., are markedly dependent on the steric effects of the amine substituents. The base strength of the amine has little effect on the adduct ^{19}F chemical shifts, but it does influence the rate of halogen redistribution. The ^{11}B and ^{13}C chemical shifts and $^{11}B-^{19}F$ coupling constants were also discussed.[126]

Ab initio m.o. calculations have been used to study binding preferences of CN^- for BX_3 and AlX_3 (where X = H, CH_3, Cl or F). Electronegative X groups favour binding via the nitrogen. The calculated transition state for the unimolecular rearrangement $CNBH_3^- \rightarrow NCBH_3^-$ is similar to that for $CNCH_3 \rightarrow NCCH_3$, but with a smaller barrier to interconversion.[127]

Borane adducts of 3-fluoro-, 3- and 4-chloro, 3- and 4-bromo- and 3- and 4-cyanopyridine have been prepared. They were characterised by i.r., ^1H and ^{11}B n.m.r. spectra, chemical analyses and differential scanning calorimetry.[128]

The crystal structure of $B(NMe_2)_3$ has been determined at -116°C. The crystals are monoclinic, space group $P2_1/n$. The average B-N bond distance is 1.439Å, which fits in well with B-N distances in other aminoboranes, although there is less π-bonding than when some of the amino-groups are replaced by e.g. chlorines. The BN_3 skeleton is accurately planar.[129]

The preparations and ^1H and ^{13}C n.m.r. properties of alkylamino-and dialkylaminopiperidinoboranes, such as (<u>14</u>), have been reported and discussed.[130]



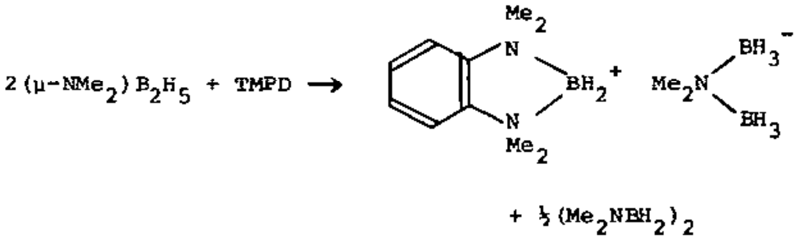
(<u>14</u>)

R_2BX (where R = Et, OMe or NMe_2; X = Cl or Br) react with $K[(OC)_5CrCN]$ according to equation (6) to form isocyanoborane

$$K[(OC)_5CrCN] + R_2BX \xrightarrow[-78^{\circ}C]{CH_2Cl_2} (OC)_5CrCNBR_2 + KX \qquad \ldots(6)$$

complexes. These were characterised by i.r., n.m.r. and mass spectra.[131]

<u>N</u>,<u>N</u>,<u>N</u>',<u>N</u>'-Tetramethyl-<u>o</u>-phenylenediamine (TMPD) reacts with μ-(dimethylamino)diborane(6), inducing an unsymmetrical cleavage



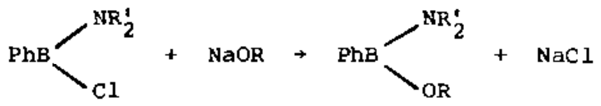
...(7)

reaction (equation 7). The product was characterised by ^{11}B n.m.r.[132] The reactions of TMPD with B_4H_{10} or $THF.B_3H_7$ were also

$$TMPD + B_4H_{10} \xrightarrow{toluene} [(TMPD)BH_2]B_3H_8 \qquad \ldots(8)$$

investigated, e.g. equation (8), and mechanisms and reaction pathways were suggested.[133]

The preparation of a series of alkoxydialkylaminophenylboranes has been reported, e.g. equation (9), where R = Me; R' = Me, ^iPr, nBu etc; R = R' = Et; R = ^iPr, R' = Et. Their ^1H and ^{13}C n.m.r. spectra are consistent with hindered rotation about the B-N



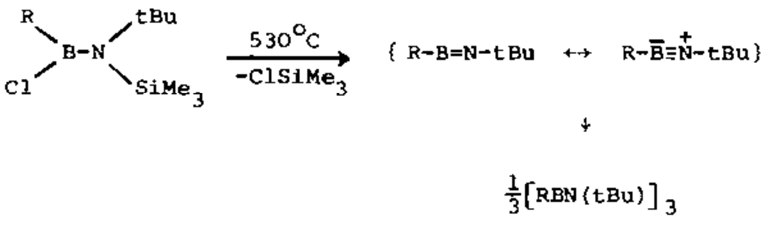
$$PhB(NR'_2)Cl + NaOR \rightarrow PhB(NR'_2)OR + NaCl \qquad ...(9)$$

bond.[134] Chlorodialkylaminophenylboranes, $PhB(NR_2)Cl$, have been prepared from $PhBCl_2$ and R_2NH, where R = Me, Et, nPr, iPr, sBu etc.[135] Variable-temperature ^{13}C n.m.r. spectra of dialkylaminofluorophenylboranes give values for $\Delta G^{\ddagger}$ for the rotational barrier about the B-N bond, e.g. for $Ph(F)B-NMe_2$ it is 19.1 kcal. mol^{-1}.[136]

Bromide abstraction from $(tmp)B(NR_2)Br$, where tmp = 2,2,6,6-tetramethylpiperidino; R = Me or Et, or $(tmp)B(R)Br$, where R = Me or Ph, in dichloromethane solutions produces tetrabromoaluminates of the dico-ordinate cations $[(tmp)=B=NR_2]^+$ or $[(tmp)=B-R]^+$. The cations were characterised by n.m.r. ($^1H, ^{11}B, ^{13}C$) and i.r. spectra, and electrical conductivity. The crystal structure of $[(tmp)=B=NMe_2]^+AlBr_4^-$ shows that the C_2NBNC_2 skeleton is allene-like, with an almost linear NBN unit (bond angle 176°). The BN bond distances are consistent with a fairly high bond order. The thermal stability of the diamido is greater than that of the monoamido compounds.[137]

Bis(di-isopropylamino)chloroborane and $AlCl_3$ react under rigorously anhydrous conditions to produce the ionic compound $[(iPr)_2N=B=N(iPr)_2]^+AlCl_4^-$. This gave i.r. bands in the range 1830-1900 cm^{-1} due to the N=B=N unit.[138]

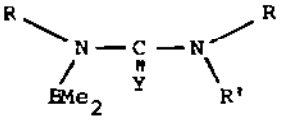
The boron imides, RB=N(tBu), where R = Et, Pr or Bu, storable at -80°C, are formed at 530°C by the elimination of $ClSiMe_3$ from the aminoboranes $Cl-(R)B-[N(tBu)SiMe_3]$. ν BN is seen ca. 2010 cm^{-1}, showing that there is considerable BN triple bond character. The imides trimerise to borazines, leading to an overall reaction (10).[139]



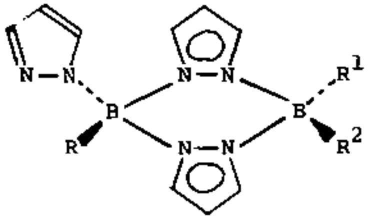
$$R(Cl)B-N(tBu)SiMe_3 \xrightarrow[-ClSiMe_3]{530^\circ C} \{R-B=N-tBu \leftrightarrow R-\bar{B}\equiv\overset{+}{N}-tBu\} \rightarrow \tfrac{1}{3}[RBN(tBu)]_3 \qquad ...(10)$$

$LiBH_4$ reacts with $(Me_3Si)_2NB(Cl)N(H)SiMe_3$ to produce $(Me_3Si)_2NBH_2$, $[Me_3SiN(H)BH_2]_3$ and $[Me_3SiNBH]_3$. A number of related reactions were also reported.[140] Reductions of ((organosilyl)amino)(alkylamino)boranes, e.g. $sBu_2NB(Cl)N(SiMe_3)_2$, by various hydrides were studied to clarify the reaction pathway for reactions between $LiBH_4$ and chlorobis(amino)boranes containing an (organosilyl)amino group.[141]

New syntheses of open-chain and cyclic N-borylureas and -thioureas have been reported. Thus, N,N,N'-triorganylureas or -thioureas react with bromodimethylborane to give (15), where R= Me or iPr; Y = O; R' = Me, iPr, Et; R = Me, Y = S, R' = Et.



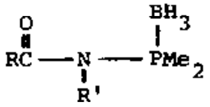
(15)



(16)

N.m.r. spectra have been reported for pyrazole derivatives of boron, e.g. (16), where R,R^1,R^2 = Me, Ph, CF_3, H etc.[143]

Vibrational assignments and a normal coordinate analysis have been described for $HPF_2.BH_3$, on the basis of Raman (liquid, solid) and i.r. (gaseous, solid) spectra of five isotopic species. The force field is very similar to that of $F_3P.BH_3$, even though the two compounds are very different in stability.[144] Mean amplitudes of vibration have been calculated from literature spectroscopic data for $X_3P.BY_3$, where X = H, D or F; Y = H, D, F, Cl, Br or I. The potential barriers to internal rotation were also calculated.[145]



(17)

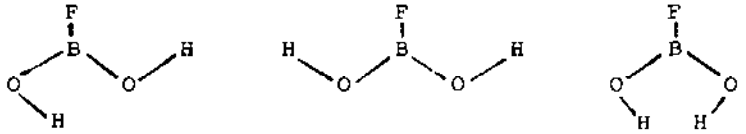
$Me_2(BH_3)PCl$ reacts with the lithium salts of acetamide, N-methylacetamide or N-methylformamide to produce (17), where R = H, R' = Me; R = Me, R' = H; R=R' = Me.[146]

3.1.7 Compounds containing B-O or B-S Bonds.

Rate constants have been measured for the reactions of gas-phase boron atoms with H_2O, H_2O_2, alcohols and ethers. Products included BO, BO_2, BOH etc.[147]

Calculated values have been tabulated for the bond dissociation energies of the diatomic molecules XY, where X = B, Al, Ga, In or Tl; Y = O, S, Se, Te, Po or F, Cl, Br, I, At. Those for XPo, XAt, GaS and GaSe have been estimated for the first time.[148]

Electron diffraction data for gas-phase $CsBO_2$ could not be used to decide unambiguously between a linear and an angular model for the molecular structure. The B-O distance was 1.266(6)Å.[149]



(18)

A theoretical study of the stabilities of the planar conformers of $BF(OH)_2$, (18 a-c), suggests that (b) is not formed from BF_3 and excess H_2O. The forms (a) and (b) are almost equal in energy, but there is a high barrier to their interconversion.[150]

The He(I) photoelectron spectrum of the 1:1 complex $Me_2O.BF_3$ has been obtained. The peaks were assigned with the help of *ab initio* and semi-empirical m.o. calculations. The results indicated a net transfer of 0.09 electron from Me_2O to BF_3.[151]

The hydrated sodium borate, $Na_2[BO_2(OH)]$, is orthorhombic (space group Pnma). Dense sheets of Na-O polyhedra are linked by isolated $BO_2(OH)$ triangles and by hydrogen bonds.[152]

The suggested disproportionation reaction of dimethoxyborane, equation (11), was studied. Careful investigation was unable to

$$6HB(OMe)_2 \rightleftarrows B_2H_6 + 4B(OMe)_3 \qquad \ldots(11)$$

detect B_2H_6 in the gas-phase, although it is present in the liquid. Optimised conditions for the production of $HB(OMe)_2$ were established.[153]

The compound $B(OTeF_5)_3$ forms hexagonal crystals, space group $P6_3/m$. The molecule has D_{3h} symmetry, and the boron environment is strictly trigonal planar. The average B-O bond length is 1.358(6)Å.[154]

Bis(oxalato)- and bis(malonato)borates have been prepared in heterogeneous reactions from boric acid, the dicarboxylic acid and dicarboxylate salts, by refluxing in benzene. They were characterised by i.r., Raman and ^{11}B n.m.r. spectra; the vibrational spectrum of $B(C_2O_4)_2^-$ was discussed in detail.[155]

X-ray diffraction showed that $B(O_2CMe)(acac)$ forms monoclinic crystals, space group $P2_1/c$. The discrete molecular units have symmetry close to C_{2v}, with four-coordinate (pseudo-tetrahedral) boron, and unidentate acetato ligands.[156]

The quadrupole coupling constant C_Q and the electric field asymmetry parameter η were determined directly from the dispersive mode n.m.r. line shape of the ^{11}B resonance in borate glass.[157]

Ammonium halides salt out orthoboric acid from aqueous solutions, due to hydrogen-bond formation.[158] KCl, on the other hand, salts-in orthoboric acid, while other alkali metal halides salt it out, in the order: LiI>NaI>KI>LiBr>NaBr>KBr>LiCl>NaCl.[159]

Solubility diagrams have been constructed for the systems $X-EtCOOH-H_2O$, where $X = H_3BO_3$, CaB_4O_7 or MgB_6H_{10}. All measurements were carried out at 50°C.[160]

H_3BO_3 and dibutylamine interact in water at 25°C to give $[Bu_2NH_2]^+[H_4B_3O_7]^-.2H_2O$, in which the anion is a resonance-stabilised cyclic trimetaborate.[161] A very similar process occurs for H_3BO_3 and diethylenetetramine.[162]

The fine structure of the ^{11}B n.q.r. spectrum of datolite, $HCaBSiO_5$, is due to dipole-dipole interactions between ^{11}B and ^1H nuclei. The results confirmed the proton positions determined by ^1H n.m.r.[163]

A new form of silver(I) orthoborate has been prepared: $AgBO_3$-II. This forms rhombohedral crystals (space group $R\bar{3}c$), and is a stacking variant of the previously-known $AgBO_3$-I.[164] Ni_2NbBO_6 is orthorhombic (space group Pnma), and contains NiO_6 and NbO_6 octahedra linked by corner-shared BO_4 tetrahedra. It is isostructural with Fe_3BO_6.[165]

Three types of compound have been found and described in the Ln_2O_3-WO_3-B_2O_3 ternary systems, where Ln = La-Nd, Sm or Dy. These are: $Ln(BO_2)WO_4$ (Ln = La-Nd); $Ln_2B_2WO_9$ (Ln = Pr-Dy); and $Ln_4B_2WO_{12}$ (Ln = La-Ho).[166] Phase equilibria have been studied in the B_2O_3-Ho_2O_3-NiO system at 1000°C. Three solid phases were characterised: $Ni(BO_2)_2$, $HoNi(BO_2)_5$ and $Ni_3(BO_3)_2$.[167]

Investigation of the B_2O_3-CuO-Li_2O ternary system revealed the formation of $2Li_2O.CuO.B_2O_3$; $Li_2O.2CuO.B_2O_3$ and $Li_2O.CuO.2B_2O_3$.[168] Palladium metaborate, PdB_2O_4, is tetragonal, space group $I\bar{4}2d$, and isotypical with the Cu(II) analogue.[169]

$Cu_{15}[(B_2O_5)_2(BO_3)_6O_2]$,i.e. $3CuO.B_2O_3$, crystallises in the space group $P\bar{1}$. It possesses a layer structure, containing almost planar B_2O_5 groups, planar, isolated BO_3 groups, isolated O^{2-} ions, and four-coordinate (square planar) Cu^{2+}.[170]

$CaK_2[B_4O_5(OH)_4].8H_2O$ forms orthorhombic crystals, space group $P2_12_12_1$. Each tetraborate ion is hydrogen-bonded to 2 water molecules and another tetraborate within a layer.[171] A structure refinement has been reported for $CaNa[B_5O_7(OH)_4].3H_2O$. The pentaborate ions are linked into chains, and these chains are connected by clusters of Ca-O and Na-O polyhedra.[172]

The new phase $3Na_2O.5B_2O_3.2H_2O$ has been synthesised at 523K under hydrothermal conditions. It is in fact $Na_3(B_5O_9).H_2O$, and crystallises in the space group $Pca2_1$. The polyanion $B_5O_9{}^{3-}$ consists of three tetrahedra and two triangles. The polyanions are linked to give an open B-O framework, with three series of channels, parallel to *a*, *b* and *c* (these contain Na^+ and H_2O).[173]

D.T.A. and i.r. spectra were used to characterise $MgB_6H_{10}.8H_2O$ and $CaB_4O_7.6H_2O$, isolated from the systems H_3BO_3-$M(OOCEt)_2$-H_2O (M = Mg or Ca) at 0°C.[174] The thermal transformations of kaliborite, $KMg_2B_{11}O_{14}(OH)_{14}.2H_2O$, have been studied, and i.r. spectra and X-ray powder diffraction patterns of heated specimens obtained.[175] Similar methods were used to deduce the thermal transformations of preobrazhenskite, $Mg_3[B_{11}O_{15}(OH)_9]$.[176]

A theoretical study of the relative stabilities of the known molecules XBS (X = F or Cl) and their unreported isomers BSX suggests that the latter are potentially stable.[177] *Ab initio* m.o. studies have been reported for the sulphido-borons R-B≡S, where R = H, CH_3, NH_2, OH, F or Cl. The geometries were optimised by the gradient method, using the double-zeta basis set.[178]

The trimethylsilylthioboranes, $(Me_3Si)\text{-}S\text{-}BRR'$, where R = R' = $-NMeCH_2CH_2NMe-$, $-O-C_6H_4-O-$ or $-S-CH_2CH_2-S-$, have been prepared in good yield from $(Me_3Si)SLi$ and XBRR'. They can be distilled under high vacuum without decomposition.[179]

3.1.8 Boron Halides.

Decomposition temperatures in the heterogeneous BCl_3/H_2 system have been determined at various surfaces. The decomposition

$$BCl_3(g) + B(s) \rightarrow 3BCl(ads) \qquad \ldots(12)$$

$$BCl(ads) + \tfrac{1}{2}H_2 \rightarrow B(ads) + HCl(g) \qquad \ldots(13)$$

$$B(ads) \rightarrow B(s) \qquad \ldots(14)$$

involves production of boron, by reactions such as (12)-(14).[180]

MNDO m.o. calculations have been carried out for BCl_3, B_2Cl_4, B_4Cl_4, their molecular cations, and all singly- and doubly-charged ions occurring in their mass-spectra, together with the corresponding neutral fragments.[181]

B_8Cl_8 can be prepared in 88% yield by the thermal decomposition of dilute B_2Cl_4, 20% by weight in CCl_4, at 100°C. The choice of solvent is crucial. Several reactions of B_8Cl_8 were reported. Thus B_8Cl_8 in CCl_4 at 200°C gives BCl_3 and B_9Cl_9; B_8Cl_8 and tBuLi from $B_9(tBu)_9$; and B_8Cl_8 with excess liquid Al_2Me_6 give $Me_nB_9Cl_{9-n}$ (n = 0-4). At 100°C, B_8Cl_8 accepts hydrogen from pentane, liberating pentene.[182]

$B_{10}Cl_{10}^{2-}$ is oxidised by $Pb(OAc)_4$ in the presence of Lewis acids to give a blue-violet radical anion, $B_{10}Cl_{10}^{\dot{-}}$. This is sufficiently stable for its i.r., e.s.r. and electronic spectra to be measured. It is a strong oxidising agent, and the oxidising powers of a series of radical anions are: $B_{10}Cl_{10}^{\dot{-}} > B_9I_9^{\dot{-}} > B_9Br_9^{\dot{-}} > B_9Cl_9^{\dot{-}}$.[183] Evidence was also found for the formation of $B_{10}Cl_{10}^{\dot{-}}$ by the oxidation of $B_{10}Cl_{10}^{2-}$ by $SOCl_2$.[184]

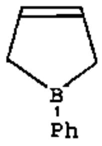
New routes have been found to produce halogenated B_8 and B_9 boron cages. Heating $B_{10}Cl_{10}$ or $B_{11}Cl_{11}$ with hydrogen gives B_9Cl_8H and $B_9Cl_7H_2$ respectively. B_8Br_8 and B_9Br_9 are prepared from B_8Cl_8 and B_9Cl_9 by treatment with $AlBr_3$. At least 6 of the bromine atoms in B_9Br_9 can be replaced by methyl groups (using $SnMe_4$).[185]

Ligand exchange has been studied in the Bu_4NBH_4/Bu_4NBBr_4 system in benzene. The anions BH_3Br^-, $BH_2Br_2^-$ and $BHBr_3^-$ can all be detected at the appropriate molar ratios. BH_3Br^- decomposes at 20°C, the others at 140°C, 160°C respectively. The bromo-anions are more stable than their chloro-analogues.[186] Bu_4NBH_4 reacts with iodine at 20°C in benzene to form $BH_{4-n}I_n^-$ (n = 1-4) at the appropriate molar ratios. The degrees of dissociation of these are in the order: $BI_4^- < BHI_3^- < BH_2I_2^- << BH_3I^-$. Chloro-alkanes react with Bu_4NBH_4 to produce the analogous chloro-anions.[187]

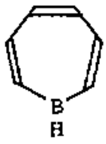
The thermal decomposition of B_2I_4 in the range 100-400°C, with removal of BI_3, yields a mixture of B_9I_9 (85%) and B_8I_8 (15%).[188]

3.1.9 Boron-containing Heterocycles.

(1,3-Diene)magnesium addition compounds and boron halides react to form 3-borolenes in good yield. Thus $Mg(C_4H_6).2THF$ and $PhBCl_2$ give (19).[189]



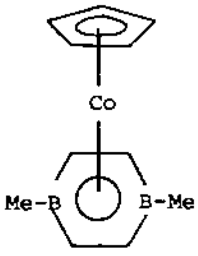
(19)



(20)

Ab initio m.o. calculations on the unknown borepin, (20), using STO-3G and 4-31G basis sets give an optimum planar structure, which would be a weakly conjugated system.[190]

Semiempirical INDO m.o. calculations have been carried out on (21), and its He(I) photo-electron spectrum has been obtained. The dibora-ligand is attached to the Co *via* the metal $3d_{xz}$ orbital.[191]



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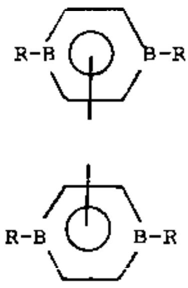

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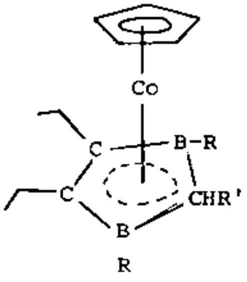
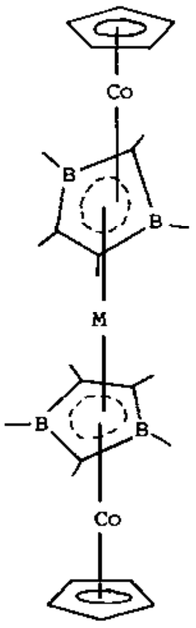


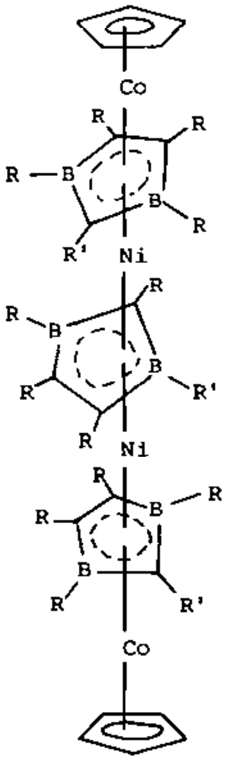
(23)

The novel 6π-electron anion in $Na_2[FcB\{C_2H_2\}_2BFc]$, where HFe = $Fe(C_5H_5)_2$, is formed by the reduction of the 1,4-dibora-2,5-cyclohexadiene $FcB[CH{=}CH]_2BFc$. Seventeen transition metal complexes of Co, Rh, Ni or Pt with $RB[C_2H_2]_2BR$ have been prepared and characterised, e.g. (22), where R = OMe, Me, Ph or Fe.[192]

(23), where R = Et, R' = Me or R = Me, R' =H, are prepared from Δ^4-1,3-diborolenes and $CpCo(CO)_2$. The structure was determined by X-ray diffraction.[193]



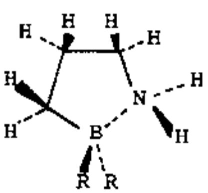
(24)



(25)

Further extensions to the chemistry of sandwich complexes have occurred. Thus the μ,η^5-1,3-diborolenyl tetradecker compounds (24), where M = Ni, Zn, Fe or Co, have been made and characterised, showing that 1,3-diborolene can produce tetradecker sandwich compounds with from 42 to 46 valence electrons.[194] A pentadecker compound has also been made for the first time, i.e. (25), where R = Et, R' = Me. This was characterised by n.m.r. and X-ray diffraction.[195]

I.r. bands due to dipropyl(γ-aminopropyl)borane can be assigned and rationalised in terms of the structure (26), where R = propyl.[196]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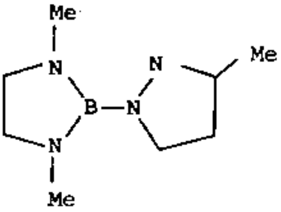
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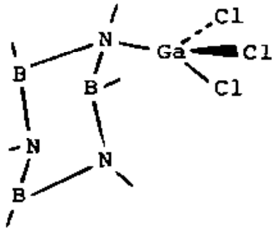
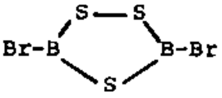

(28)

The preparation and chemical reactions of monomeric pyrazol-1-ylboranes, such as (27), have been reported. The best preparation is by the condensation of 1,3-dimethyl-1,3,2-diazaboracyclopentane with pyrazoles.[197]

Hexamethylborazine forms a 1:1 adduct with $GaCl_3$; this is isostructural with the $AlBr_3$ analogue. The BN heterocycle becomes non-planar, with approximate C_s symmetry, (28). The adduct is fluxional at room temperature.[198]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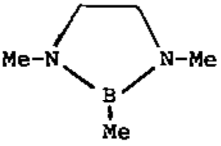
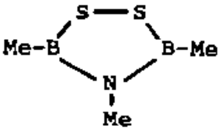

(30)

Substituent exchange reactions between (29) and (30) occur *via* adduct formation, but definite compounds could not be isolated unless the thia-compound is pure.[199]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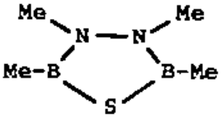
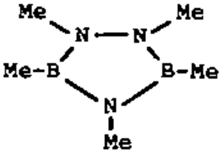
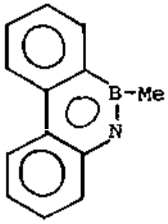
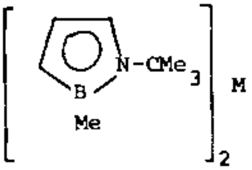

(32)


(33)

The formation of bromo-derivatives from the methylated compounds (31) and (32) follows the endocyclic reaction mechanism.[200] Rapid exchange of the ring hydrazino and the ring disulphide group occurs in the reactions of (32) or (33) with (29). The "bridge exchange" is accompanied by a much slower boryl group exchange, detected by ^{10}B labelling.[201]



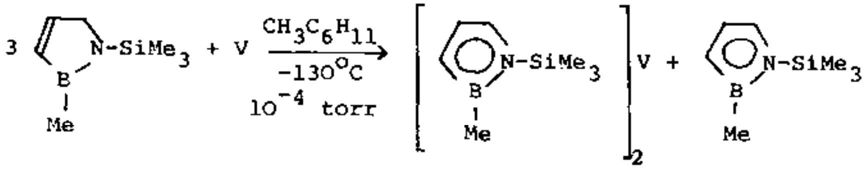
(34)



(35)

A study has been made of the π-donor complexes of heteroaromatic B-N compounds (hexamethylborazine or (34)) and iodine. The results suggest that the complexation occurs *via* the π-donor interaction rather than the n-donor interaction.[202]

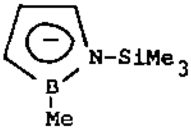
The complexes (35), where M = Fe or Co, are prepared by the reaction of 1-t-butyl-2-methyl-1,2-azaborolinyl-lithium with MBr_2. $TiBr_4$ gave an analogous titanium dibromide complex. The metal



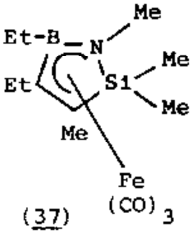
...(15)

atom reaction (15) was also described.[203] A separate report was also given of exactly analogous reactions with V replaced by Fe or Co. In these cases, the sandwich complexes could each be separated (by fractional sublimation) into staggered and eclipsed conformers. These were identified by X-ray diffraction.[204]

A different route to these sandwich complexes consists of reacting lithium 2,2,6,6-tetramethylpiperidide with 2-methyl-1-(trimethylsilyl)-Δ^3-1,2-azaboroline to produce (36). This reacts with MBr_2 (M = Fe or Co) in THF at -78°C to give the final products.[205]

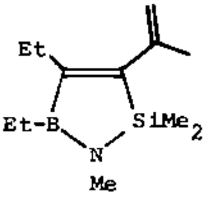


(36)

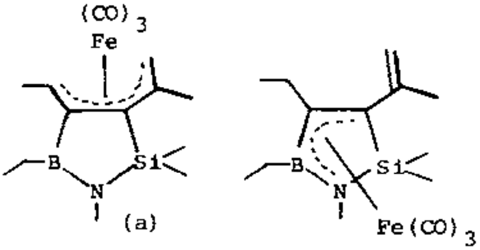


(37)

4,5-Diethyl-1,2,2,3-tetramethyl-Δ^3-1,2,5-azasilaboroline acts as a four-electron donor. Thus, with $Fe_2(CO)_9$ it forms (37), whose structure was elucidated by X-ray diffraction.[206]

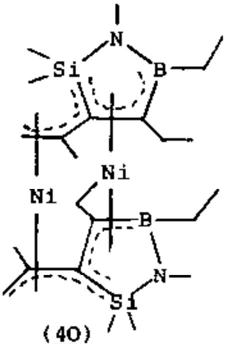


(38)



(39) (b)

Hexa-alkyl-Δ^3-1,2,5-azasilaborolines can form π-complexes in different ways, e.g. (38) reacts with $Fe_2(CO)_9$ to give a mixture of (39a) and (39b). Ttt-1,5,9-cyclododecatrienenickel, on the other hand, produces (40).[207]



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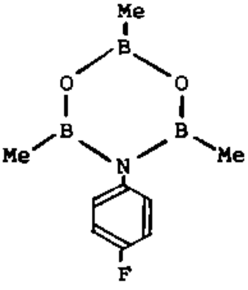
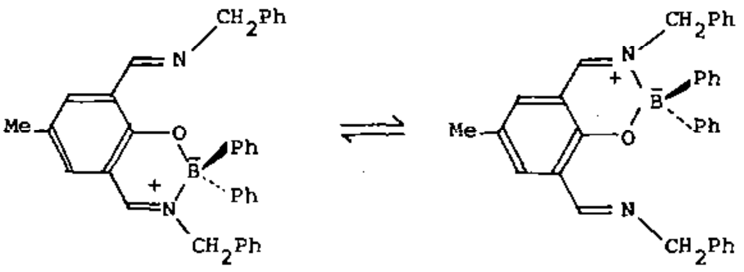


(41)

(41) is prepared from p-fluorophenyl-N-sulphinylamine and 3,5-dimethyl-1,2,4-trithia-3,5-diborolane (together with several other products). It forms orthorhombic crystals (space group Pnma). The p-fluorophenyl group lies at right angles to the

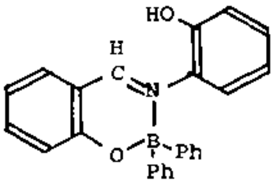
heterocyclic ring plane.[208]

Racemisation of dissymmetric diarylboron salicylideneiminato chelates involves B-N bond dissociation to give planar three-coordinate boron; it does not take place *via* a planar, four-coordinate boron intermediate, as previously suggested. The evidence was based on studies of equilibria such as (16).[209]



...(16)

The crystal structure of (42), as its 1:1 adduct with methanol, confirms the presence of the 6-membered heterocyclic ring as shown, and not the alternative structure, (43).[210]



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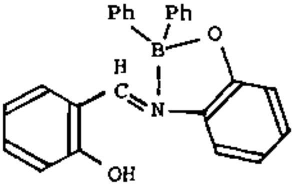
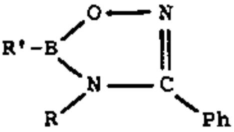


(43)

The preparations and some properties have been reported for some new 2,4-diphenyl-2-diethylamino-4-phenyl-1,3,5,2-oxadiazaboroles, (44), where R' = Ph, R = H, Me, Et, nPr or nBu; R'=NEt$_2$, R = H or nPr.[211]



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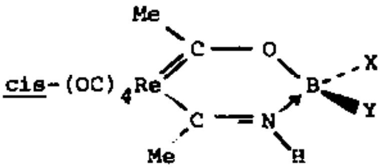
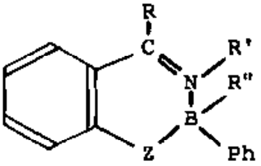


(45)

The complexes (<u>45</u>) have been prepared, where X = Y = Cl, Br or I; X = Cl, Y = Ph, from the rhena-acetylacetonimine complex *via* NaH reduction, and treatment with excess BX_2Y in CH_2Cl_2. I.r. and ^1H n.m.r. data were presented.[212]

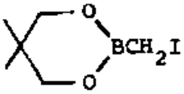
The chelates (<u>46</u>), where R = H or Me; R',R" = Me, Ph, OH or NHPh; Z = O or NH, are prepared by reacting the appropriate carbonyl component with a primary amine, or hydrazine with an organoboric acid.[213] Mass-spectral data were also given for these compounds.[214]



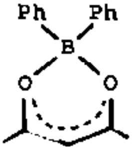
(<u>46</u>)

^{17}O chemical shifts have been measured for various cyclic organo-boron-oxygen compounds (borolanes, borinanes, 9-borabicyclo[3.3.1]nonanes, boroxins). These show that the screening of the oxygen depends upon the B-O (p-p)π-bonds.[215]

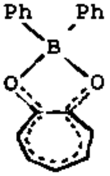
The key step in a facile new preparation of iodomethaneboronic esters, e.g. (<u>47</u>), is a tin hydride reduction of dichloromethaneboronic esters.[216]



(<u>47</u>)

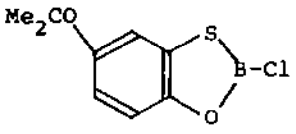


(<u>48</u>)

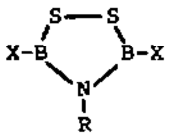


(<u>49</u>)

Crystal and molecular structure determinations have been carried out for (acetylacetonato)diphenylboron, (<u>48</u>), and (tropolonato)-diphenylboron, (<u>49</u>). Each contains discrete molecules with approximately tetrahedral boron. The acetylacetonato complex forms two crystalline modifications.[217]



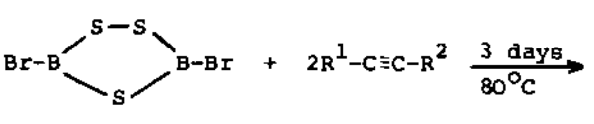
(50)



(51)

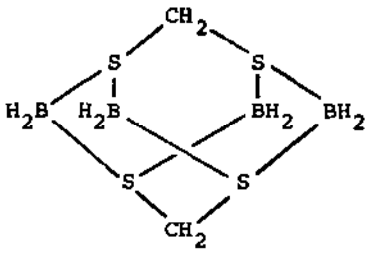
Reaction of (50) with phenol, thiophenol etc. leads to substitution at the boron atom.[218] Trimethylsilyl- and pentafluorophenyl-N-sulphinylamine react with 3,5-dihalogeno-1,2,4-trithia-3,5-diborolanes to give (51), where X = Cl, Br; R = $SiMe_3$, C_6F_5. Several related species were also described.[219]

Numerous reactions of 3,5-dibromo-1,2,4-trithia-3,5-diborolane have been described, producing a wide range of boron containing heterocycles, e.g. equation (17), where R^1 = H, R^2 = Ph, nBu, nPr, CH_2Br; $R^1 = R^2$ = Ph, Et; $R^1 = CH_3$, R^2 = nPr etc.[220]



...(17)

Hydroboration of CS_2 by BH_3.THF produces a new cage-compound, $[CH_2(SBH_2)_2]_2$, with an adamantane-like $C_2B_4S_4$ skeleton, (52). This was characterised by ^{11}B n.m.r., and mass spectra, and the structure was determined by X-ray diffraction. The mean B-S bond distance is close to 1.93Å.[221]



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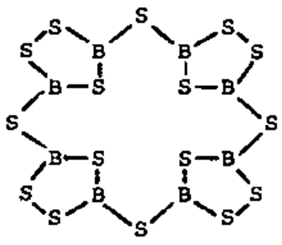


(53)

The recently-prepared B_8S_{16}, (53), is formally similar to the porphine nucleus, although not isoelectronic. Hückel m.o. calculations show that the HOMO-LUMO gap (π-π^* transition energy) in B_8S_{16} is large compared to that in porphine. The extra electrons in B_8S_{16} reside in orbitals which are more antibonding than bonding, hence there is a smaller π-delocalisation energy than in porphine. B_8S_{16} is not likely to be a good ligand for either simple cations or transition metals.[222]

3.1.10 Metal Borides.

Metal boride systems which catalyse hydrodesulphurisation and coal liquefaction are produced by reactions of borane anions with transition metal salts at 400°C and 2000 psi of H_2. $B_5H_8^-$ gives the most active systems, especially with Co and Ni. The products were not fully characterised, but residual hydrogen was present.[223]

$(Mn_{1-x}Cr_x)_3B_4$, where $0 \leqslant x \leqslant 1$, and $(Mn_{1-x}Mo_x)_3B_4$, where $(0 \leqslant x \leqslant 0.8)$, can be prepared from the elements. Their magnetic properties were examined; all possess the Ta_3B_4-type of structure.[224]

The new ternary metal borides EuM_4B_4, where M = Os or Ir, have been prepared from the elements. They crystallise with the $NdCo_4B_4$ structure type. Their magnetic properties were examined in the temperature range 1.8K to 800K, as were those of the solid solutions ROs_4B_4-RIr_4B_4 (R = Ce, Pr, Sm).[225]

$LuRh_4B_4$ forms orthorhombic crystals, space group Ccca. The boron atoms are present as pairs, with a B-B distance of 1.4Å. The heavy lanthanides Ho, Er, Tm, Yb form isotypic compounds.[226]

3.2 ALUMINIUM

3.2.1 Aluminium Hydrides.

SCF-MO calculations have been performed on the reactants and product of the model reaction (18), on a symmetric π-complex

$$H_2AlH^* + H_2C{=}CH_2 \rightarrow H_2AlCH_2CH_2H^* \qquad \ldots(18)$$

formed from the reactants, and on the system at various points along the reaction path. The best description of the reaction involves concerted bond making/breaking via a four-centre (Al, H*, C, C) transition state. A symmetric π-complex is a possible intermediate in the reaction.[227]

^{60}Co γ-irradiation of $(NBu_4)(AlH_4)$ at 77K produces two species, identified by e.s.r. as $\cdot AlH_3^-$ and a hydroxylated impurity anion. The results confirm that the former has a pyramidal structure, and that the Al 3s population is similar to that for Si in the isoelectronic $\cdot SiH_3$.[228]

The crystal structure of $(Cp_2YCl)_2AlH_3.Et_2O$ shows that it is polymeric, made up of $Cp_2Y(\mu-Cl)_2YCp_2$ fragments with aluminium hydride monoetherate units linked with each other _via_ Y-H-Al bridges. The aluminium coordination is trigonal bipyramidal.[229]

The soluble calcium alkoxyalanates, $Ca[AlH_{4-n}(OR)_n]_2$, where n = 1-3, R = iPr, iBu, tBu, $i-C_5H_{11}$, C_6H_{11}, $CH_3OCH_2CH_2$, are prepared by partial alcoholysis of $Ca(AlH_4)_2$ in toluene. X-ray powder diffraction and i.r. spectra (νAl-H) show that these are generally individual molecular species.[230] Other simple syntheses of calcium alkoxyalanates involve $NaAlH_4$, $CaCl_2$ and the appropriate alcohol.[231]

The heat capacity of $NaAlH_4$ has been measured in the temperature range 11-335K. These gave ΔH_f^o ($NaAlH_4$, cryst.,0) = -99.1 kJ mol^{-1}, ΔG_f^o($NaAlH_4$, cryst., 298.15) = -38.0 kJ mol^{-1}. Values of the free energy of decomposition, equation (19), for the

$$MAlH_4 \rightarrow MH + Al + \tfrac{3}{2}H_2 \qquad \ldots(19)$$

crystalline compounds, at 298.15K, are (ΔG_d^o) are 2.1 kJ mol^{-1} (M = Na), -22.3 kJ mol^{-1} (M = Li).[232] Heat capacity measurements (12-320K) were also reported for $RbAlH_4$.[233]

Geometry-optimised 3-21G _ab initio_ m.o. calculations on $[R_3Al{-}{-}{-}H{-}{-}{-}AlR_3]^-$, where R = H or Me, show that the lowest energy is associated with Al---H---Al being linear. Rotational barriers and bending energies were calculated to be small. The optimum structure for $[H_3Al{-}{-}{-}Cl{-}{-}{-}AlH_3]^-$ was, however, bent.[234]

Exchange of hydrogen with isopropoxy groups takes place in reactions of MgH_2 with $Al(O-i-Pr)_3$ in THF. A variety of mixed

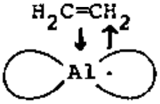
$$MgH_2 + 2Al(O\text{-}i\text{-}Pr)_3 \xrightarrow{THF} Mg[Al(O\text{-}i\text{-}Pr)_3H]_2 \qquad \ldots(20)$$

$$Mg[Al(O\text{-}i\text{-}Pr)_3H]_2 \rightarrow i\text{-}PrOMgAl(O\text{-}i\text{-}Pr)_2H_2 + Al(O\text{-}i\text{-}Pr)_3 \qquad \ldots(21)$$

'isopropoxy-hydride' complexes were identified and characterised. Thus a 1:2 mixture of MgH_2 and $Al(O-i-Pr)_3$ reacts according to equation (20). The product has νAl-H at 1800 and 1760cm^{-1}, νAl-O at 675 cm^{-1} and MgO at 430 cm^{-1}. There was some evidence for the further reaction, (21).[235]

3.2.2 Compounds containing Al-C Bonds.

Ab initio m.o. calculations on the ground and first excited states of $AlCH_2$ suggest that the Al-C bond is single, compared to the double B-C bond in BCH_2 and $HBCH_2$, but that the Al-C bond in $HAlCH_2$ is intermediate between single and double. Changing the aluminium substituent electronegativity may be able to impose Al-C bond order changes between 1 and 2.[236]



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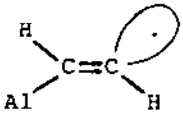


(55)

Complexes between Al and C_2H_4 or C_2H_2 in rare-gas matrices at about 4K have been studied by e.s.r. Al-monoethylene has a π-coordinated structure with donation from a half-filled aluminium p-orbital to the π* m.o. of ethylene, (54). Aluminium and acetylene, on the other hand, interact to give a σ-bonded vinylic compound, (55). There was some evidence for the formation of $Al(C_2H_4)_2$ on the photo-irradiation of $Al(C_2H_4)$.[237]

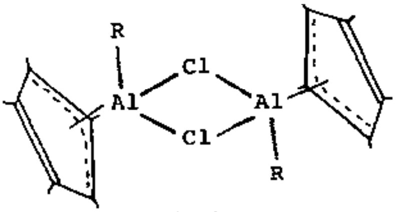
A new synthesis has been reported for $Al(CH_2SiMe_3)_3$ - from $AlBr_3$ and $LiCH_2SiMe_3$ in refluxing hexane. The product reacts further with KH to give $K[Al(CH_2SiMe_3)_3H]$.[238]

^{13}C n.m.r. data on $[M(cyclopropyl)_3]_2$, where M = Al, Ga or In, provide evidence (when M = Al) for a singly-bridged intramolecular bridge-terminal exchange process. For the gallium and indium compounds,the n.m.r. parameters are strongly dependent on temperature, solvent and concentration - this is explicable in terms of a monomer/dimer equilibrium.[239]

The crystal structure of tribenzylaluminium, $Al(CH_2Ph)_3$, shows that there is significant intermolecular interaction between the phenyl carbons and the vacant p-orbital on the aluminium.[240]

The crystal and molecular structures of tetra-*o*-tolyl(bis-(μ-*o*-tolyl)dialuminium reveal the presence of discrete bridged dimers like those in Al_2Ph_6 etc. The only unusual feature is the longer Al-Al distance (2.817Å) than expected. Tri-*o*-tolylaluminium diethyletherate contains pseudo-tetrahedral aluminium, as expected.[241]

The new compounds $[(Me_5C_5)Al(Cl)R]_2$, where R = Me, Et or iBu, have been reported, from the reactions of LiC_5Me_5 or Me_5C_5MgCl with alkylaluminium halides. The compounds with R = Me or iBu were subjected to single crystal X-ray diffraction. The structures reveal unusual η^3-Me_5C_5 coordination to central Al_2Cl_2 units, (<u>56</u>), although for R = iBu steric effects produce distortion towards an η^2-configuration.[242]



(<u>56</u>)

Dimethyl-μ-cyclopentadienylaluminium polymer forms monoclinic crystals, space group $P2_1/n$. There are no significant interactions between the infinite chains in $[Al(\mu\text{-}C_5H_5)Me_2]_n$, and the bonding in the $AlMe_2$ unit is normal.[243]

3.2.3 <u>Compounds containing Al-N Bonds</u>.

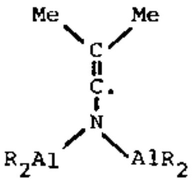
$NaAl(NH_2)_4$ reacts with alcohols or aromatic amines to form sodium alkoxyimidoaluminates, $NaAl(NH)(OR)_2$, where R = CMe_3, $CHMe_2$, CH_2CH_2OMe or Ph, or amido(arylamido)aluminates respectively. Sodium amido(alkylamido)aluminates were made from $NaAl(NH_2)_4$ and $NaAl(NHR)_4$. ^1H n.m.r. data were given for the products.[244]

Urotropine, $C_6H_{12}N_4$, and MMe_3 (M = Al, Ga, In or Tl) give stable, monomeric 1:1, 1:2 or 1:3 adducts, but no 1:4 adducts. The vibrational spectra of all of the compounds were reported and partly assigned. These clearly show the symmetry changes: $C_{3v}(1{:}1) \rightarrow C_{2v}(1{:}2) \rightarrow C_{3v}(1{:}3)$. Crystal structure determinations of $C_6H_{12}N_4.nGaMe_3$ (n = 1,2) agreed with the vibrational data.[245]

$[Alpy_4Cl_2][AlCl_4]$ forms orthorhombic crystals, space group $Pna2_1$; the cation has <u>trans</u>-geometry, with Al-N 2.070(4)Å and Al-Cl 2.279(3)Å. $Alpy_3Cl_3$ is monoclinic, space group $P2_1/c$. The $AlCl_3N_3$ unit has <u>mer</u>-geometry; the Al-N <u>trans</u> to Cl (2.076(2)Å) is significantly longer than those <u>trans</u> to each other (2.072(2)Å.[246]

It has been possible to differentiate, using i.r., between the isomers $Cl_3Al\text{-}N(Me)\text{-}C{\equiv}O$ and $Cl_3Al\text{-}O\text{-}C{=}NMe$. The former ultimately decomposes to N-trimethylisocyanuric acid.[247]

It was possible to identify by e.s.r. the organoaluminium radical (57, where R = iso-butyl). There was some evidence for the involvement of the nitrogen atomic orbitals in the delocalised spin density at the aluminium.[248]



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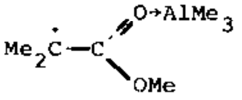

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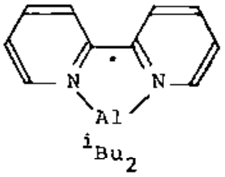


(59)

E.s.r spectra have been reported for the radicals $Me_2CCN.AlMe_3$ and $Me_2CCO_2Me.AlMe_3$, (58). These were generated by the photolysis of azo-compounds in the presence of Al_2Me_6.[249] Di-isobutylaluminium hydride, $^iBu_2AlH$, reacts with N-heterocycles (L) to form 1:1 radical species $[L(Al^iBu_2)\cdot]$, where L = pyrazine, 2,2'- or 4,4'-bipyridine, e.g. (59).[250]

8-Hydroxy-7-[(6'-sulpho-2'-naphthyl)azo]quinoline-5-sulphonic acid (H_3L) forms a chelate complex with Al(III): $[AlL(H_2O)_4]$, by coordination of the heterocyclic N and phenolic O to form a 5-membered chelate ring.[251]

3.2.4 Compounds containing Al-O or Al-S Bonds.

I.r. spectra have been reported for the reaction products of Al, Ga, In or Tl atoms with natural and ^{18}O-enriched (74%) O_2 in an Ar matrix at 14K. ν_1 and ν_2 wavenumbers were assigned for MO_2 as follows: M = Al, ν_1 1096; ν_2 496 cm^{-1}; Ga, 1088, 387cm^{-1}; In, 1083, 336cm^{-1}; Tl, 1080, 299cm^{-1}. A cyclic MO_2 structure of C_{2v} symmetry was assumed in each case. Some bands assignable to M_2O_2 were also seen.[252]

Ion cyclotron resonance spectroscopy can be used to study the chemistry of Al^+ with alkyl halides and alcohols. Al^+ induces

$$Al^+ + ROH \rightarrow R^+ + AlOH \qquad ...(22)$$

$$Al^+ + ROH \rightarrow Al(H_2O)^+ + alkene \qquad ...(23)$$

$$Al(H_2O)^+ + ROH \rightarrow Al(ROH)^+ + H_2O \qquad ...(24)$$

dehydration of alcohols to give $Al(H_2O)^+$. Ligand displacement reactions result in $Al(ligand)^+$ as the final product, equations (22) to (24).[253]

I.r. spectra were used to determine the hydrogen positions in the boehmite (γ-AlO(OH)) crystal lattice.[254] The hydrogen bond distance in γ-$AlO[O(H)_{0.33}(D)_{0.67}]$, 2.73(2)Å, has been measured by neutron powder diffraction.[255]

Aluminium and gallium hydroxides interact with RbOH at 25°C to give solubility isotherms with three crystallisation branches: $RbOH.2H_2O$, $Rb_2[M_2O(OH)_6]$ and $M(OH)_3$, where M = Al or Ga.[256]

Wavenumbers of the internal modes of $[Al(OH_2)_6]^{3+}$ have been deduced from oriented single-crystal Raman spectra of $CsAl(SO_4)_2.12H_2O$, $CsAl(SeO_4)_2.12H_2O$ and $CsAl(SO_4)_2.12D_2O$, all at 80K. They are: ν_1, 542; ν_2, 473; ν_5, 347 cm^{-1}.[257]

The proton chemical shift of $Al(H_2O)_6^{3+}$ has been measured over a range of compositions in acetone/water mixtures in the temperature range -80°C to 32°C. The temperature variation depends on the solvent composition, and is small for pure water. There was some evidence for ion-pairing in the second sphere in the acetone-rich solutions.[258]

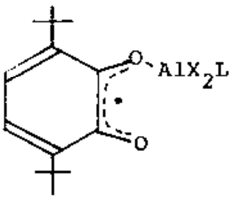
The hydrolysis-precipitation reactions of $Al(H_2O)_6^{3+}$ have been followed by high-resolution ^{27}Al n.m.r. spectroscopy, and potentiometric titration. Evidence was found for several monomers, but only one polymeric species: $[Al_{13}O_4(OH)_x]^{(31-x)-}$ [259]

High-resolution solid-state ^{27}Al n.m.r. spectra (with magic-angle spinning) were obtained for a number of zeolites with different framework structures. Sodium zeolites give one narrow peak (51.5-65.0 ppm. from $Al(H_2O)_6^{3+}$). ^{27}Al n.m.r. is most useful for probing the coordination, quantity and location of aluminium atoms in chemically treated zeolites, but it is less useful than ^{29}Si n.m.r. for direct structural determinations.[260]

A new synthesis of tetraethylaluminoxane has been carried out, and two intermediates isolated in the solid phase. These are oligoaluminoxanes, which dissolve in strong Lewis acids to form equilibrium adducts.[261]

^{27}Al n.m.r. can be used to study aluminium complexes with phosphate ligands (both simple, e.g. phosphate ion itself, and also, for example adenosine-5'-triphosphate,ATP) in aqueous solutions at approcimately 20 mM concentrations.[262]

E.s.r. spectra were measured for aluminium derivatives of semiquinones, formed by the reaction of Et_nAlCl_{3-n} (n = 0,1 or 3) with 3,6-di-t-butyl-1,2-benzoquinone. They were interpreted in terms of the presence of fluxional and non-fluxional (60), and also of (61), L = solvent, X = Et or Cl).[263]



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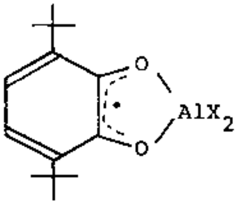


(61)

Association equilibria have been studied in aqueous solutions of $Al(NO_3)_3$, by component band analysis of the Raman-active ν_1 band of NO_3^-. Evidence was found for strongly directional perturbation of the nitrate ion.[264] U.v. spectra of $Al(NO_3)_3$, $Al_2(SO_4)_3$, $Al(ClO_4)_3$ and $AlCl_3$ aqueous solutions, give evidence of for direct Al(III)-SO_4 interaction, and also some Al(III)-NO_3 interaction.[265]

Thermographic studies have been carried out on $Al(IO_3)_3.8H_2O$, and the Ga, In and Tl iodates. The aluminium octahydrate is dehydrated in two stages, and finally decomposes (460-560°) to Al_2O_3. The gallium and indium compounds behave similarly, but the thallium compound is first reduced to thallium(I) iodate. This (420-440°C) gives Tl_5IO_6, which in turn (500-520°C) decomposes to Tl_2O and TlI.[266]

Ethyl dichlorophosphate reacts with $AlCl_3$ to produce $Al(OOPCl_2)[OOPCl(OEt)]_2$, which was characterised by infrared spectroscopy and chemical analysis.[267]

Relative ligand binding energies, $\delta D(Al^+-L)$, have been determined by ion cyclotron resonance, for 30 different organic ligands (L) i.e. alcohols, esters, ketones, aldehydes, cyanides.[268]

Equilibria between Al^{3+}, gallic acid ($C_7H_6O_5$; H_3L) and OH^- have been examined over a wide range of relative concentrations. The following species were detected: $AlOH^{2+}$,$Al_3(OH)_4^{5+}$, $Al(H_2)^+$, AlL, $Al_4L_3^{3+}$ and $Al_3(OH)_4(H_2L)^{4+}$.[269] Stability and equilibrium constants of catecholato and pyrogallato complexes of aluminium have been redetermined by iterative techniques.[270] Potentiometric and spectrophotomeric measurements have been carried out on Al(III) complexes with methylthymol blue. Complexes are formed with metal:dye ratios of 1:1 and 2:1, both in neutral form, and as protonated and hydroxo-derivatives.[271]

X-ray diffraction results on $[AlMe_3]_2$[dibenzo-18-crown-6] show that the six oxygens of the crown adopt a chair conformation. The Al-O coordination is quite strong (Al-O distance = 1.967(3)Å), but the rigidity of the ligand does not allow more than two aluminium atoms to coordinate. For $[AlMe_3]_4$[15-crown-5], however, the Al-O bonding is weaker (bond distance 2.005(6)Å), but the greater flexibility of the ligand allows coordination by four aluminium atoms.[272]

Crystalline tetramethylammonium aluminosilicates, $wNMe_4OH.xSiO_2.yAl_2O_3.zH_2O$, where w = 1-1.2, x = 1, y = 0.02-0.5, z = 8.1-9.7, have been obtained. Their structures are believed to be analogous to those of the aluminium-free silicates.[273] ^{29}Si n.m.r. results on these complexes are consistent with this.[274]

^{27}Al n.m.r. results were used to monitor the reaction of aluminoborosilicate glasses with alumina during sintering.[275] The distribution of silicon and aluminium atoms in synthetic faujasite zeolites has been determined by high-resolution solid-state ^{29}Si n.m.r. The distribution was such as to exclude Al-O-Al linkages.[276] High resolution ^{27}Al n.m.r. of solid $2CaO.Al_2O_3.8H_2O$ shows that the aluminium is present only in octahedral coordination. The compound was therefore formulated as $[Ca_2Al(OH)_6][Al(OH)_3(H_2O)_3].OH$. The compound $CaO.Al_2O_3.10H_2O$ also only contains octahedral aluminium, i.e. it is $Ca_3[Al_6(OH)_{24}].18H_2O$.[277]

Single crystals of $PbAl_2O_4$ and $PbGa_2O_4$ have been prepared from PbO/Al_2O_3 or PbO/Ga_2O_3 mixtures. Both contain three-dimensional networks, built up from MO_4 (M = Al or Ga) units linked into six-membered rings.[278] Phase relationships have been elucidated in the $SrAl_2O_4$-$SrGa_2O_4$ system.[279] A high-pressure (β) from of $SrAl_4O_7$ has been characterised. The crystals are orthorhombic, space group Cmma. It contains a three-dimensional $(Al_4O_7)_\infty$ network of AlO_6 and AlO_4 units. The Al-O bond distances in the AlO_4 units are unusually short (1.449-1.537Å).[280]

Infrared and Raman spectra have been reported for some aluminium and gallium garnets, containing $M_5O_{12}^{9-}$ (M = Al or Ga). The Al-O bonds are stronger than the Ga-O bonds, and various lanthanide cations have significant effects on the bond strengths.[281] Na_2O and alumina react to form a new sodium aluminate, $Na_{17}Al_5O_{16}$ (monoclinic, space group Cm). This contains discrete Al_5O_{16}

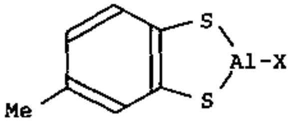
chains, built up from five corner-sharing AlO_4 units. The Al-O-Al unit is almost linear (bond angle $173(1)^{\circ}$), hence some (d-p)π-bonding must be postulated.[282] $Sr_{1.33}Pb_{0.67}Al_6O_{11}$ crystals belong to the space group Pnnm, and the aluminate framework contains both AlO_6 and AlO_4 units.[283]

Re-interpretation of earlier data shows that $5SrO.4Al_2O_3.H_2O$ forms rhombohedral crystals, space group $R\bar{3}$. The structural formula for one primitive rhombohedral cell is $Sr_{7.5}[AlO_2]_{12}(OH)_3$.[284]

Small-angle neutron scattering by hydrolysed aluminium nitrate solutions with OH:Al ratios of up to 2.25 is consistent with the presence of polynuclear species $Al_{13}O_4(OH)_{24}(H_2O)_{12}{}^{7+}$.[285] Small-angle X-ray scattering was used to study the hydrolysis-precipitation of an aqueous $AlCl_3$ solution (10^{-1}M) at 25°C. If $r = [NaOH]/[Al]_{tot} = 2$, the aluminium is present chiefly as $Al_{13}O_4(OH)_{28}{}^{3+}$. If r = 2.5 this species is still present, but so is a colloidal material, whose composition approximates to $Al(OH)_3$.[286]

High-resolution solid-state ^{27}Al n.m.r. spectra of basic aluminium sulphate and of the mineral zunyite show that both contain tridecameric aluminium-oxo-hydroxo groups, but that they are not identical in the two cases. Thus, zunyite, $\{[Al_{13}(OH,F)_{16}F_2]Si_5O_{20}Cl\}$ contains both AlO_6 and AlO_4 groups, but basic aluminium sulphate. $[Al_{13}O_4(OH)_{25}(H_2O)_{11}](SO_4)_3.16H_2O$ contains only AlO_4.[287]

Toluene 3,4-dithiol(H_2TDT) and trimethylaluminium (in 3:2 molar ratio) form polymeric $Al_2(TDT)_3$. A 1:1 reaction gives (TDT)AlMe, (62, X = Me).[288] Dimethylaluminium chloride and H_2TDT give (TDT)AlCl, (62, X = Cl).[289] $Me_3Al.HNMe_2$ and H_2TDT form a cyclic dithiolate derivative, "(TDT)AlMe.$HNMe_2$". Other amine adducts of trimethylaluminium give more complex reactions.[290]



(62)

3.2.5 Aluminium Halides.

M.o. calculations of cation migration barriers in $LiAlF_4$ and $MgAlF_5$ show that no metastable states exist for the face- or corner-bridged structures. The potential energy curve near the equilibrium structure (edge-bridged) is shallow, allowing for easy distortion.[291]

There are 3 crystal modifications of $BaAlF_5$: α(low temperature)-orthorhombic, isotypic with $BaGaF_5$; β-monoclinic and γ(high temperature)-monoclinic. The α→β tranformation is irreversible, and takes place slowly, beginning at 666°C. β→γ is reversible, and takes place at 789°C.[292]

Interactions have been studied in the fluoroaluminate glasses in the systems CaF_2-AlF_3 and MgF_2-CaF_2-AlF_3. The aluminium-containing species is generally AlF_6^{3-}.[293]

Activities and phase diagram data have been found for the NaF-AlF_3-Al_2O_3 system by e.m.f. and cryoscopic measurements. Standard thermodynamic data were tabulated for β-Al_2O_3(s), Na_3AlF_6(s), $Na_5Al_3F_{14}$(s) and $NaAlF_4$(l).[294] Unit cell dimensions have been determined for $Ag_2M^{II}M^{III}F_7$, where M^{III} = Al, Ga or In; M^{II} = Mg, Mn, Co, Cu or Zn. All are isostructural with Na_2MgAlF_7.[295]

Single crystals of colourless Ba_2ZnMF_9 (where M = Al or Ga) have been prepared for the first time. The aluminium compound is orthorhombic (space group Pnma), containing double chains of ZnF_6 and AlF_6 octahedra, these produce rings built up from 4 of each type of octahedron. The gallium compound has a similar structure, but distorted such that the crystals are monoclinic.[296] $Ba_2M^{II}AlF_9$, where M^{II} = Ni, Co or Mg, are all isostructural with Ba_2ZnAlF_9.[297] The low-temperature form of $Ba_3Al_2F_{12}$ has been prepared as single crystals for the first time. They belong to the space group Pnnm, and contain the anionic unit $[(F_{4/1}AlF_{2/2})_4]^{8-}$.[298]

A low-temperature molten salt can be prepared from aluminium chloride and 1-n-butyl-t-(dimethylamino)pyridinium chloride ([BuDMAP]Cl). At 40°C the system is liquid with ratios (BuDMAP)Cl:$AlCl_3$ of from 0.95:1 to 2.0:1.[299] Dialkylimidazolium chloroaluminate melts have been revealed as useful room-temperature ionic liquids for electrochemistry, spectroscopy and synthesis.[300]

The crystal-structures of $LiAlCl_4$ (space group $P2_1/c$) and $NaAlCl_4$ ($P2_12_12_1$) have been investigated over a range of temperatures. The dimensions of the $AlCl_4$ tetrahedra do not alter within the ranges 293-364K (for $LiAlCl_4$) or 293-393K (NaAlCl).[301]

$NaAlCl_4.1.5SO_2$ forms monoclinic crystals, space group $P2_1/n$. The structure is built up from $AlCl_4$ tetrahedra, NaO_2Cl_4 and NaO_3Cl_3 octahedra.[302] Crystalline $CuAlCl_4$ is prepared by heating CuCl and $AlCl_3$ in a quartz tube at 533K. The crystals are tetragonal, space group $P\bar{4}2c$, in which the chlorines form a cubic close packed lattice, with Cu and Al each occupying $^1/8$ of the tetrahedral holes.[303] $NS_2^+AlCl_4^-$ (prepared from S_4N_4 and $AlCl_3$ in CH_2Cl_2 solution) forms orthorhombic crystals, space group Pnma.[304]

^{27}Al n.m.r. studies have been carried out on $AlCl_3$ solutions in diethyl ether. At high concentrations $AlCl_4^-$ is formed; at low temperatures and in dilute solutions both $AlCl_4^-$ and $AlCl_3.OEt_2$ can be detected. At 25°C in dilute solutions, however, only one signal is seen, due to the average of all the species in solution. In THF solutions the $AlCl_3$ undergoes more extensive dissociation, and the main species in equilibrium are $AlCl_3.2THF$, $AlCl_4^-$ and $AlCl_2(THF)_2^+$. In monoglyme, dissociation to $AlCl_4^-$ and $[AlClL_5]^{2+}$ (where L = one oxygen donor atom) is almost quantitative in dilute solutions. At higher concentrations $AlCl_3.L$ is also present.[305]

Infrared and Raman spectra were reported for the $AlCl_3/MeCN$ system, together with ^{35}Cl and ^{27}Al n.m.r. data, in the $[CH_3CN]/[AlCl_3]$ molar ratio range from 5.6 to 80. There was evidence for only one anion, $AlCl_4^-$, but a variety of cations: $[Al(CH_3CN)_{6-n}Cl_n]^{(3-n)+}$, where n = 0, 1 or 2. In concentrated solutions the new species $[Al(CH_3CN)_5]^{3+}$ was detected.[306] Infrared, Raman and ^{27}Al n.m.r. studies on the $AlCl_3/CH_3CN/CH_3NO_2$ system show that neutral and ionic complexes are in equilibrium. The systems $AlCl_3/CH_3CN/NMe_4Cl$ and $AlCl_3/CH_3CN/H_2O$ are, however, wholly ionic.[307]

An X-ray structure determination on $h^6\text{-}C_6H_6Ti(Cl_2AlCl_2)_2$ confirmed earlier structural proposals. The structure is very similar to that of the hexamethylbenzene analogue.[308]

ΔH and ΔS for the reactions (25) and (26), where E = Al or Ga, have been determined by gas-phase spectrophotometry in the

$$NiCl_2(s) + ECl_3(g) \rightleftharpoons NiECl_5(g) \qquad \ldots(25)$$

$$NiCl_2(s) + E_2Cl_6(g) \rightleftharpoons NiE_2Cl_8(g) \qquad \ldots(26)$$

temperature range 300-840°C, and by analysis of the quenched condensates. ΔS is practically independent of E (ca. 70 J mole^{-1} K^{-1} for (25), 43 J mole^{-1}K^{-1} for (26), but for (25) ΔH is more positive for E = Ga, hence the gallium complexes are less stable.[309]

Vibrational spectra have been analysed and force fields calculated for the μ-halo-hexahaloaluminates $Al_2X_7^-$ (where X = Cl, Br or I). Almost complete vibrational assignments were proposed.[310]

The solubility of sodium chloride in molten $NaAlCl_4$ was

$$2AlCl_4^- \rightleftharpoons Al_2Cl_7^- + Cl^- \qquad ...(27)$$

$$3Al_2Cl_7^- \rightleftharpoons 2Al_3Cl_{10}^- + Cl^- \qquad ...(28)$$

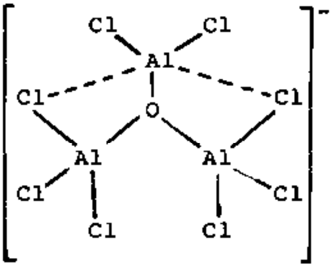
$$2Al_3Cl_{10}^- \rightleftharpoons 3Al_2Cl_6 + 2Cl^- \qquad ...(29)$$

investigated by potentiometric measurements with chlorine/chloride electrode cells in the temperature range 200-300°C. The data were explicable in terms of 3 equilibria, (27)-(29), and pK values were estimated for all of these.[311]

Infrared spectra of samples from the KCl-$AlCl_3$ system show that KAl_2Cl_7 is present, and that the stretching modes of the Al-Cl-Al bridge are at 306/325cm^{-1} (ν_s) and 387cm^{-1} (ν_{as}).[312] Equilibrium vapour pressure measurements over KCl-$AlCl_3$ melts (containing 75.0, 66.6 or 62.8 mole % $AlCl_3$) also suggest the formation of KAl_2Cl_7 - for which a number of thermodynamic parameters were calculated.[313]

The crystal structure of the low-temperature modification of $TiAl_2Cl_8$ has been determined by vibrational frequency correlations and neutron powder-diffraction. The chlorines form a slightly distorted h.c.p. lattice, with titanium in octahedral and Al in tetrahedral holes in every second layer. The bonding leads to the formation of chains in the structure.[314]

Some novel chloro-oxoaluminates, e.g. (<u>63</u>), (<u>64</u>), have been prepared and characterised as counterions of the cationic products of the Friedel-Crafts synthesis of arene-transition metal compounds.[315]



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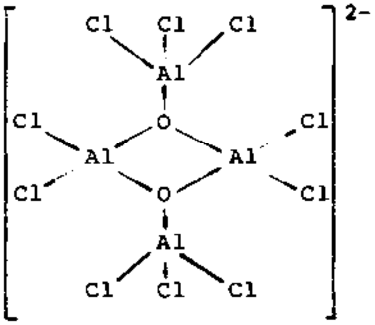


(64)

Electrical conductivity has been measured for $SbCl_3$-$AlCl_3$ melts containing 2.5-60 mole % of $AlCl_3$.[316]

Crystal structure determinations have been carried out on MI_3 (M = Al, Ga or In) - all contain a distorted c.c.p. iodine lattice with metal atoms in tetrahedral holes. GaI_3 and InI_3 are isotypic, and contain M_2I_6 units. AlI_3 has an infinite chain structure - isotypic with the "asbestos-like" form of SO_3.[317]

3.2.6 Intermetallic Phases containing Aluminium.

$SrAl_2$ belongs to the KHg_2 structure type at room temperature and pressure. At ca. 60 kbar and 1050°C this transforms to a new modification with the $MgCu_2$ structure.[318]

$GdAl_2Si_2$ crystallises with the $CaAl_2Si_2$-type structure. It is an unusual compound in that it has 17 valence electrons per formula unit, and possesses metallic conductivity.[319]

The compound $Ca_3Al_2Ge_3$ can be prepared from its constituent elements. It crystallises with orthorhombic symmetry, space group Pnma. The structure contains $AlGe_4$ tetrahedra linked by corners to produce a three-dimensional network with channels containing calcium atoms.[320]

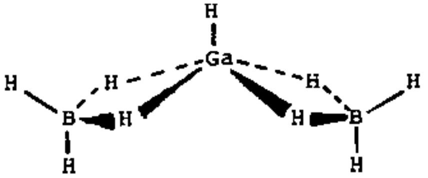
Ca_3AlAs_3 crystallises in the orthorhombic system, and belongs to the point group Pnma. The $AlAs_4$ tetrahedra present are linked into chains *via* common corners. Ba_3AlSb_3 is also orthorhombic, space group Cmca, but here $AlSb_4$ tetrahedra are edge-linked to give isolated Al_2Sb_6 groups.[321]

New ternary phases have been characterised in each of the systems $NbZn_{2-x}Al_x$ and $TaZn_{2-x}Al_x$. Thus, NbZnAl and TaZnAl both have the $MgZn_2$-type structure (space group $P6_3/mmc$), while $NbZn_{1.25}Al_{0.75}$ possesses the $AuCu_3$ structure (space group Pm3m).[322]

3.3 GALLIUM

3.3.1 Gallium Hydrides.

Electron diffraction of gaseous $Ga(BH_4)_2H$ shows that the molecules are monomeric, (65). The best fit was achieved for an unsymmetrical $Ga(\mu\text{-}H)_2B$ unit, with $rGaH_b$ 176.2(1.5) and 189.1(2.5)pm, and rBH_b 125.0(8.1) and 145.6(3.3)pm.[323]



(65)

The heat capacities of $NaGaH_4$, $KGaH_4$ and $RbGaH_4$ have been determined by adiabatic calorimetry in the temperature range 15-317K ($KGaH_4$) or 11-320K (the rest). Values of thermodynamic functions were calculated from these data.[324,325]

3.3.2 Compounds containing Ga-C Bonds.

Infrared and Raman data have been recorded and assigned for $(AsMe_4)[(CD_3)_{4-n}M^{III}Cl_n]$, where M = Ga or In; n = 1 to 3. Together with data on the CH_3 analogues those results were used to determine the molecular force fields in the methylchlorogallate and -indate ions. Both M-Cl and M-C stretching force constants increase markedly in the series $[(CH_3)_{4-n}M^{III}Cl_n]^-$ from n = 0 to n = 4.[326]

An X-ray diffraction study has been carried out on $[(THF)(C_2H_3)GaFe(CO)_4]_2$. The Ga-Fe distance is 2.516(3)Å, Ga-C(vinyl) 2.069(5)Å, and Ga-O(THF) 2.129(4)Å. Significant distortions were found in the structure, and these were ascribed to partial ionic bonding.[327]

3.3.3 Compounds containing Ga-N or Ga-P Bonds.

The infrared and Raman spectra of $Me_3Ga.NH_3$ and $Me_3Ga.ND_3$ in the solid state at 77K are assignable in terms of C_{3v} molecular symmetry. No A_2 modes were observed, although there was evidence for a lower site-symmetry. Splitting of the A_1 modes indicated that there are 2 or more molecules per unit cell. The Ga-N stretching force constant (1.08 mdyn Å^{-1}) was much lower than that in $Me_3N.GaH_3$ (2.43 mdyn Å^{-1}).[328] Analogous spectroscopic data were obtained for $Me_3N.GaCl_3$. These also were consistent with C_{3v} molecular symmetry, but a normal coordinate analysis revealed extensive coupling of modes, and the largest Ga-N stretching force constant yet calculated.[329]

$(Me_3Si)_2NH$ reacts with $MeGaCl_2$ or $nBuGaCl_2$ to form $[R(Cl)GaN(H)SiMe_3]_2$, where R = Me or nBu. These are crystalline solids, dissolving in benzene as dimers. The crystal structure of the methyl compound shows that it contains a planar, four-membered Ga_2N_2 ring, with equivalent substituents trans to each other. Infrared and ^1H n.m.r. data were recorded and partially assigned.[330]

The stabilities and enthalpies of complexes formed by N_3^- with Ga(III) and In(III) were measured in aqueous solution (I = 1; 25°C). For gallium, the only species which can be studied is GaN_3^{2+}, while for indium all of the species $In(N_3)_n^{3-n}$ (n = 1 to 4) are formed.[331]

A detailed assignment and discussion of the infrared and Raman spectra of solid $Me_3P.GaCl_3$ has been presented. The vibrational assignment was complete except for the torsional modes. The Ga-P stretching force constant (2.01mdyn Å^{-1}) is similar to that in $Me_3P.GaH_3$. There is extensive vibrational coupling between Ga-P stretching, $GaCl_3$ and PC_3 stretching and symmetric deformations.[332]

3.3.4 Compounds containing Ga-O or Ga-S Bonds.

The Raman spectrum of a single crystal of β-Ga_2O_3 was obtained in the temperature range 4-1000K. The temperature dependence of Raman band halfwidths can be explained in terms of anharmonicity, creation of defects, and order-disorder phase transitions.[333]

Infrared spectra have been reported for the gallates $LnGaO_3$ (Ln = La, Pr or Nd), with the perovskite structure, together with Raman data for $NdGaO_3$. The Ga-O bonds parallel to the C_2 axis are stronger than the others.[334]

Heating $Na_8Ga_2O_7$ with lithium oxide produces single crystals of $Li_3Na_2GaO_4$. The same compound can be formed as a powder by heating together all of the binary oxides. The crystals contain isolated GaO_4 units, with Ga-O distances in the range 1.836-1.876Å.[335]

Mixing solutions of sodium vanadate (pH 12.6, 9-8 or 5.0) and gallium(III) nitrate (pH 2.0) produces the single-phase species $Ga_2O_3.V_2O_5.6H_2O$, $2Ga_2O_3.3V_2O_5.15H_2O$ and $Ga_2O_3.2V_2O_5.9H_2O$. These are thought to be $GaVO_4.3H_2O$, $Ga_4(V_2O_7)_3.15H_2O$ and $Ga_2V_4O_{13}.9H_2O$

respectively.[336]

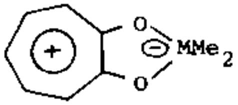
$Pb_9Ga_8O_{21}$, prepared for the first time from the individual oxides, crystallises with cubic symmetry (space group T_h^6-Pa3). The gallium is all present as GaO_4 tetrahedra.[337]

A series of two-electron reduced gallato tungstates has been isolated.[338] $K_7GaPbW_{11}O_{39}.16H_2O$ is orthorhombic, space group Pnma. The GaO_4 unit has a Ga-O bond length of 1.80Å.[339] The hexamolybdogallates $BaH[Ga(OH)_6Mo_6O_{18}].3H_2O$ and $M^{II}(NH_4)[Ga(OH)_6Mo_6O_{18}].nH_2O$ (where M^{II} = Ca, Sr or Ba) have been synthesised and studied by X-ray diffraction and infrared spectroscopy.[340]

^{19}F n.m.r. spectra of $GaCl_3$ solutions in ROH (R = Me, Et or nPr) containing F^- produced evidence for the formation of the following outer-sphere complexes: $[Ga(ROH)_6]^{3+}.F^-.Cl^-$; $[Ga(ROH)_5(H_2O)]^{3+}.F^-.Cl^-$; $[Ga(ROH)_5(H_2O)]^{3+}.F^-.F^-$ and $[Ga(ROH)_4(H_2O)_2]^{3+}.F^-$.[341]

Kinetics and equilibria have been studied between gallium(III) and salicylic acid, 5-chloro-, 5-nitro- and 3,5-dinitrosalicylic acid in aqueous solution, with $[H^+]$ in the range 0.0075-0.2M and ionic strength 0.2M. GaL^+ and $Ga(HL)^+$ were detected for the first three, but only GaL^+ for the last ligand.Complex formation constants were determined.[342]

MMe_3, where M = Ga or In, and α-tropolone react to give (66). Both were found to be monomeric in solution, with an almost planar 7-/5-ring bicyclic structure, approximating to C_{2v} symmetry. For M = Ga the solid is dimeric.[343]



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Solution equilibria were determined between Ga(III) or In(III) and the hexadentate ligands N,N',N"-tris(2,3-dihydroxy-5-sulphonatobenzyl)-1,3,5-tris(aminomethyl)benzene (MECAMS) or N,N',N"-tris-(2,3-dihydroxy-5-sulphonatobenzyl)-1,5,10-triazadecane (3,4-LICAMS) or the bidentate catechol N,N-dimethyl-2,3-dihydroxy-5-sulphonatobenzamide (DMBS). Increased acidity led to protonation of the hexadentate sequestering agents (monitored by following ν(C=O) by F.T.I.R.). The catechol derivative formed 1:3 complexes.[344]

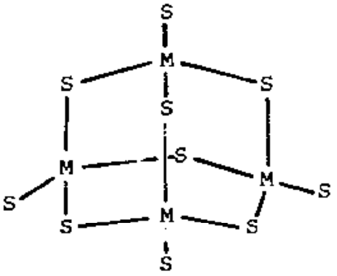
Eight tris(β-diketonato)gallium(III) and seven tris(β-diketonato) indium(III) complexes have been prepared: $M(RCOCHCOR')_3$, where $R' = CHF_2$ or CF_3; R = Me, Ph etc; M = Ga or In. All are fluxional; ^{19}F n.m.r. spectra show four resonances in the non-exchanging regions, due to cis- and trans-isomers.[345]

$La_{3.3\underline{3}}Ga_6O_2S_{12}$ forms tetragonal crystals, belonging to the space group $P\bar{4}2_1m$. The Ga, S and O are all four-coordinate. The structure is built up from sheets of GaS_4 and $GaOS_3$ tetrahedra, parallel to the 010 plane. The La atoms bind together the $(Ga_3S_6O)_n^{5n-}$ sheets.[346] $LaGaS_3$ is monoclinic, space group $P2_1/b$, and contains four-coordinate, tetrahedral Ga.[347]

Phase diagrams have been determined for the GaS-PbS and GaS-Pb systems. Only small regions of solid solution formation were found.[348] The Ga_2S_3-PbS section of the Ga-Pb-S system has been investigated. Only one compound is found, $PbGa_2S_4$, which melts without decomposition at 875°C.[349]

The crystal structure of the 3R-polytype of $Fe_2Ga_2S_5$ has been determined. The crystals are rhombohedral, space group $R\bar{3}m$, containing double layers of FeS_6 octahedra enclosed between two single layers of GaS_4 tetrahedra.[350]

$(CeO)_4Ga_2S_5$ is tetragonal, space group I4/mmm. The gallium is four-coordinated by sulphur atoms, although there is a deficit of both Ga^{3+} and S^{2-}.[351] In the orthorhombic crystals of $(NdO)_4Ga_2S_5$ (space group Pbca) the tetrahedral GaS_4 units are linked into sheets.[352]



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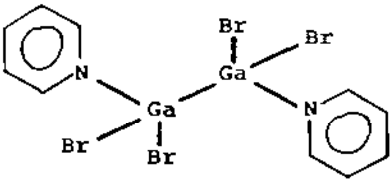
Nucleophilic degradation of M_2S_3 (where M = Ga or In) with sulphide (as an alkali metal salt in aqueous solution at 90°C for 4 hours) forms $M_4S_{10}^{8-}$. Raman spectra show that the structures of these are the same in solid and solution. X-ray crystallography reveals that these novel anions possess an adamantane-like structure, (<u>67</u>).[353]

3.3.5 Gallium Halides.

$^{35,37}Cl$ and $^{69,71}Ga$ n.q.r. spectra have been reported for the charge-transfer complexes of $GaCl_3$ with ketones and nitriles.[354]

MCl_3, where M = Ga or In, and $NaMn(CO)_5$ react to form $Na\{Cl_{4-n}M[Mn(CO)_5]_n\}$, where n = 1, 2 or 3. Indium(III) butyrate and $NaMn(CO)_4L$, where L = CO or PPh_3, produce $(C_3H_7CO_2)_2InMn(CO)_4L$, with five-coordinate indium. TlCl and $NaRe(CO)_5$ initially give $TlRe(CO)_5$, but this disproportionates to Tl and $Tl[Re(CO)_5]_3$. Heating the latter produces $Re_2(CO)_8[\mu\text{-}TlRe(CO)_5]_2$.[355]

^{35}Cl or ^{81}Br and ^{69}Ga n.q.r. spectra have been reported for $L_2{}^{2+}Ga_2X_6{}^{2-}$ (L = NMe_4, NEt_4; X = Cl or Br). The halogen n.q.r. frequency is considerably lower in the Ga(II) than in Ga(III) compounds. The ^{69}Ga signals were in the range 22-24MHz.[356]



(<u>68</u>)

$Ga_2Br_4py_2$, (<u>68</u>), forms monoclinic crystals (space group C2/m). The Ga-Ga bond length is 2.421Å, and the complex adopts the <u>trans</u>-conformation, as shown.[357] The crystal and molecular structures of Ga_2Br_4(1,4-dioxan) show that the Ga-Ga bond length in this case is 2.395Å, and that the structure is very like that of the chloro-analogue.[358]

Phase diagrams have been established for the systems GaI_2-$MGaI_4$, where M = Na, K, Rb or Cs. Continuous solid solutions are formed for M = K, Na or Rb. For M = Cs there was some evidence of compound formation.[359]

Ga_2I_4 and Ga_2I_3 have been prepared as small single crystals by heating the elements in sealed glass ampoules. The Ga_2I_3 was found to be identical to material formerly described as "GaI". Its crystals were monoclinic, space group $P2_1/c$, and it could be formulated as $(Ga^+)_2(Ga_2I_6)^{2-}$, with a Ga-Ga distance of 238.7(5)pm.

The crystals of Ga_2I_4, i.e. $Ga^+GaI_4^-$, were rhombohedral, space group R3c.[360]

3.3.6 Intermetallic Phases containing Gallium.

The intermetallic compound $Na_{22}Ga_{39}$ is orthorhombic, space group Pnma. Most of the gallium atoms are arranged in a non-compact framework of icosahedra, with a few gallium atoms of lower coordination number.[361]

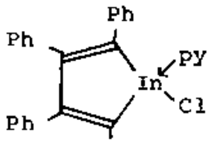
The new compound Na_7Ga_{13}-I crstallises in the trigonal-rhombohedral system, with the space group R3m. The Ga atoms form Ga_{12} icosahedra and Ga_{15} clusters. These are linked to give a three-dimensional network, and the resultant structure is related to that of $MgCu_2$.[362] The form Na_7Ga_{13}-II has a very similar structure, but here the crystals are orthorhombic, space group Pnma.[363]

3.4 INDIUM

3.4.1 Compounds containing In-C Bonds.

The structures of MMe_3, where M = In or Tl, have been studied by gas-phase electron diffraction. Both gave patterns consistent with planar MC_3 skeletons and freely-rotating methyl groups. The M-C bond distances were 2.161(3)Å (In) and 2.206(3)Å (Tl).[364]

C.N.D.O. molecular-orbital calculations have been carried out on InC_5H_5, of C_{5v} symmetry. The bonding between indium and the organic fragment is essentially a covalent interaction involving indium 5s and 5p orbitals, and the ring p_π orbitals. The lone pairs of electrons on the In has a very significant effect.[365]



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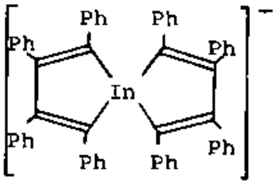

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1,4-Dithio-1,2,3,4-tetraphenylbutadiene and $InCl_3$-py interact to form (69). With $InCl_4^-$, on the other hand, the spiro-anion (70) is formed.[366]

3.4.2 Compounds containing In-N or In-P Bonds.

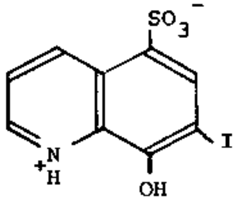
Neutral In(II) complexes $In_2X_4L_2$, where X = Br or I; L_2 = N,N,N',N'-tetramethylethylenediamine or L = PEt_3, are prepared by the reaction of InX_2 with the donor in benzene or toluene solution. Other donors, and for X = Cl all donors, produce decomposition to In^o. The vibrational spectra of the adducts show that $X_2In-InX_2$ units are present.[367]

Related adducts which have been reported are $In_2X_4L_4$, where X = Cl, Br or I, L = piperidine, piperazine, or morpholine; X = Br or I, L = pyridine or DMSO, and species containing O or S donors i.e. $In_2X_4L_2$ (X = Cl, Br or I; L = 1,4-dioxan, tetrahydropyran, THF or tetrahydrothiophen; X = Br or I; L =DMSO). Solid-state Raman spectra show that all contain In-In bonds.[368]

Reaction of InL_3, where L = $N(SiMe_3)_2$, with trimethylphosphine oxide, Me_3PO (= L'), gives a 1:1 complex $InL_3(L')$. This dissociates on heating *in vacuo*.[369]

In(I) halides dissolve in toluene in the presence of neutral donor ligands at or below 0°C. The simplest solute species in the InBr-toluene-N,N,N',N'-tetramethylethylenediamine(TMEN) system is InBr.3TMEN. This precipitates solid InBr.0.5TMEN. Above 0°C disproportionation of InX occurs. Solutions of InX, where X = Br or I, can oxidatively insert into C-X bonds to give organo-indium(III) halides.[370]

The equilibria and mechanism of interaction of In(III) with ferron, 8-hydroxy-7-iodo-quinolinium-5-sulphonate, H_2L, (71), have been investigated. Two complexes were observed, $[InL]^+$ and $[In(HL)]^{2+}$; these are thought to be formed by 3 parallel paths, differing in their dependence on $[H^+]$.[371]



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3.4.3 Compounds containing In-O or In-S Bonds.

The hydrolysis of In^{3+} has been studied for [In] from 0.2 to 0.75M. The results were explicable in terms of the formation of only two polynuclear ions: $In_2(OH)_2{}^{4+}$ and $In_4(OH)_6{}^{6+}$. Formation constants were determined for these.[372]

Potentiometric titration was used to examine the hydrolysis of In(III) at 25°C, in the presence of 0.10 mol. dm^{-3} KNO_3. These data were interpretable in terms of $[In(OH)]^{2+}$, $[In(OH)_2]^+$ and $[In_p(OH)_p]^{2p+}$.[373] Equilibrium constants for the hydrolysis of In(III) in H_2O-dioxan solutions have been measured at dioxan mole fractions of 0.25 and 0.48.[374]

$InCl_3[OP(NMe_2)_3]_2$ has been prepared by the extraction of $InCl_3$ from an aqueous solution into $CHCl_3$ containing hexamethylphosphoramide. The crystal structure of this confirms that it contains five-coordinate indium. The HMPA molecules are axial, with average bond distances of 2.18Å (In-O) and 2.36Å (In-Cl). Infrared and Raman spectra are consistent with these data.[375]

Investigation of solubility in the Li_2SeO_4-$In(SeO_4)_3$-H_2O system at 20°C shows that there is no chemical interaction, unlike the situation for other alkali metal cations.[376]

Zinc indium double oxides, $Zn_kIn_2O_{k+3}$, where k = 2-5 or 7, can be synthesised by sintering stoichiometric mixtures of the initial oxides. The vibrational spectra (50-1000 cm^{-1}) were reported.[377a] Infrared and Raman spectra of crystalline $SrIn_2O_4$ were analysed to give a general assignment of vibrational modes. A normal coordinate analysis was performed using the polymer chain approximation.[377b]

The double molybdate $K_5In(MoO_4)_4$ forms monoclinic crystals, space group Aa. InO_6 and MoO_4 units are present, which condense to form infinite chains of $\{[In(MoO_4)_4]^{5-}\}_\infty$.[378] In_6WO_{12} crystals are rhombohedral, space group $R\bar{3}$, of the Y_6UO_{12} type. The InO_4 tetrahedra share corners as in the fluorite structure.[379]

$In_6La_{10}O_6S_{17}$ forms orthorhombic crystals, space group Immm. The indium atoms are present in both four- and six-coordinate sites, all coordinated by S atoms, not oxygen.[380] The complex species $In_{32}ON_{17}F_{43}$ forms cubic crystals, space group Ia3. The structure is related to that of fluorite, with infinite strings of corner-sharing $In(O,F)_6N_2$ distorted cubes, lying along the four <111> directions.[381]

A study of interactions in the indium-molybdate system showed that heteropolycomplexes such as the 12-molybdatoindate are formed, but less readily than for the analogous gallium-containing systems.[382]

$Al_2In_4S_9$ and $Ga_2In_4S_9$ are formed by chemical vapour transport reactions. They crystallise in the space group $P\bar{3}m1$. Parts of the $AlInS_3$-In_2S_3 phase diagram was shown.[383]

3.4.4 Indium Halides.

Infrared and Raman spectra have been described for $MInF_4$ and M_3InF_6, where M = Na, K, Rb or Tl. Internal anion modes and lattice modes could be correlated with crystal structure and coordination changes.[384]

Crystal structures have been determined for the tetra-n-butylammonium salts of $InCl_4^-$, $InBr_4^-$, $InBrCl_3^-$ and $InBr_3Cl^-$. All are isomorphous, orthorhombic and belong to the space group Pnma. $InCl_4^-$ is a distorted tetrahedron, of C_{3v} symmetry, with In-Cl distances of 2.344(3) and 2.355(3)Å. $InBr_4^-$ preserves regular T_d symmetry, with In-Br 2.378(5)Å. The mixed species both have disordered structures, and it is difficult to discern structural differences.[385]

Phase diagrams have been determined for the systems InX_3-KX-H_2O, where X = Cl or Br, at 21°C. The following double salts were detected: $3KCl.InCl_3.H_2O$, $2KCl.InCl_3.H_2O$; $3KBr.InBr_3.1.5H_2O$, $2KBr.InBr_3.H_2O$, $KBr.InBr_3.2H_2O$ and $3KBr.2InBr_3$. All are incongruently saturating at 21°C.[386]

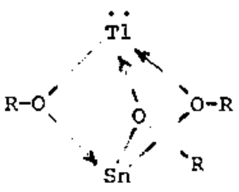
3.5. THALLIUM

3.5.1 Thallium(I) Compounds.

The infrared spectrum of the $Tl_2^{2+}CO_3^{2-}$ triple ion isolated in an argon matrix has been obtained. The carbonate ion gives bands consistent with C_{2v} symmetry due to cation/anion interaction. The results were very similar to analogous systems with alkali metal carbonates.[387]

A new cage molecule involving Tl(I) has been prepared, i.e. $Tl(O^tBu)_3Sn$, the structure of which is (72), as shown by X-ray diffraction. It is prepared from $[Tl(O^tBu)]_4$ and $[SnO^tBu)_2]_2$.[388]

Thallium(I) chloride and $[Me_2Si(Me_3CO)(Me_3CNLi)]_2$ react to form (73), which is monomeric and highly reactive.[389]



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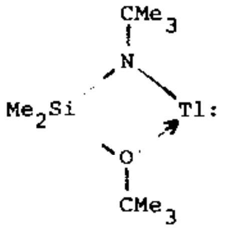

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The thallium(I) derivative of $HC_5(CO_2Me)_5$ has been prepared: $Tl[C_5(CO_2Me)_5]$. The thallium is irregularly five-coordinate, with two chelating carbonyl groups from one anion, and 3 others from separate anions. All of the carbonyl oxygens of each anion are coordinated to four different metal cations.[390]

$Te(OH)_6.Tl_2SO_4$ is monoclinic, belonging to the space group $P2_1/a$. There are two types of thallium present, one seven-, the other eight-coordinate. The Tl-O distances lie in the range 2.8 to 3.3Å.[391]

Thallium lanthanide double vanadates, $Tl_3Ln(VO_4)_2$, where Ln = Y-Lu or Sc, can be obtained by solid-phase synthesis. All decompose above 450°C to the individual vanadates.[392]

The following new ternary thallium chalcogenides: $Tl_4Si_2S_6$, $Tl_4Si_2Se_6$ and $Tl_4Ge_2Se_6$, have been synthesised from the elements. All of them are isostructural with $Tl_4Ge_2S_6$, and contain the anions $Si_2S_6^{4-}$ etc.[393] Single crystals of Tl_4GeS_4 and Tl_4GeSe_4 can be obtained from the Tl_2S-GeS_2 or Tl_2Se-$GeSe_2$ systems. The physical properties of these crystals were reported.[394] $Tl_2Sn_2S_3$ is made from Tl_2S/SnS mixtures; it forms monoclinic crystals, space group C2/c. The thallium is four-coordinated by sulphur atoms (with Tl-S in the range 2.81 - 3.13Å).[395]

The phase diagrams of the Ge-S-Tl,[396] Ag-Se-Tl,[397] and Ag-Te-Tl systems have been determined.[398] A number of new ternary phases were identified.

3.5.2 Thallium(III) Compounds.

The crystal structure of dimethyl(dibenzo-18-crown-6)thallium(III) 2,4,6-trinitrophenolate shows that the linear $Me_2Tl(III)$ unit is threaded through the crown ether, with the TlC_2 group held perpendicular to the plane containing the six ether oxygen atoms and the thallium atom.[399]

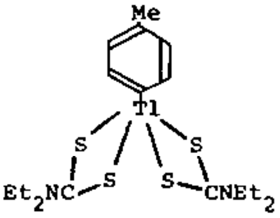
Crystal structures have been determined for complexes between dimethylthallium(III) picrate and two isomers of dicyclohexano-18-crown-6. The linear Me_2Tl^+ is surrounded by six oxygen atoms in each isomer, which has cyclohexano-rings in the chair conformation (these are related by a centre of symmetry, in the cis-anti-cis isomer; and by a pseudo-plane of symmetry, in the cis-syn-cis isomer). At each cyclohexano-ring the $Tl-O_{ax}$ bond is longer than $Tl-O_{eq}$.[400]

Equilibrium constants have been determined for the hydrolysis of the Tl(III) ion in water-dioxan mixtures. An increase in these constants with increasing dioxan concentration can be explained by positive energies of resolvation of the thallium ion on going from H_2O to the mixed solvents.[401]

Thallium(III) acetate monohydrate, $Tl(OAc)_3.H_2O$, forms monoclinic crystals, space group $P2_1/c$. The thallium is coordinated irregularly by eight oxygen atoms, with Tl-O distances of between 2.17 and 2.87Å.[402]

Evidence has been found for complexes of hexamethylphosphoramide (HMPA) with TlX_3 and $PhTlX_2$ (where X = Cl or Br), i.e. $TlX_3(HMPA)_2$ and $PhTlX_2(HMPA)$. They were characterised by infrared, Raman and ^1H n.m.r. spectra, molecular weights and conductivity.[403]

The thermal decomposition of $TlPO_4.2H_2O$ up to 700°C was followed by thermal analysis, X-ray diffraction, infrared and n.m.r. spectra. Dehydration takes place in two stages (85-330°C), followed (615-680°C) by reduction of Tl(III) to Tl(I), giving a polyphosphate.[404]



(74)

The crystal structure of (74) shows that the dithiocarbamate ligands are unsymmetrically bidentate, with Tl-S distnaces of 2.591(2)Å and 2.728(3)Å.[405]

$Tl^{III}MF_6$ (where M = Ga, In or Sc) are all prepared from the binary fluorides. All give crystals isostructural with VF_3, with a statistical distribution of the metal ions.[406]

The structures of $TlCl_4^{3-}$ were determined from X-ray diffraction on concentrated aqueous solutions of Tl(III) and chloride ion. The Tl-Cl distances were: $TlCl_4^-$(T_d): 2.43(1)Å; $TlCl_6^{3-}$(O_h): 2.59(1)Å. There was no evidence for polynuclear species, and the data were consistent with the Raman spectra of such solutions.[407]

X-ray diffraction by concentrated aqueous solutions of Tl(III) and various concentrations of Br^- gave the structures of $TlBr_n(H_2O)_m^{3-n}$,where n = 0,2,3,4. At high $[Br^-]:[Tl^{3+}]$ ratios there was evidence for $TlBr_n^{3-n}$, where n>4. No polynuclear species were found in the systems studied.[408]

Tetrabromo- and tetraiodothallates(III) of alkali metal cations crystallise from aqueous solutions as cubic hydrates, $MTlX_4.nH_2O$, where M = Li,Na,K,Rb,Cs or NH_4; X = Br or I; n = 1 or 2. The iodo-compounds retained their cubic structure on dehydration, but the bromo-species underwent structural changes.[409]

Crystals of $[N^nBu_4][TlI_4]$ are monoclinic, space group $P2_1$. The TlI_4^- ion is very close to regular tetrahedral, with Tl-I bond lengths between 2.723(4) and 2.840(5)Å. Assignments of vibrational spectra were made for this salt at room and liquid nitrogen temperatures.[410]

REFERENCES.

1 D.A.Ramsay and P.J.Sarre, J. Chem. Soc., Faraday Trans. 2, 78(1982)1331.
2 R.Klein, P.Rosmus and H.J.Werner, J. Chem. Phys., 77(1982)3559.
3 A.J.Stone and M.J.Alderton, Inorg. Chem., 21(1982)2297.
4 D.Laurie and P.G.Perkins, Inorg. Chim. Acta, 63(1982)53.
5 C.W.Chiu, A.B.Burg and R.A.Beaudet, Inorg. Chem., 21(1982)1204.
6 M.A.Toft, J.B.Leach, F.L.Himpsl and S.G.Shore, Inorg. Chem., 21(1982)1952.
7 M.L.McKee and W.N.Lipscomb, Inorg. Chem., 21(1982)2846.
8 M.Kameda and G.Kodama, Inorg. Chem., 21(1982)1267.
9 R.L.DeKock and T.P.Fehlner, Polyhedron, 1(1982)521.
10 N.W.Alcock, H.M.Colquhoun, G.Haran, J.F.Sawyer and M.G.H.Wallbridge, J. Chem. Soc., Dalton Trans., (1982)2243.
11 M.A.Nelson, M.Kameda, S.A.Snow and G.Kodama, Inorg. Chem., 21(1982)2898.
12 D.F.Gaines, J.A.Heppert, D.E.Coons and M.W.Jorgenson, Inorg. Chem., 21(1982)3662.
13 J.A.Heppert and D.F.Gaines, Inorg. Chem., 21(1982)4117.
14 D.D.Bray, R.M.Kabbani and E.H.Wong, Acta Crystallogr., B38(1982)957.
15 T.Whelan, P.Brint, T.R.Spalding, W.S.McDonald and D.R.Lloyd, J.Chem. Soc., Dalton Trans., (1982)2469.
16 M.E.O'Neill and K.Wade, Inorg. Chem., 21(1982)461.
17 D.J.Fuller and D.L.Kepert, Inorg. Chem., 21(1982)163.
18 R.B.King, Polyhedron, 1(1982)133.
19 W.E.Geiger, D.E.Brennan and J.L.Little, Inorg. Chem., 21(1982)2529.
20 K.S.Wong, W.R.Scheidt and T.P.Fehlner, J. Am. Chem. Soc., 104(1982)1111.
21 C.P.Marabella and J.H.Enemark, J. Organomet. Chem., 226(1982)57.
22 J.Emri and B.Györi, Polyhedron, 1(1982)673.
23 M.I.Memon, W.F.Sherman and G.R.Wilkinson, J. Raman Spectrosc., 13(1982)96.
24 M.I.Memon, G.R.Wilkinson and W.F.Sherman, J. Mol. Struct., 80(1982)113.
25 R.Bonaccorsi, P.Palla and J.Tomasi, J. Mol. Struct., 87(1982)187.
26 H.Nöth, Z. Naturforsch., 37b(1982)1499.
27 C.J.Dain, A.J.Downs and D.W.H.Rankin, Angew. Chem., Int. Ed. Engl., 21(1982)534.
28 A.I.Sizov and B.M.Bulychev, Russ. J. Inorg. Chem., 26(1981)1421.
29 G.Dell'Amico, F.Marchetti and C.Floriani, J. Chem. Soc., Dalton Trans., (1982)2197.
30 J.A.Marsella and K.G.Caulton, J. Am. Chem. Soc., 104(1982)2361.
31 A.P.Hitchcock, N.Hao, N.H.Werstiuk, M.J.McGlinchey and T.Ziegler, Inorg. Chem., 21(1982)793.
32 M.Y.Darensbourg, R.Bau, M.W.Marks, R.R.Burch, J.C.Deaton and
33 C.A.Ghilardi, S.Midollini and A.Orlandini, Inorg. Chem., 21(1982)4096.
S.Slater, J. Am. Chem. Soc., 104(1982)6961.
34 P.G.Egan and K.W.Morse, Polyhedron, 1(1982)299.
35 U.Mirsaidov, A.Kurbonbekov and M.Khikmatov., Russ. J. Inorg. Chem., 26(1981)1538.
36 A.Kurbonbekov, M.Khikmatov and U.Mirsaidov, Russ. J. Inorg. Chem., 26(1981)1199.
37 L.V.Titov, L.A.Gavrilova, U.Mirsaidov, T.G.Vershinnikova, G.N.Boiko and V.Ya.Rosolovskii, Russ. J. Inorg. Chem., 27(1982)1104.

38 V.D.Makhaev, A.P.Borisov, B.P.Tarasov and K.N.Semenenko, Russ. J. Inorg. Chem., 26(1981)1417.
39 S.G.Shore, S.H.Lawrence, M.I.Watkins and R.Bau, J. Am. Chem. Soc., 104(1982)7669.
40 G.B.Jacobsen and J.H.Morris, Inorg. Chim. Acta, 59(1982)207.
41 G.B.Jacobsen, J.H.Morris and D.Reed, J. Chem. Res.(S), (1982)319.
42 S.J.Andrews, A.J.Welch, G.B.Jacobsen and J.H.Morris, J. Chem. Soc., Chem. Commun., (1982)749.
43 C.E.Housecroft and T.P.Fehlner, Inorg. Chem., 21(1982)1739.
44 J.E.Crook, N.N.Greenwood, J.D.Kennedy and W.S.McDonald, J. Chem. Soc., Chem. Commun., (1982)383.
45 J.Bould, N.N.Greenwood and J.D.Kennedy, J. Chem. Soc., Dalton Trans., (1982)481.
46 T.L.Venable and R.N.Grimes, Inorg. Chem., 21(1982)887.
47 T.L.Venable, E.Sinn and R.N.Grimes, Inorg. Chem., 21(1982)904.
48 M.B.Fischer, D.F.Gaines and J.A.Ulman, J. Organomet. Chem., 231(1982)55.
49 J.Bragin, D.S.Urevig and M.Diem, J. Raman Spectrosc., 12(1982)86.
50 W.K.Pelin, T.R.Spalding and R.P.Brint, J. Chem. Res.(S), (1982)120.
51 M.J.Calhorda and D.M.P.Mingos, J. Organomet. Chem., 229(1982)229.
52 M.J.Calhorda, D.M.P.Mingos and A.J.Welch, J. Organomet. Chem., 228(1982)309.
53 R.Ahmad, J.E.Crook, N.N.Greenwood, J.D.Kennedy and W.S.McDonald, J. Chem. Soc., Chem. Commun., (1982)1019.
54 E.H.Wong and M.G.Gatter, Inorg. Chim. Acta, 61(1982)95.
55 E.H.Wong, M.G.Gatter and R.M.Kabbani, Inorg. Chem., 21(1982)4022.
56 T.L.Venable, E.Sinn and R.N.Grimes, Inorg. Chem., 21(1982)895.
57 J.Bould, J.E.Crook, N.N.Greenwood, J.D.Kennedy and W.S.McDonald, J. Chem. Soc., Chem. Commun., (1982)346.
58 J.Bould, N.N.Greenwood, J.D.Kennedy and W.S.McDonald, J. Chem. Soc., Chem. Commun., (1982)465.
59 S.K.Boocock, J.Bould, N.N.Greenwood, J.D.Kennedy and W.S.McDonald, J. Chem. Soc., Dalton Trans., (1982)713.
60 D.F.Gaines and G.A.Steehler, J. Chem. Soc., Chem. Commun., (1982)122.
61 A.V.Agafonov, L.A.Butman, K.A.Solntsev, A.N.Vinokurov, N.A.Zhukova and N.T.Kuznetsov, Russ. J. Inorg. Chem., 27(1982)35.
62 L.A.Leites, S.S.Bukalov, A.P.Kurbakova, M.M.Kaganski, Yu.L.Gaft N.T.Kuznetsov and I.A.Zakharova, Spectrochim. Acta, 38A(1982)1047.
63 N.T.Kuznetsov, L.A.Zemskova and E.G.Ippolitov, Russ. J. Inorg. Chem., 26(1981)1343.
64 M.A.Beckett, J.E.Crook, N.N.Greenwood, J.D.Kennedy and W.S.McDonald, J. Chem. Soc., Chem. Commun., (1982)552.
65 Y.M.Cheek, N.N.Greenwood, J.D.Kennedy and W.S.McDonald, J. Chem. Soc., Chem. Commun., (1982)80.
66 E.D.Jemmis, J. Am. Chem. Soc., 104(1982)7017.
67 B.Wrackmeyer, Z. Naturforsch., 37b(1982)412.
68 R.L.DeKock, T.P.Fehlner, C.E.Housecroft, T.V.Lubben and K.Wade, Inorg. Chem., 21(1982)25.
69 T.L.Venable, W.C.Hutton and R.N.Grimes, J. Am. Chem. Soc., 104(1982)4716.
70 R.Wilczynski and L.G.Sneddon, Inorg. Chem., 21(1982)506.
71 B. Oh and T.Onak, Inorg. Chem., 21(1982)3150.

72 G.Siwapinyoyos and T.Onak, Inorg. Chem., 21(1982)156.

73 B.Štibr, S.Heřmanek, Z.Janoušek, Z.Plzák, J.Dolanský and J.Plešek, Polyhedron, 1(1982)822.

74 T.P.Hanusa, Polyhedron, 1(1982)663.

75 A.I.Yanovskii, Yu.T.Struchkov, V.N.Kalinin and L.I.Zakharkin, J. Struct. Chem., 23(1982)232.

76 D.C.Busby and M.F.Hawthorne, Inorg. Chem., 21(1982)4101.

77 B.Štibr, J.Plešek and A.Zobáčova, Polyhedron, 1(1982)824.

78 V.S.Mastryukov, E.G.Atavin, A.V.Golubinskii, L.V.Vilkov, V.I.Stanko and Yu.V.Gol'tyapin, J. Struct. Chem., 23(1982)41.

79 V.V.Grushin, T.P.Tolstaya, I.N.Lisichkina and A.N.Vanchikov, Doklady Chem., 264(1982)163.

80 L.I.Zakharkin, A.I.Kovredov, V.A.Ol'shevskaya and Zh.S.Shaugumbekova, J. Organomet. Chem., 226(1982)217.

81 V.V.Grushin, T.B.Tolstaya and I.N.Lisichkina, Doklady Chem., 261(1981)456.

82 E.C.Reynhardt, A.Watton and H.E.Petch, J. Magn. Reson., 46(1982)453.

83 V.I.Bregadze, V.Ts.Kampel, A.Ya.Usyatinsky, O.B.Ponomareva, and N.N.Godovikov, J. Organomet. Chem., 233(1982)C33.

84 G.K.Barker, M.P.Garcia, M.Green, F.G.A.Stone, H.E.Parge and A.J.Welch, J. Chem. Soc., Chem. Commun., (1982)688.

85 A.J.Borelli, J.S.Plotkin and L.G.Sneddon, Inorg. Chem., 21(1982)1328.

86 L.Borodinsky and R.N.Grimes, Inorg. Chem., 21(1982)1921.

87 L.Borodinsky, E.Sinn and R.N.Grimes, Inorg. Chem., 21(1982)1928.

88 W.E.Geiger and D.E.Brennan, Inorg. Chem., 21(1982)1963.

89 R.B.Maynard and R.N.Grimes, J. Am. Chem. Soc., 104(1982)5983.

90 R.N.Grimes, R.B.Maynard, E.Sinn, G.A.Brewer and G.J.Long, J. Am. Chem. Soc., 104(1982)5987.

91 G.K.Barker, M.P.Garcia, M.Green, F.G.A.Stone and A.J.Welch, J. Chem. Soc., Chem. Commun., (1982)46.

92 B.Štibr, Z.Janoušek, K.Baše, J.Dolanský, S.Heřmanek, K.A.Solntsev, L.A.Butman, I.I.Kuznetsov and N.T.Kuznetsov, Polyhedron, 1(1982)833.

93 S.Ya.Dvurechenskaya, V.V.Volkov, S.V.Tkachev and L.S.Den'kina, Russ. J. Inorg. Chem., 27(1982)981.

94 L.I.Zakharkin, V.V.Kobak, A.I.Yanovski and Yu.T.Struchkov, J. Organomet. Chem., 228(1982)119.

95 T.P.Hanusa, J.C.Huffman and L.J.Todd, Polyhedron, 1(1982)77.

96 L.Borodinsky, E.Sinn and R.N.Grimes, Inorg. Chem., 21(1982)1686.

97 Ľ.Mátel, F.Macášek, P.Rajec, S.Heřmanek and J.Plešek, Polyhedron, 1(1982)511.

98 W.C.Kalb, Z.Demidowicz, D.M.Speckman, C.Knobler, RG.Teller and M.F.Hawthorne, Inorg. Chem., 21(1982)4027.

99 G.K.Barker, M.P.Garcia, M.Green, F.G.A.Stone and A.J.Welch, J. Chem. Soc., Dalton Trans., (1982)1679.

100 G.Z.Suleimanov, V.I.Bregadze, N.A.Koval'chuk and I.P.Beletskaya, J. Organomet. Chem., 235(1982)C17.

101 F.Morandini, B.Longato and S.Bresadola, J. Organomet. Chem., 239(1982)377.

102 F.Watari, Inorg. Chem., 21(1982)1442.

103a D.J.Brauer, H.Bürger and G.Pawelke, J. Organomet. Chem., 238(1982)267.

103b W.Kosmus and K.Kalcher, Monatsh., 113(1982)265.

104 H.C.Brown, D.Basavaiah and S.U.Kulkarni, J. Organomet. Chem., 225(1982)63.

105 G.E.Herberich and G.Pampaloni, J. Organomet. Chem., 240(1982)121.

106 J.R.Bews and C.Glidewell, J. Mol. Struct., 90(1982)151.
107 M.M.Kappes, J.S.Uppal and R.H.Staley, Organometallics, 1(1982)1303.
108 J.B.Holbrook, B.C.Smith, C.E.Housecroft and K.Wade, Polyhedron, 1(1982)701.
109 J.D.Odom, S.V.Saari, A.B.Nease, Z.Szafran, and J.R.Durig, J. Raman Spectrosc., 12(1982)111.
110 R.Contreras and B.Wrackmeyer, Spectrochim. Acta, 38A(1982)941.
111 R.L.Tapping, Inorg. Chem., 21(1982)1691.
112 B.Wrackmeyer, Z. Naturforsch., 37b(1982)788.
113 V.Dimitrov, K.-H.Thiele and A.Zschunke, Z. Anorg. Allg. Chem., 494(1982)144.
114 M.V.Garad and J.W.Wilson, J. Chem. Res.(S), (1982)132.
115 U.Sicker, A.Meller and W.Maringgele, J. Organomet. Chem., 231(1982)191.
116 C.Eaborn, N.Retta, J.D.Smith and P.B.Hitchcock, J. Organomet. Chem., 235(1982)265.
117 H.Klusik and A.Berndt, J. Organomet. Chem., 232(1982)C21.
118 H.Klusik and A.Berudt, J. Organomet. Chem., 234(1982)C17.
119 W.Biffar and H.Nöth, Chem. Ber., 115(1982)934.
120 L.R.Thorne and W.D.Gwinn, J. Am. Chem. Soc., 104(1982)3822.
121 D.C.Reuter, L.R.Thorne and W.D.Gwinn, J. Phys. Chem., 86(1982)4737.
122 A.Lötz and J.Voitlander, J. Magn. Reson., 48(1982)1.
123 I.Wilson and H.C.Kelly, Inorg. Chem., 21(1982)1622.
124 P.R.Laurence and C.Thomson, J. Mol. Struct., 88(1982)37.
125 K.H.Scheller, R.B.Martin, B.F.Spielvogel and A.T.McPhail, Inorg. Chim. Acta, 57(1982)227.
126 A.Fox, J.S.Hartman and R.E.Humphries, J. Chem. Soc., Dalton Trans., (1982)1275.
127 D.S.Marynick, L.Throckmorton and R.Bacquet, J. Am. Chem. Soc., 104(1982)1.
128 S.Ferrence, J.Iwamoto, S.Levy, N.Massey, R.Williams and D.R.Martin, Inorg. Chim. Acta, 58(1982)131.
129 G.Schmid, R.Boese and D.Bläser, Z. Naturforsch., 37b(1982)1230.
130 R.H.Cragg and T.J.Miller, J. Organomet. Chem., 235(1982)143.
131 M.Höfler and H.Löwenich, J. Organomet. Chem., 226(1982)229.
132 P.C.Keller, Inorg. Chem., 21(1982)444.
133 P.C.Keller, Inorg. Chem., 21(1982)445.
134 R.H.Cragg and T.J.Miller, J. Organomet. Chem., 235(1982)135.
135 R.H.Cragg and T.J.Miller, J. Organomet. Chem., 232(1982)201.
136 R.H.Cragg, T.J.Miller and D.O'N.Smith, J. Organomet. Chem., 231(1982)C41.
137 H.Nöth, R.Staudigl and H.-U.Wagner, Inorg. Chem., 21(1982)706
138 J.Higashi, A.D.Eastman and R.W.Parry, Inorg. Chem., 21(1982)716.
139 P.Paetzold and C. von Plotho, Chem. Ber., 115(1982)2819.
140 W.R.Nutt and R.L.Wells, Inorg. Chem., 21(1982)2469.
141 W.R.Nutt and R.L.Wells, Inorg. Chem., 21(1982)2473.
142 W.Maringgele, Chem. Ber., 115(1982)3271.
143 W.J.Layton, K.Niedenzu and S.L.Smith, Z. Anorg. Allg. Chem., 495(1982)52.
144 R.C.Taylor and V.D.Dunning, J. Mol. Struct., 95(1982)23.
145 A.Sebestyén, L.Megyeri and V.Vizi, J. Mol. Struct., 89(1982)259.
146 C.H.Yoder and L.A.Miller, J. Organomet. Chem., 228(1982)31.
147 T.G.DiGiuseppe, R.Estes and P.Davidovits, J. Phys. Chem., 86(1982)260.

148 A.I.Cherkesov, Russ. J. Inorg. Chem., 26(1981)1703.

149 V.A.Kulikov, V.V.Ugarov and N.G.Rambidi, J. Struct. Chem., 23(1982)156.

150 S.P.So, J. Mol. Struct., 89(1982)255.

151 D.C.Frost, W.M.Lau, C.A.McDowell and N.P.C.Westwood, J. Phys. Chem., 86(1982)1917.

152 S.Menchetti and C.Sabelli, Acta Crystallogr., B38(1982)1282.

153 P.M.Jeffers and S.H.Bauer, Inorg. Chem., 21(1982)2516.

154 J.F.Sawyer and G.J.Schrobilgen, Acta Crystallogr., B38(1982)1561.

155 E.Bessler and J.Weidlein, Z. Naturforsch., 37b(1982)1020.

156 F.A.Cotton and W.H.Ilsley, Inorg. Chem., 21(1982)300.

157 P.W.France and M.Wadsworth, J. Magn. Reson., 49(1982)48.

158 V.G.Skvortsov, A.K.Molodkin and N.R.Tsekhanskaya, Russ. J. Inorg. Chem., 26(1981)1045.

159 V.G.Skvortsov, A.K.Molodkin and N.R.Tsekhanskaya, Russ. J. Inorg. Chem., 26(1981)1204.

160 B.Kh.Khazikanova, B.A.Beremzhanov, R.F.Savich and V.G.Kalacheva, Russ. J. Inorg. Chem., 26(1981)1671.

161 V.G.Skvortsov, S.A.Mikhailov, A.K.Molodkin, R.S.Tsekhanskii, N.S.Rodionov and O.V.Petrova, Russ. J. Inorg. Chem., 27(1982)885.

162 V.G.Skvortsov, R.S.Tsekhanskii, A.K.Molodkin, V.P.Dolganev and N.S.Rodionov, Russ. J. Inorg. Chem., 27(1982)1370.

163 O.V.Falaleev and E.P.Zeer, J. Mol. Struct., 83(1982)257.

164 M.Jansen and G.Brachtel, Z. Anorg. Allg. Chem., 489(1982)42.

165 G.B.Ansell, M.E.Leonowicz, M.A.Modrick, B.M.Wanklyn and F.R.Wondre, Acta Crystallogr., B38(1982)892.

166 E.M.Reznik, B.F.Dzhurinskii and I.V.Tananaev, Russ. J. Inorg. Chem., 27(1982)118.

167 O.A.Aliev and Dzh.I.Zul'fugarly, Russ. J. Inorg. Chem., 26(1981)1795.

168 G.K.Abdullaev, P.F.Rza-Zade and Kh.S.Mamedov, Russ. J. Inorg. Chem., 27(1982)1037.

169 W.Depmeier and H.Schmid, Acta Crystallogr., B38(1982)605.

170 H.Behm, Acta Crystallogr., B38(1982)2781.

171 X.Solans, M.Font-Albana, J.Solans and M.V.Domenech, Acta Crystallogr., B38(1982)2438.

172 S.Menchetti, C.Sabelli and R.Trosti-Ferroni, Acta Crystallogr., B38(1982)3072.

173 S.Menchetti, C.Sabelli and R.Trosti-Ferroni, Acta Crystallogr., B38(1982)2987.

174 B.Kh.Khazikanova, B.A.Beremzhanov, V.G.Kalacheva and R.F.Savich, Russ. J. Inorg. Chem., 26(1981)1104.

175 I.G.Saiko, G.N.Kononova, K.I.Petrov and A.Ya.Tavrovskaya, Russ. J. Inorg. Chem., 27(1982)190.

176 I.G.Saiko, G.N.Kononova, K.I.Petrov and A.Ya.Tavrovskaya, Russ. J. Inorg. Chem., 26(1981)1732.

177 S.P.So, J. Mol. Struct., 90(1982)29.

178 T.-K.Ha, M.-T.Nguyen and L.G.Vanquickenborne, J. Mol. Struct., 90(1982)99.

179 K.Hennemuth, A.Meller and M.Wojnowska, Z. Anorg. Allg. Chem., 489(1982)47.

180 M.Luthardt, E.Than and G.Marx, Z. Chem., 22(1982)231.

181 J.R.Bews and C.Glidewell, J. Mol. Struct., 89(1982)333.

182 S.L.Emery and J.L.Morrison, J. Am. Chem. Soc., 104(1982)6790.

183 E.H.Wong, M.G.Gatter and R.M.Kabbani, Inorg. Chim. Acta, 57(1982)25.

184 C.A.Young, H. van Willigen and R.F.Lee, Inorg. Chim. Acta, 65(1982)L241.

185 A.J.Markwell, A.G.Massey and P.J.Portal, Polyhedron, 1(1982)134.
186 L.A.Gavrilova, L.V.Titov and V.Ya.Rosolovskii, Russ. J. Inorg. Chem., 26(1981)955.
187 L.A.Gavrilova, L.V.Titov and V.Ya.Rosolovskii, Russ. J. Inorg. Chem., 26(1981)1116.
188 A.G.Massey and P.J.Portal, Polyhedron, 1(1982)319.
189 G.E.Herberich, B.Hessner and D.Söhnen, J. Organomet. Chem., 233(1982)C35.
190 J.M.Schulman, R.L.Disch and M.L.Sabio, J. Am. Chem. Soc., 104(1982)3785.
191 M.C.Böhm, M.Eckert-Maksić, R.Gleiter, G.E.Herberich and B.Hessner, Chem. Ber., 115(1982)754.
192 G.E.Herberich and B.Hessner, Chem. Ber., 115(1982)3115.
193 W.Siebert, J.Edwin and H.Pritzkow, Angew. Chem., Int. Ed. Engl., 21(1982)148.
194 W.Siebert, J.Edwin, H.Wadepohl and H.Pritzkow, Angew. Chem., Int. Ed. Engl., 21(1982)149.
195 M.W.Whiteley, H.Pritzkow, U.Zenneck and W.Siebert, Angew. Chem., Int. Ed. Engl., 21(1982)453.
196 B.La Serna, M.Hernández and J.Fernández Bertrán, J. Mol. Struct., 95(1982)271.
197 F.Alam and K.Niedenzu, J. Organomet. Chem., 240(1982)107.
198 K.Anton and H.Nöth, Chem. Ber., 115(1982)2668.
199 H.Nöth and R.Staudigl, Chem. Ber., 115(1982)813.
200 H.Nöth and R.Staudigl, Chem. Ber., 115(1982)3011.
201 H.Nöth and R.Staudigl, Chem. Ber., 115(1982)1555.
202 J.E.Frey, G.M.Marchand and R.S.Bolton, Inorg. Chem., 21(1982)3239.
203 G.Schmid, S.Amirkhalili, U.Höhner, D.Kampmann and R.Boese, Chem. Ber., 115(1982)3830.
204 S.Amirkhalili, U.Höhner and G.Schmid, Angew. Chem., Int. Ed. Engl., 21(1982)68.
205 S.Amirkhalili, R.Boese, U.Höhner, D.Kampmann, G.Schmid and P.Rademacher, Chem. Ber., 115(1982)732.
206 R.Köster, G.Seidel, S.Amirkhalili, R.Boese and G.Schmid, Chem. Ber., 115(1982)738.
207 R.Köster and G.Seidel, Angew. Chem., Int. Ed. Engl., 21(1982)207.
208 A.Meller, C.Habben, M.Noltemeyer and G.M.Sheldrick, Z. Naturforsch., 37b(1982)1504.
209 A.J.Boulton and C.S.Prado, J. Chem. Soc., Chem. Commun., (1982)1008.
210 R.Allmann, E.Hohaus and S.Olenik, Z. Naturforsch., 37b(1982)1450.
211 R.H.Cragg and T.J.Miller, J. Chem. Soc., Dalton Trans., (1982)907.
212 C.M.Lukehart and M.Raja, Inorg. Chem., 21(1982)2100.
213 E.Hohaus, Z. Anorg. Allg. Chem., 484(1982)41.
214 E.Hohaus, K.D.Klöppel, B.Paschold and H.-R.Schulten, Z. Anorg. Allg. Chem., 493(1982)41.
215 B.Wrackmeyer and R.Köster, Chem. Ber., 115(1982)2022.
216 P.G.M.Wuts and P.A.Thompson, J. Organomet. Chem., 234(1982)137.
217 S.J.Rettig and J.Trotter, Can. J. Chem., 60(1982)2957.
218 K.Andrä and A.Straube, Z. Anorg. Allg. Chem., 490(1982)191.
219 A.Meller and C.Habben, Monatsh., 113(1982)139.
220 C.Habben, W.Maringgele and A.Meller, Z. Naturforsch., 37b(1982)43.

221 H.Binder, W.Diamantikos, K.Dermentzis and H.-D.Hausen, Z. Naturforsch., 37b(1982)1548.

222 B.Gimarc and N.Trinajstić, Inorg. Chem., 21(1982)21.

223 A.Bonny, R.Brewster and A.Welborn, Inorg. Chim. Acta, 64(1982)L3.

224 T.Ishii, M.Shimada and M.Koizumi, Inorg. Chem., 21(1982)1670.

225 K.Hiebl, P.Rogl and M.J.Sienko, Inorg. Chem., 21(1982)1128.

226 K.Yvon and D.C.Johnston, Acta Crystallogr., B38(1982)247.

227 O.Gropen and A.Haaland, Acta Chem. Scand., A36(1982)435.

228 M.C.R.Symons and L.Harris, J. Chem. Soc., Faraday Trans.1, 78(1982)3109.

229 E.B.Lobkovskii, G.L.Soloveichik, A.B.Erofeev, B.M.Bulychev and V.K.Bel'skii, J. Organomet. Chem., 235(1982)151.

230 S.Cuccinella, G.Dozzi and G. del Piero, J. Organomet. Chem., 224(1982)1.

231 G.Dozzi, S.Cuccinella and M.Bruzzone, J. Organomet. Chem., 224(1982)13.

232 K.S.Gavrichev, V.E.Gorbunov and S.I.Bakum, Russ. J. Inorg. Chem., 26(1981)1100.

233 K.S.Gavrichev, V.E.Gorbunov and S.I.Bakum, Russ. J. Inorg. Chem., 26(1981)1551.

234 J.M.Howell, A.M.Sapse, E.Singman and G.Snyder, J. Am. Chem. Soc., 104(1982)4758.

235 A.B.Goel, E.C.Ashby and R.C.Mehrotra, Inorg. Chim. Acta., 62(1982)161.

236 C.M.Cook and L.C.Allen, Organometallics, 1(1982)246.

237 P.H.Kasai, J. Am. Chem. Soc., 104(1982)1165.

238 O.T.Beachley, C.Tessier-Youngs, R.G.Simmons and R.B.Hallock, Inorg. Chem., 21(1982)1970.

239 R.D.Thomas and J.P.Oliver, Organometallics, 1(1982)571.

240 A.F.M.M.Rahman, K.F.Siddiqui and J.P.Oliver, Organometallics, 1(1982)881.

241 M.Barber, D.Liptak and J.P.Oliver, Organometallics, 1(1982)1307.

242 P.R.Schonberg, R.T.Paine, C.F.Campana and E.N.Duesler, Organometallics, 1(1982)799.

243 B.Teclé, P.W.R.Corfield and J.P.Oliver, Inorg. Chem., 21(1982)458.

244 O.Křiž, F.Mareš and B.Čásenský, Coll. Czech. Chem. Commun., 47(1982)384.

245 H.Krause, K.Sille, H.-D.Hausen and J.Weidlein, J. Organomet. Chem., 235(1982)253.

246 P.Pullmann, K.Hensen and J.W.Bats, Z. Naturforsch., 37b(1982)1312.

247 E.Montoneri, L.Giuffre, M.Fornaroli,M.Tempesti and P.M.Spaziante, Bull. Soc. Chim. Fr., I, (1982)211.

248 N.S.Enikolopyan, F.S.D'yachkovskii, Z.M.Dzhabieva, P.E.Matkovskii and A.F.Shestakov, Doklady Chem., 261(1981)535.

249 S.Brumby, J. Chem. Soc., Chem. Commun., (1982)677.

250 W.Kaim, Z. Naturforsch., 37b(1982)783.

251 K.Hayashi, K.-I.Okamoto, J.Hidaka and H.Einaga, J. Chem. Soc., Dalton Trans., (1982)1377.

252 L.V.Serebrennikov, S.B.Osin and A.A.Maltsev, J. Mol. Struct., 81(1982)25.

253 J.S.Uppal and R.H.Staley, J. Am. Chem. Soc., 104(1982)1229.

254 A.B.Kiss, P.Gadő, and G.Keresztury, Spectrochim. Acta, 38A(1982)1231.

255 A.N.Christensen, M.S.Lehmann and P.Convert, Acta Chem. Scand., A36(1982)303.

256 B.N.Ivanov-Emin, G.Z.Kaziev, G.A.Lovetskaya, T.B.Aksenova and B.E.Zaitsev, Russ. J. Inorg. Chem., 26(1981)1661.

257 S.P.Best, R.S.Armstrong and J.K.Beattie, J. Chem. Soc., Dalton Trans., (1982)1655.

258 J.W.Akitt, J. Chem. Soc., Faraday Trans.1, 78(1982)289.

259 J.-Y.Bottero, J.-P.Marchal, J.-E.Poirier, J.Cases and F.Fiessinger, Bull. Soc. Chim. Fr. I, (1982)489.

260 C.A.Fyfe, G.C.Gobbi, J.S.Hartman, J.Klinowski and J.M.Thomas, J. Phys. Chem., 86(1982)1247.

261 A.Wolińska, J. Organomet. Chem., 234(1982)1.

262 S.J.Karlik, G.A.Elgavish, R.P.Pillai and G.L.Eichorn, J. Magn. Reson., 49(1982)164.

263 A.G.Davies, Z.Florestańczyk, A.Lusztyk and J.Lusztyk, J. Organomet. Chem., 229(1982)215.

264 D.W.James and R.L.Frost, Austral. J. Chem., 35(1982)1793.

265 J.F.McIntyre, R.T.Foley and B.F.Brown, Inorg. Chem., 21(1982)1167.

266 B.N.Ivanov-Emin, V.I.Rybina, N.U.Venskovskii, G.Z.Kaziev and B.E.Zaitsov, Russ. J. Inorg. Chem., 26(1982)1730.

267 N.M.Karayannis, L.L.Pytlewski and C.M.Mikulski, Inorg. Chim. Acta, 64(1982)L97.

268 J.S.Uppal and R.H.Staley, J. Am. Chem. Soc., 104(1982)1235.

269 L.-O.Öhman and S.Sjöberg, Acta Chem. Scand., A36(1982)47.

270 R.A.Hancock and S.T.Orszulik, Polyhedron, 1(1982)313.

271 S.Murakami and T.Yoshino, Polyhedron, 1(1982)405.

272 J.L.Atwood, D.C.Hrncir, R.Shakir, M.S.Dalton, R.D.Priester and R.D.Rogers, Organometallics, 1(1982)1021.

273 D.Hoebbel, G.Garzó, K.Ujszászi, G.Engelhardt, B.Fahlke and A.Vargha, Z. Anorg. Allg. Chem., 484(1982)7.

274 G.Engelhardt, D.Hoebbel, M.Tarmak, A.Samoson and E.L.Lippmaa, Z. Anorg. Allg. Chem., 484(1982)22.

275 W.Schiller, D.Müller and G.Scheler, Z. Chem., 22(1982)44.

276 M.T.Melchior, D.E.W.Vaughan and A.J.Jacobson, J. Am. Chem. Soc., 104(1982)4859.

277 W.Gessner, D.Müller, H.-J.Behrens and G.Scheler, Z. Anorg. Allg. Chem., 486(1982)193.

278 K.-B.Plötz and Hk.Müller-Buschbaum, Z. Anorg. Allg. Chem., 488(1982)38.

279 Z.R.Kadyrova and N.A.Sirazhiddinov, Russ. J. Inorg. Chem., 27(1982)109.

280 K.-I.Machida, G.-Y.Adachi, M.Shimada and M.Koizumi, Acta Crystallogr., B38(1982)889.

281 M.C.Saine, E.Husson and H.Brusset, Spectrochim. Acta, 38A(1982)25.

282 M.G.Barker, P.G.Gadd and S.C.Wallwork, J. Chem. Soc., Chem. Commun., (1982)516.

283 K.-B.Plötz and Hk.Müller-Buschbaum, Z. Anorg. Allg. Chem., 491(1982)253.

284 L.S.Dent Glasser, A.P.Henderson and R.A.Howie, Acta Crystallogr., B38(1982)24.

285 A.N.Christensen, M.S.Lehmann and A.Wright, Acta Chem. Scand., A36(1982)779.

286 J.-Y.Bottero, D.Tchoubar, J.M.Cases and F.Fiessinger, J. Phys. Chem., 86(1982)3667.

287 F. von Lampe, D.Müller, W.Gessner, A.-R.Grimmer and G.Scheler, Z. Anorg. Allg. Chem., 489(1982)16.

288 A.A.Carey and E.P.Schram, Inorg. Chim. Acta, 59(1982)75.

289 A.A.Carey and E.P.Schram, Inorg. Chim. Acta, 59(1982)79.

290 A.A.Carey and E.P.Schram, Inorg. Chim. Acta, 59(1982)83.

291 L.A.Curtiss, Inorg. Chem., 21(1982)4100.

292 R.Domesle and R.Hoppe, Z. Anorg. Allg. Chem., 495(1982)16.
293 D.Ehrt, M.Krauss, C.Erdmann and W.Vogel, Z. Chem., 22(1982)315.
294 Å.Sterten, K.Hamberg and I.Maeland, Acta Chem. Scand., A36(1982)329.
295 J.Koch, C.Hebecker and H.John, Z. Naturforsch., 37b(1982)1659
296 T.Fleischer and R.Hoppe, Z. Anorg. Allg. Chem., 492(1982)83.
297 T.Fleischer and R.Hoppe, Z. Anorg. Allg. Chem., 493(1982)59.
298 R.Domesle and R.Hoppe, Z. Anorg. Allg. Chem., 495(1982)27.
299 G.T.Cheek and R.A.Osteryoung, Inorg. Chem., 21(1982)3581.
300 J.S.Wilkes, J.A.Levisky, R.A.Wilson and C.L.Hussey, Inorg. Chem., 21(1982)1263.
301 E.Perenthaler, H.Schulz and A.Rabenau, Z. Anorg. Allg. Chem., 491(1982)259.
302 K.Peters, A.Simon, E.-M.Peters, H.Kühnl and B.Kozlowski, Z. Anorg. Allg. Chem., 492(1982)7.
303 K.Hildebrandt, P.G.Jones, E.Schwarzmann and G.M.Sheldrick, Z. Naturforsch., 37b(1982)1129.
304 U.Thewalt, K.Berhalter and P.Müller, Acta Crystallogr., B38(1982)1280.
305 H.Nöth, R.Rurlander and P.Wolfgardt, Z. Naturforsch., 37b(1982)29.
306 M.Dalibart, J.Derouault, P.Granger and S.Chappelle, Inorg. Chem., 21(1982)1040.
307 M.Dalibart, J.Derouault and P.Granger, Inorg. Chem., 21(1982)2241.
308 U.Thewalt and F.Stollmaier, J. Organomet. Chem., 228(1982)149
309 F.P.Emmenegger, P.Favre and M.Kluczkowskii, Inorg. Chem., 21(1982)2934.
310 A.Manteghetti and A.Potier, Spectrochim. Acta, 38A(1982)141.
311 H.A.Hjuler, A.Mahan, J.H. von Barner and N.J.Bjerrum, Inorg. Chem., 21(1982)402.
312 A.I.Morozov and O.A.Solovkina, Russ. J. Inorg. Chem., 27(1982)186.
313 A.I.Morozov, O.A.Solovkina and V.I.Evdokimov, Russ. J. Inorg. Chem., 27(1982)1172.
314 J.Justness, E.Rytter and A.F.Andresen, Polyhedron, 1(1982)393
315 U.Thewalt and F.Stollmaier, Angew. Chem., Int. Ed. Engl., 21(1982)133.
316 C.Petrovic, G.Mamantov, M.Sørlie, M.H.Lietzke and G.P.Smith, J. Phys. Chem., 86(1982)4598.
317 R.Kniep, P.Blees and W.Poll, Angew. Chem., Int. Ed. Engl., 21(1982)386.
318 G.Cordier, E.Czech and H.Schäfer, Z. Naturforsch., 37b(1982)1442.
319 R.Nesper, H.G. von Schnering and J.Curda, Z. Naturforsch., 37b(1982)1514.
320 G.Cordier and H.Schäfer, Z. Anorg. Allg. Chem., 490(1982)136.
321 G.Cordier, G.Savelsberg and H.Schäfer, Z. Naturforsch., 37b(1982)975.
322 A.Drašner and Ž.Blažina, Z. Naturforsch., 37b(1982)1225.
323 M.T.Barlow, C.J.Dain, A.J.Downs, G.S.Laurenson and D.W.H. Rankin, J. Chem. Soc., Dalton Trans., (1982)597.
324 V.E.Gorbunov, K.S.Gavrichev and S.I.Bakum, Russ. J. Inorg. Chem., 27(1982)891.
325 V.E.Gorbunov, K.S.Gavrichev and S.I.Bakum, Russ. J. Inorg. Chem., 27(1982)1082.
326 A.Haaland and J.Weidlein, Acta Chem. Scand., A36(1982)805.
327 J.C.Vanderhooft, R.D.Ernst, F.W.Cagle, R.J.Neustadt and T.H.Cymbaluk, Inorg. Chem., 21(1982)1876.

328 J.R.Durig, C.B.Bradley and J.D.Odom, Inorg. Chem., 21(1982)1466.
329 J.R.Durig and K.K.Chatterjee, J. Mol. Struct., 95(1982)105.
330 W.R.Nutt, R.E.Stimson, M.F.Leopold and B.H.Rubin, Inorg. Chem., 21(1982)1909.
331 E.Avsar, Acta Chem. Scand., A36(1982)627.
332 J.R.Durig and K.K.Chatterjee, J. Mol. Struct., 81(1982)167.
333 D.Doby and G.Lucazeau, J. Mol. Struct., 79(1982)419.
334 M.C.Saine, E.Husson and H.Brusset, Spectrochim. Acta, 38A(1982)19.
335 J.Köhler and R.Hoppe, Z. Anorg. Allg. Chem., 495(1982)7.
336 L.F.Chernysh, A.P.Nakhodnova and V.G.Pitsyuga, Russ. J. Inorg. Chem., 26(1981)1443.
337 K.-B.Plötz and Hk.Müller-Buschbaum, Z. Anorg. Allg. Chem., 484(1982)153.
338 F.Zonnevijlle, C.M.Tourné and G.F.Tourné, Inorg. Chem.,
339 G.F.Tourné, C.M.Tourné and A.Schouten, Acta Crystallogr., B38(1982)1414.
340 M.V.Mokhosoev, L.V.Tumurova and L.G.Maksimova, Russ. J. Inorg. Chem., 27(1982)62.
341 S.P.Petrosyants and Yu.A.Buslaev, Doklady Chem., 263(1982)102.
342 R.Corigli, F.Secco and M.Venturini, Inorg. Chem., 21(1982) 2992.
343 I.Waller, T.Halder, W.Schwarz and J.Weidlein, J. Organomet. Chem., 232(1982)99.
344 V.L.Pecoraro, G.B.Wong and K.N.Raymond, Inorg. Chem., 21(1982)2209.
345 D.T.Haworth, J.W.Beery and M.Das, Polyhedron, 1(1982)9.
346 A.Mazurier, M.Guittard and S.Jaulmes, Acta Crystallogr., B38(1982)379.
347 M.Julien-Pouzol, S.Jaulmes and C.Dagron, Acta Crystallogr., B38(1982)1566.
348 Z.D.Melikova and P.G.Rustamov, Russ. J. Inorg. Chem., 27(1982)749.
349 V.M.Golovei, V.A.Oblonchik and M.I.Golovei, Russ. J. Inorg. Chem., 26(1981)1067.
350 L.Dogguy-Smiri and N.-H.Dung, Acta Crystallogr., B38(1982)372.
351 S.Jaulmes, E.Godlewski, M.Palazzi and J.Etienne, Acta Crystallogr., B38(1982)1707.
352 J.Dugué and M.Guittard, Acta Crystallogr., B38(1982)2368.
353 B.Krebs, D.Voilker and K.-O.Stiller, Inorg. Chim. Acta, 65(1982)L101.
354 L.A.Popkova, E.N.Guryanova and A.F.Volkov, J. Mol. Struct., 83(1982)341.
355 H.-J.Haupt, F.Neumann and B.Schwab, Z. Anorg. Allg. Chem., 485(1982)234.
356 T.Okuda, N.Yashida, M.Hiura, H.Ishihara, K.Yamada and H.Negita, J. Mol. Struct., 96(1982)169.
357 R.W.H.Small and I.J.Worrall, Acta Crystallogr., B38(1982)86.
358 R.W.H.Small and I.J.Worrall, Acta Crystallogr., B38(1982)250.
359 P.I.Fedorov, N.S.Malova and I.Yu.Rodimtseva, Russ. J. Inorg. Chem., 27(1982)1350.
360 G.Gerlach, W.Hönle and A.Simon, Z. Anorg. Allg. Chem., 486(1982)7.
361 R.G.Ling and C.Belin, Acta Crystallogr., B38(1982)1101.
362 U.Frank-Cordier, G.Cordier and H.Schäfer, Z. Naturforsch., 37b(1982)119.
363 U.Frank-Cordier, G.Cordier and H.Schäfer, Z. Naturforsch., 37b(1982)127.

364 T.Fjeldberg, A.Haaland, R.Seip, Q.Shen and J.Weidlein, Acta Chem. Scand., A36(1982)495.

365 C.S.Lin and D.G.Tuck, Can. J. Chem., 60(1982)699.

366 C.Peppe and D.G.Tuck, Polyhedron, 1(1982)549.

367 M.J.Taylor, D.G.Tuck and L.Victoriano, Can. J. Chem., 60(1982)690.

368 I.Sinclair and I.J.Worrall, Can. J. Chem., 60(1982)695.

369 D.C.Bradley and Y.C.Gao, Polyhedron, 1(1982)307.

370 C.Peppe, D.G.Tuck and L.Victoriano, J. Chem. Soc., Dalton Trans., (1982)2165.

371 B.Perlmutter-Hayman, F.Secco and M.Venturini, J. Chem. Soc., Dalton Trans., (1982)1945.

372 G.Biedermann and D.Ferri, Acta Chem. Scand., A36(1982)611.

373 P.J.Brown, J.Ellis and R.N.Sylva, J. Chem. Soc., Dalton Trans., (1982)1911.

374 Yu.B.Yakovlev and L.I.Ravlenko, Russ. J. Inorg. Chem., 28(1981)1424.

375 S.P.Sinha, T.T.Pakkanen, T.A.Pakkanen, and L.Niinistö, Polyhedron, 1(1982)355.

376 I.V.Tananaev and N.V.Kadoshnikova, Russ. J. Inorg. Chem., 27(1982)1193.

377a N.V.Filatkina, N.V.Porotnikov and K.I.Petrov, Russ. J. Inorg. Chem., 27(1982)939.

377b N.V.Porotnikov, O.I.Kondratov, K.I.Petrov and L.N.Margolin, Russ. J. Inorg. Chem., 27(1982)25.

378 O.V.Kudin, V.A.Efremov, V.K.Trunov and Yu.A.Velikodnyi, Russ. J. Inorg. Chem., 26(1982)1464.

379 D.Michel and A.Kahn, Acta Crystallogr., B38(1982)1437.

380 L.Gastaldi, D.Carré and M.P.Pardo, Acta Crystallogr., B38(1982)2365.

381 N.Asriat, J.P.Laval, B.Frit and G.Roult, Acta Crystallogr., B38(1982)1088.

382 S.V.Malabenskii and L.P.Tsyganok, Russ. J. Inorg. Chem., 27(1982)1276.

383 M.Schulte-Kellinghaus and V.Krämer, Z. Naturforsch., 37b(1982)390.

384 G.Cuveiller, J.C.Champarnaud-Mesjard, G.Gaudreau and S.Turrell, J. Mol. Struct., 79(1982)345.

385 M.A.Khan and D.G.Tuck, Acta Crystallogr., B38(1982)803.

386 J.Wignacourt, G.Mairesse, P.Barbier, A.Lorriaux-Rubbens and F.Wallart, Can. J. Chem., 60(1982)1747.

387 S.J.David and B.S.Ault, J. Phys. Chem., 86(1982)4618.

388 M.Veith and R.Rösler, Angew. Chem., Int. Ed. Engl., 21(1982)858.

389 M.Veith and R.Rösler, J. Organomet. Chem., 229(1982)131.

390 M.I.Bruce, J.K.Walton, M.L.Williams, S.R.Hall, B.W.Skelton and A.H.White, J.Chem. Soc., Dalton Trans., (1982)2209.

391 R.Zilber, A.Durif and M.T.Averbuch-Pouchot, Acta Crystallogr., B38(1982)1554.

392 A.K.Molodkin, Yu.E.Bogatov, V.I.Moskalenko, T.N.Susanina, I.G.Zhuravleva, V.V.Kurilkin and Z.N.Melo, Russ. J. Inorg. Chem., 27(1982)797.

393 G.Eulenberger, Monatsh., 113(1982)859.

394 E.Yu.Peresh, L.S.Shpyrko, V.I.Tkachenko, V.I.Starosta, A.A.Kikineshi, K.A.Batori and V.S.D'ordyai, Russ. J. Inorg. Chem., 27(1982)268.

395 S.Del Bucchia, J.C.Jumas, E.Philippot and M.Maurin, Z. Anorg. Allg. Chem., 487(1982)199.

396 M.B.Babanly, N.A.Kulieva and I.S.Sattar-Zade, Russ. J. Inorg. Chem., 27(1982)1340.

397 M.B.Babanly and A.A.Kuliev, Russ. J. Inorg. Chem., 27(1982)1336.

398 M.B.Babanly and A.A.Kuliev, Russ. J. Inorg. Chem., 27(1982)867.

399 K.Henrick, R.W.Matthews, B.L.Podejma and P.A.Tasker, J. Chem. Soc., Chem. Commun., (1982)118.

400 D.L.Hughes and M.R.Truter, J. Chem. Soc., Chem. Commun., (1982)727.

401 Yu.B.Yakovlev and R.I.Ravlenko, Russ. J. Inorg. Chem., 27(1982)649.

402 R.Faggiani and I.D.Brown, Acta Crystallogr., B38(1982)2473.

403 S.Blanco, J.B.Casas, A.Sanchez, J.Sordo, J.M.F.Solis and M.Gayoso, J. Chem. Res.(S), (1982)328.

404 T.V.Khomutova, A.A.Fakeev, B.M.Nirsha, O.I.Evstaf'eva, V.F.Chuvaev, V.M.Agre and N.P.Kozlova, Russ. J. Inorg. Chem., 27(1982)943.

405 Ch.Burschka, Z. Anorg. Allg. Chem., 485(1982)217.

406 R.Lösch, Ch.Hebecker and Z.Ranft, Z. Anorg. Allg. Chem., 491(1982)199.

407 J.Glaser, Acta Chem. Scand., A36(1982)451.

408 J.Glaser and G.Johansson, Acta Chem. Scand., A36(1982)125.

409 H.W.Rotter and G.Thiele, Z. Naturforsch., 37b(1982)995.

410 J.Glaser, P.L.Goggin, M.Sandström and V.Litsko, Acta Chem. Scand., A36(1982)55.