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Chapter 3

ELEMENTS OF GROUP 3

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3.1 BORON

3.1.1 Boranes

A fully numerical Hartree-Fock approach has been developed for diatomic molecules, leading to an improved Hartree-Fock limit for BH.[1] A set of full CI calculations has been reported for BH, using a double-zeta plus polarisation basis. 99% of the correlation energy is obtained by using SDTQ-CI calculations at the geometries examined.[2]

Preliminary *ab initio* calculations of the potential surface of BH_2^+ suggest that bent (C_{2v} or near C_{2v}) geometries are the most

$$B^+(^1S) + H_2 \rightarrow BH^+(B'^2\Sigma^+) + H \qquad ...(1)$$

$$B^+(^1S) + H_2 \rightarrow BH^+(A^2\pi) + H \qquad ...(2)$$

favoured for the intermediates in reactions (1) and (2).[3]

A new method has been proposed for the canonical numbering, stereochemical descriptors and unique linear notations for polyhedral clusters. Examples were given of the application of this to boranes, borane anions, metal carbaborane complexes etc.[4]

A systematic structural nomenclature described for polyboron hydrides and similar systems has now been extended to include capped polyhedral systems,[5] non-closed structures, their hetero- (including metallo-) analogues and derivatives.[6]

Ab initio calculations (using a 3-21G basis set) on the course of reaction of ethylene with $H_3B.OH_2$ (a model for hydroboration in ether solvents) show that the mechanism is essentially an S_N2 displacement of the solvent by the olefin. H_2O plays no major role in transition state, but BH_3 never becomes wholly free.[7]

A method for determining B_2H_6 in organic solvents has been devised from a study of the coulometric titration of B_2H_6-ether and B_2H_6-DMF complexes.[8]

The reactions of B_2H_6 with aromatic heterocycles, containing one or more six-membered rings with only one nitrogen per ring, have been studied. Hydroboration frequently occurs, *via* intermediate borane adduct formation.[9]

Calculations on a series of boranes, from B_2H_6 up to $B_{20}H_{16}$, suggest that in their crystals the potential energy barriers for large amplitude molecular reorientations are of the same order of magnitude as the lattice energies.[10]

^{11}B n.m.r. data on quadrupolar relaxation in B_3H_7X show that the relaxation times fall in the sequence $X = NMe_3 < NMe_2H < NMeH_2 < NH_3 < CH_3CN$, and $X = Cl^- < NCS^- < BH_3CN^- < CN^-$.[11]

Protonation of boranes and carbaboranes, B_4H_{10}, B_nH_{n+4} (n = 2,5 or 6), $C_2B_nH_{n+2}$ (n = 3,4,5 or 10), CB_5H_9, $B_nH_n^{2-}$ (n = 4,6 or 7), has been studied by MNDO calculations. The calculated proton affinities, and protonated structures, were reported. The calculations predict B-B edge protonation for B_6H_{10} and 1,6-$C_2B_4H_6$; B-B-B face protonation for $B_6H_6^{2-}$, $B_7H_7^{2-}$, 2,4-$C_2B_5H_7$ and 1,12-$C_2B_{10}H_{12}$; proton attack yielding a three-centre B-H_2 bond for B_2H_6, B_4H_{10} and B_5H_9; carbon protonation for 1,5-$C_2B_3H_5$ and 2-CB_5H_9; and formation of a two-centre B-H bond for $B_4H_4^{2-}$. The sites of protonation correlate with the electronic structures of the substrates. Some 3-21G *ab initio* calculations were also performed.[12]

Pentaborane(9), in the presence of catalytic amounts of $PdBr_2$, reacts with various alkenes (e.g. ethylene, propylene, 1-butene) to give excellent yields of 1- and 2-substituted alkenylpentaboranes. These are the first such reactions in which Pd(II) acts as a catalyst in the absence of an additional oxidising agent.[13]

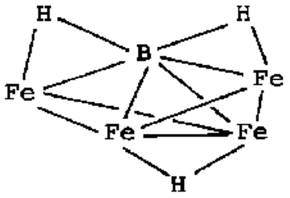
Rearrangements of various deuterium-labelled derivatives of B_5H_8 in Et_2O were studied by ^{11}B and ^2H n.m.r. Two pathways for intramolecular exchange were identified at temperatures below 65°C. One allows for movement from bridging to basal terminal positions, while the second (of higher energy) allows migration from basal terminal positions to the apex of the molecule. Exchange involving the apex of pentaborane appears only to occur when a substituent is one of the migrating groups.[14]

A one-step synthesis has been reported for 1,2'-$[B_5H_8]_2$, a $PtBr_2$-catalysed dehydrodimerisation of B_5H_9 in essentially quantitative yield. Only one of three possible isomers was produced, suggesting that both electrophilic attack and oxidative addition of pentaborane(9) at the metal are important.[15]

3.1.2 Borane Anions and their Metallo-derivatives

Nb_2Cl_{10} and $NbCl_4$ react with hydridotris- and hydridobis(1-pyrazolyl)borate salts to produce several Nb(V) and Nb(IV) (1-pyrazolyl)borates, e.g. $K\{NbCl_5[HB(pz)_3]\}$, $Nb_2Cl_6[H_2B(pz)_2]_2$ etc. νBH modes were assigned from i.r. spectra, and structures were suggested, based on ^1H n.m.r.[16]

$B_2H_6Fe_2(CO)_6$ reacts with excess $Fe_2(CO)_9$ in pentane at 25°C to form a new ferraborane, $HFe_4(CO)_{12}BH_2$. This was characterised by single crystal X-ray crystallography. This contains an $HFe_4(CO)_{12}$ "butterfly" fragment with BH_2 bridging the "wing-tips", (1). The structure is closely similar to the isoelectronic $HFe_4(CO)_{12}CH$. The compound can be described as an arachno-, four-atom cluster with an interstitial boron atom, or as a saturated, 62-electron complex with a BH_2 ligand contributing five electrons. The orientation of the BH_2 with respect to the iron "butterfly" is explicable in terms of the special properties of the frontier orbitals of the Fe_4 fragment.[17]



(1)

The compounds $M(BH_3Me)_4$, where M = Zr,Th,U or Np, have been synthesised, using reaction (3). The molecular structures were

$$MCl_4 + 4LiBH_3Me \xrightarrow{C_6H_5Cl} M(BH_3Me)_4 + 4LiCl \qquad ...(3)$$

determined by X-ray diffraction. All are monomeric, with tetrahedral coordination by four BH_3Me groups, via tridentate hydrogen bridges. The M-B distances are: Zr, 2.335±0.003Å; Th, 2.56±0.05Å; U, 2.49±0.02Å; Np, 2.487±0.006Å.[18]

The possibility of a general synthesis of lithium organotrihydroborates, $LiRBH_3$, was investigated by reactions of organolithium compounds with $BH_3.THF$, $BH_3.SMe_2$ or $BH_3.NMe_3$. RLi with $BH_3.THF$ give all possible $LiR_{4-n}BH_n$, except that n = 0 is not found for bulky R. With $BH_3.SMe_2$, RLi forms higher proportions of $LiRBH_3$, especially at low temperatures, e.g. $LiMe_2CHBH_3$ and $LiMe_3CBH_3$ in good yield, although some $LiBH_4$ is always present. $BH_3.NMe_3$ only reacts with RLi above 80°C, but $LiPhBH_3.TMEDA$ and $LiPhCH_2BH_3.TMEDA$ could be formed.[19]

U.v. photolysis of solutions containing BH_4^-, BH_3CN^- or $(Bu^tO)_3BH^-$ in liquid NH_3 leads to electron detachment from the anions, and proton loss, producing borane radical anions e.g.

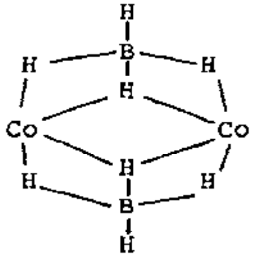
$\cdot BH_3^-$.[20]

Ab initio calculations on $LiBH_4$ and $NaBH_4$ are consistent with a non-rigid model for these molecules.[21]

Exposure of $Na^+BH_4^-$ or $Na^+BD_4^-$ to ^{60}Co γ-rays at 77K produces a species with large proton hyperfine coupling to two equivalent protons (or deuterons) and a small coupling to two other protons (deuterons), together with a strongly anisotropic coupling to ^{11}B. These are consistent with the formation of a $\cdot BH_4$ radical of C_{2v} symmetry (cf. D_{2d} geometry for the isoelectronic $\cdot CH_4^+$).[22]

A single-crystal neutron diffraction study of $Hf(BH_4)_4$ shows that the molecule is monomeric, with rigorous T_d symmetry, and tridentate BH_4^- coordination. The following bond lengths were determined: Hf-B, 2.281(8)Å; Hf-H_{br}, 2.130(9)Å; B-H_{br}, 1.235(10)Å; B-H_t, 1.150(19)Å.[23]

$Co_2(BH_4)_2[Ph_2P(CH_2)_5PPh_2]_2 \cdot 0 \cdot 5C_6H_6$, one of several intermediates in reactions involving Co^{II}, $NaBH_4$ and α, ω-bis(diphenylphosphino)-alkanes, is a phosphine-bridged binuclear species in which each of the two BH_4 groups also bridges the two Co(I) units by a new type of bond: M-H-BH_2-H-M. A further unusual feature of the structure is that one hydrogen atom of each of the two central BH_2 groups also acts as a bridging ligand. This central unit is thus (2).[24]



(2)

$\Delta G^\ddagger$ for the fluxional process in $[(MeO)_3P]_2CuBH_4$ was estimated from data on $[(MeO)_3P]_2CuBH_3(CO_2Et)$. The difference in $\Delta G^\ddagger$ for the copper complex, compared to the bidentate vanadium complex is thought to be due to differences in B-H bond strengths rather than differences in geometry.[25]

CO_2 and COS react with $(R_3P)_2Cu(\eta^2$-$BH_4)$ under very mild conditions to form $(R_3P)_2Cu(\eta^2$-OXCH), where X = O or S.[26]

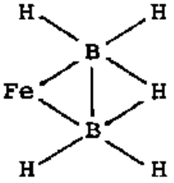
An X-ray structure determination for $Sc\{\eta$-$C_5H_3(SiMe_3)_2\}_2(\mu$-$H)_2BH_2$ confirms the bidentate bonding of BH_4^-, with the Sc...B distance

2.52(3)Å. The analogues with Y or Yb are also bidentate, but rapid bridging $\rightleftharpoons$ terminal hydrogen exchange takes place. For La, Pr, Nd and Sm the BH_4^- units are tridentate.[27]

Lanthanum and cerium tetrahydroborates can be prepared from $LaCl_3$ or $CeCl_3$ and $NaBH_4$ in an aromatic solvent. Non-solvated $M(BH_4)_3$ (M = La or Ce) can be prepared from tetrahydrofuran adducts *in vacuo* at 100-110°C.[28] Lanthanide chlorides react with $NaBH_4$ in 1,2-dimethoxyethane (DME) to form crystalline $NaLn(BH_4)_4.4DME$ (Ln = Gd or Tb), amorphous $NaLn(BH_4)_4.3DME$ (Ln = Dy, Ho, Er or Tm), and the ether-soluble $NaLn(BH_4)_4.4DME$ (Ln = Yb or Lu).[29]

A theoretical study has been made of $B_2H_7^-$: *ab initio* m.o. calculations at the MP2/6-31G* level confirm that a single, bent B-H-B bridge is preferred. However, other details of the experimental structure are not reproduced very well.[30]

The valence-level photoelectron spectrum of $Cp(OC)_2Fe\text{-}B_2H_5$ has been measured in the gas-phase with HeI and NeI radiation. The assignment proposed was based on spectra of model compounds, and also m.o. calculations on the compound, compared with $(OC)_4Fe(C_2H_4)$ and free $B_2H_5^-$ and C_2H_4. The $B_2H_5^-$ ligand can be considered as a side-bound $B_2H_4^{2-}$, as a π-ligand, with a proton in the π-lobe opposite the metal, (3). The proton has a significant effect on the bonding, as the Fe-B interaction is quite different from the Fe-C interaction in the C_2H_4 complex.[31]



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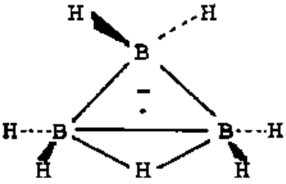
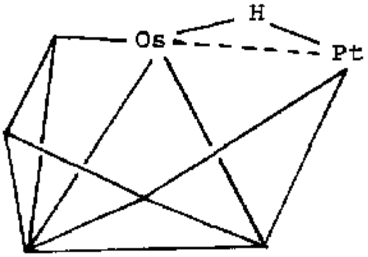


(4)

Thermal transformations have been studied for the Na^+ and NMe_4^+ salts of $B_3H_8^-$, in the range 100-280°C. Formation of lower members of the series of polyhedral ions, e.g. $B_6H_6^{2-}$, requires higher temperatures than for higher members, e.g. $B_{12}H_{12}^{2-}$.[32] Kinetics of thermal decomposition have been measured for NaB_3H_8 at 80-100°C under static isothermal conditions. The solid-phase decomposition follows a first-order law, releasing B_5H_9 and H_2, in the molar ratio 2:1.[33] The radical anion of triborane(7), $B_3H_7^{\wedge}$, is generated by hydrogen abstraction from $B_3H_8^-$. It was studied by e.s.r., and MNDO-UHF calculations. The structure is believed to be cyclic, of C_{2v} symmetry, with a single bridging hydrogen, (4).[34]

$Os(CO)ClH(PPh_3)_3$ reacts under mild conditions with arachno-$B_3H_8^-$ or nido-$B_5H_8^-$ to form the first-known air-stable polyhedral osmaboranes: arachno-$[(HOsB_3H_8)(CO)(PPh_3)]$ and nido-$[(OsB_5H_9)(CO)(PPh_3)_2]$ respectively. The ^{11}B and ^1H n.m.r. properties of these are very similar to those of the iridium analogues, arachno-$[(H_2IrB_3H_8)(PPh_3)_2]$ and nido-$[(IrB_5H_8)(CO)(PPh_3)_2]$. Mild thermolysis of the OsB_5H_9 compound produces nido-$[OsB_4H_8](CO)(PPh_3)_2$.[35]

The first X-ray diffraction characterisation of a polyhedral metallaborane osmium compound has also been reported, for $(Ph_3P)_2(CO)\overline{Os(PhMe_2P)ClH}PtB_5H_7$. This has a seven-vertex nido-osmaplatinaborane cluster, based on a dodecahedron, with one 5-connected vertex missing, and the metal atoms at adjacent (2,7) positions in the five-membered open face, linked by Os-H-Pt bridging, (5).[36]



(5)

Bonding in the closo-boron hydride anions, $B_nH_n^{2-}$, where n = 5 to 12, can be considered in terms of the sum of all possible, n(n-1)/2, boron-boron interactions. The bonding energy, u, between each pair of boron atoms was only taken to depend on the internuclear distance, d, by the relationship:

$$u = \frac{1}{d^2} - \frac{1}{d} .$$

The scheme can rationalise the details of molecular geometry and can give an assessment of the relative importance of possible intramolecular rearrangement pathways.[37] MNDO calculations were also carried out on $B_nH_n^{2-}$ (for n = 6 to 12) to assess the accuracy of a recent theory of their electronic structure and bonding (A.J.Stone, Mol. Phys., 41(1980)1339). The assumptions of this theory were fully supported by the results, and the theory can also be applied to closo-carbaborane systems.[38]

[μ-1,2-(MeCO.O)-2-H-2,10-$(PPh_3)_2$-closo-$ClIrB_8H_7$], an Ir(III) complex, has a structure containing a closo-ten-vertex cluster, following Wade's rules. This has a bicapped Archimedean square antiprismatic structure. The Ir(III) contributes three orbitals and two electrons, and occupies a 5-connected vertex. This should be compared with the unusual iso-nido- cluster structure of the previously-reported species [$(PPh_3)(Ph_2PC_6H_4)\{IrB_8H_8(OMe)$-$C(OH)\}$].[39]

Polyhedron edge-bonding or -antibonding characteristics of the non-degenerate tenth and eleventh molecular orbitals of D_{3h} tricapped trigonal-prismatic 9-atom homonuclear clusters were used to rationalise the edge lengths in such clusters. The skeletal bonding is strongest, and the clusters closest to spherical, for 20 skeletal bonding electrons, as in, for example, $B_9H_9^{2-}$.[40]

The thermal decomposition of $(H_3O)_2B_{10}Cl_{10}$ has been re-examined under dynamic vacuum. The major 9-vertex products are $H_2B_9Cl_7$, HB_9Cl_8 and B_9Cl_9. At ambient temperature, no differences in the ^{11}B n.m.r. chemical shifts of the halogen-substituted boron atoms in HB_9Cl_8 can be resolved at 29.8MHz. Some other products of decomposition include $B_{10}Cl_{10}$, $B_{11}Cl_{11}$ and $B_{12}Cl_{12}$. Mass spectral data show that the species B_nCl_n, where n = 13 to 20, are also present.[41]

The new heterobimetallic, "B-frame", compound nido-[$(Me_3P)_2Pt(Ph_3P)(Ph_2P\overline{C_6H_4)HIrB}_9H_{10}$] has been prepared, with an overall yield of 40%, from nido-decaborane. The structure was established by X-ray diffraction. It is the first nido-eleven-vertex cluster, with non-adjacent metal atoms to be so characterised.[42]

The crystal structure of $[Et_4N^+][B_{11}H_{10}SMe_2^-]$ shows that it has eleven-vertex, closo-geometry similar to those reported for $B_{11}H_9Se_3^{2-}$, $C_2Me_2B_9H_9$ etc. (including metalla-derivatives). Hence, closo-, C_{2v}, geometry is adopted by all those eleven-vertex polyhedral boranes, carbaboranes and metallacarbaboranes with the correct number of electrons.[43]

The molecular structure of the unusual seventeen-vertex macropolyhedral trimetallaborane, $(PhMe_2P)_4Pt_3B_{14}H_{16}$, may be interpreted in terms of either a formal *pentadecahapto*-complex of a 7,7'-bis(*arachno*-heptaboranyl)-type ligand, coordinated η^4, η^5 and η^7 to three metal centres, or a *nido*-type 2,7,10-trimetallaundecaborane cluster linked to an *iso*-*arachno*-6,8-dimetallanonaborane cluster, having three adjacent PtBPt vertices in common.[44]

Heating *nido*-$B_9H_{12}^-$ under reflux with $[Os(CO)_3Cl_2]_2$ in CH_2Cl_2 leads to edge fusion of two borane units to produce *anti*-$[B_{19}H_{21}]^-$. The osmium compound probably forms an intermediate metallaborane.[45]

3.1.3 Carba- and other Non-metal Heteroboranes

The magnitude of the $^1J(^{11}B^1H)$ coupling constants in *closo*-carbaboranes can be correlated with structural characteristics such as the number of adjacent cage carbon atoms and the cage "umbrella" angle. Both of these appears to contribute significantly to changes in the observed spin-coupling constants, hence smaller "umbrella" angles give larger $^1J(^{11}B^1H)$ values.[46]

Gas-phase pyrolysis of $1,5\text{-}C_2B_3H_5$ in a hot/cold reactor (400°C/0°C) gave a complex mixture of products. Major ones were a boron-boron bonded dimer, $2{:}2'\text{-}[1,5\text{-}C_2B_3H_4]_2$ and a trimer, $2{:}2',3'{:}2''\text{-}[1,5\text{-}C_2B_3H_4][1',5'\text{-}C_2B_3H_3][1'',5''\text{-}C_2B_3H_4]$. However, a number of previously unknown species were also identified: a B-C bonded dimer, $1{:}2'\text{-}[1,5\text{-}C_2B_3H_4]_2$, two B-B/B-C linked trimers $2{:}2',1'{:}2''$- and $2{:}2',3'{:}1''\text{-}[1,5\text{-}C_2B_3H_4][1',5'\text{-}C_2B_3H_3][1'',5''\text{-}C_2B_3H_4]$, and a new tetracarbon *nido*-carbaborane, $C_4B_7H_{11}$. Similar studies on the pyrolysis of $1,6\text{-}C_2B_4H_6$ showed only polymeric products, but a mixture of $1,5\text{-}C_2B_3H_5$ and $1,6\text{-}C_2B_4H_6$ gave a good yield of $2{:}2'\text{-}[1',5'\text{-}C_2B_3H_4][1,6\text{-}C_2B_4H_5]$.[47]

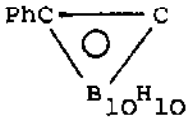
The adduct $Me_3N.5\text{-}BrC_2B_5H_6$ undergoes quantitative halogen exchange with CH_2Cl_2, forming $5\text{-}ClC_2B_5H_6$.[48]

Decaborane(14) reacts with sodium nitrite in THF to form $[9\text{-}THF\text{-}6\text{-}NO_2\text{-}B_{10}H_{12}]^-$. Protonation of this with concentrated H_2SO_4 or dilute HCl gave the azaboranes $6\text{-}NB_9H_{12}$ or $4\text{-}NB_8H_3$ respectively. The former yields adducts $9\text{-}L\text{-}6\text{-}NB_9H_{12}$, with L = Me_2S, MeCN or Ph_3P. Reduction, using $LiAlH_4$ in THF, of $9\text{-}MeCN\text{-}6\text{-}NB_9H_{12}$ gave the anion $6\text{-}NB_9H_{13}^-$. An analogous series of reactions starting from $KHSO_3$ gave $6\text{-}SB_9H_{11}$ and $4\text{-}SB_8H_{12}$, while Na_2SeO_3 formed $7,8\text{-}Se_2B_9H_9$. The structure of $4\text{-}NB_8H_{13}$ was confirmed by X-ray diffraction.[49]

Cis-3-hexene reacts with 6-SB_9H_{11}, forming 9-C_6H_{13}-6-SB_9H_{10}. This in turn reacts with additional *cis*-3-hexene at higher temperatures to give multiple hydroboration in high yield.[50] Alkyl isocyanides and $B_9H_{11}E$ (where E = S or Se) react at room temperature to give initially a mixture of two isomeric $B_9H_{11}E.CNR$ compounds. One of these reacted further to produce a good yield of the carbaborane derivative $B_9H_9ECNH_2R$. $B_9H_{11}S$ reacts with NaCN, giving Na[$B_9H_{11}S.CN$]. Passage of the latter through an acidic ion-exchange column converted it to $B_9H_9SCNH_3$.[51]

Infrared spectra were reported for solid complexes of *o*- and *m*-$B_{10}Cl_{10}C_2H_2$ with O- and N-bases. These could be related to the CH...O and CH...N hydrogen-bonding characteristics.[52]

Cyclic compounds containing two symmetrically-placed 1,2-dicarba*closo*dodecaboranyl or two 7,8-dicarbaundecaborate(10) fragments have been synthesised. These have -S-S- or -S-CH_2-CH_2-S- bridges (undegraded species) or -S-CH_2-S- or -S-CH_2-CH_2-S- bridges (degraded species).[53]



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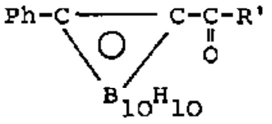


(*7*)

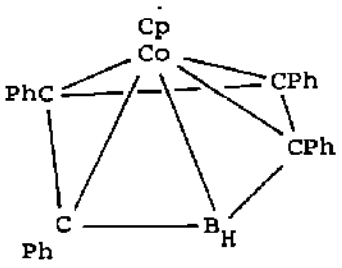
C-Lithiumcarbaboranes react with LnI_2 (where Ln = Sm, Eu or Yb) to form RLnI, where R = (*6*). These in turn react with Me_3SiCl to give trimethylsilylcarbaboranes and with R'CO_2H to give (*7*).[54]

Thermolysis of 7,8-$C_2B_9H_{13}$ gives a 10% yield of iso-$C_4B_{18}H_{22}$. ^{11}B n.m.r. spectra confirmed the structure previously suggested for this, i.e. 3-(8'-*nido*-5,6-$C_2B_8H_{11}$)-1,2-$C_2B_{10}H_{11}$.[55]

3.1.4 Metallo-heteroboranes

The borane adduct, BH_3.THF, and the cobaltacycle Cp(Ph_3P)CoC_4Ph_4 interact to give the *nido*-cobaltacarbaborane, 3,4,5,6-Ph_4-1,3,4,5,-6-CpCoC_4BH, (*8*), in a yield of 20%. This suggests a new general route to carbon-rich metallocarbaboranes.[56]

$K_2C_8H_8$ and VCl_3 react with the *nido*-carbaborane ion $[2,3\text{-}Et_2C_2B_4H_5]^-$ in THF at 0°C to give $(\eta^8\text{-}C_8H_8)V(Et_2C_2B_4H_4)$. X-ray diffraction shows that the C_8H_8 is an η^8-planar system: it is the first example of such for a first row transition metal other



(8)

than titanium. The stability of this compound can be related to the ability of $R_2C_2B_4H_4{}^{2-}$ ligands to stabilise unusual organometallic structures and metal-hydrocarbon bonding modes.[57]

Thermally-generated iron atoms react with toluene and the small carbaborane 2,3-$Et_2C_2B_4H_6$ at low temperatures to give the (arene)-ferracarbaborane 1-(η^6-MeC_6H_5)Fe-2,3-$Et_2C_2B_4H_4$. The expected sandwich structure was confirmed by X-ray diffraction.[58]

Iron(II) chloride and $C_8H_8{}^{2-}$ in THF react with $Et_2C_2B_4H_5{}^-$ forming a 1,3,5-cyclooctatriene complex, (η^6-C_8H_{10})Fe($Et_2C_2B_4H_4$), and 2 minor products, (η^6-C_6H_6)Fe($Et_2C_2B_4H_4$) and ($C_{16}H_{18}$)Fe($Et_2C_2B_4H_4$). The main product was characterised by i.r., mass, ^{11}B, ^1H and ^{13}C n.m.r. spectra, and by X-ray diffraction of the C,C'-dimethyl homologue. The metallocarbaborane fragment consists of a 7-vertex FeC_2B_4 pentagonal-bipyramidal cage, as expected.[59]

(η^6-C_8H_{10})Fe($Et_2C_2B_4H_4$) reacts in turn with benzene and other arenes in the presence of $AlCl_3$, to give the air-stable crystalline (η^6-arene)Fe($Et_2C_2B_4H_4$). X-ray diffraction shows that the arene ring is planar, centred over the iron atom, and parallel to the C_2B_3 ring of the carbaborane ligand. (η^6-C_8H_{10})Fe($Et_2C_2B_4H_4$) reacts with N,N,N',N'-tetramethyl-1,2-diaminoethane, with loss of apical boron, and formation of (η^6-C_8H_{10})Fe($Et_2C_2B_3H_5$), containing a planar carbaborane ligand.[60]

Crystals of 3-η-cyclopentadienyl-1,2-dimethyl-1,2-dicarba-3-cobalta-closo-octaborane, 1,2-Me_2-3,1,2-(η-C_5H_5)$CoC_2B_5H_5$, are monoclinic, belonging to the space group $P2_1/n$. The cyclopentadienyl-substituted cobaltacarbaborane cage has closed, dodecahedral-type geometry, with the C and Co adjacent. This agrees with the structure proposed from spectroscopic data.[61]

The molecular structure of 3':2-[2',4'-$C_2B_5H_6$][1,8,5,6-(η-C_5H_5)-$Co_2C_2B_5H_6$] has been determined by single crystal X-ray diffraction.

This confirms the structure proposed from spectroscopic results, i.e. a two-cage complex with a 1,8,5,6-$(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_6$ cobaltacarbaborane unit linked to a 2',4'-$C_2B_5H_6$ cage via a two-centre B-B single bond. The metalla-fragment is based on a tricapped trigonal prism, while the 2',4'-$C_2B_5H_6$ is based on a pentagonal bipyramid.[62]

Several products have been reported from the reaction of $IrCl(PPh_3)_3$ with the arachno-anion $CB_8H_{13}^-$. One of these was shown to be a novel closo-iridium(III) species, 1-(PPh_3)-2-H-2,2-$(PPh_3)_2$-2,10-$IrCB_8H_8$. Comparison with related species indicates that several pathways are possible for such cage-closure reactions, and that the presence of a varying number of cage-carbon atoms is valuable in elucidating such processes.[63]

Nido-5,6-$C_2B_8H_{12}$ can be used to prepare the new compounds nido-9-$(\eta\text{-}C_5H_5)$-7,8,9-$C_2NiB_8H_{11}$; nido-9-$(\eta\text{-}C_5H_5)$-$\mu_{10,11}$-(Ph_3PAu)-7,8,9-$C_2NiB_8H_{10}$ and closo-1,3-$(\eta\text{-}C_5H_5)_2$-1,2,3,4-$CrCCrCB_8H_{10}$. The structures were determined by X-ray diffraction. The last compound has a short Cr-Cr distance (2.272(2)Å) - evidence for multiple bonding between the chromium atoms in this dimetallacarbaborane.[64]

$Pt_2(\mu\text{-COD})(PEt_3)_4$ reacts with nido-5,6-$C_2B_8H_{12}$ in diethyl ether at room temperature to produce [9-H-9,9-$(Et_3P)_2$-$\mu_{10,11}$-H-7,8,9-$C_2PtB_8H_{10}$]. This forms orthorhombic crystals, belonging to the space group $P2_12_12_1$. The cage structure is close to that of a nido-icosahedron, with a $\overline{\mathrm{CCPtBB}}$ open face. The B-B bond is thought to be hydrogen-bridged, but the hydrogen atom was not located. Thermolysis of this compound leads to loss of H_2, and formation of [9-H-9,10-$(Et_3P)_2$-7,8,9-$C_2PtB_8H_9$]. This formally platinum(II) species shows distortion towards a closed octadecahedral structure.[65]

Several new chromium complexes of carbaboranes have been prepared. Thus $Et_4C_4B_8H_8^{2-}$ and $CrCl_2$, with $Na^+C_5H_5^-$ in cold THF form the red paramagnetic $CpCr[Et_4C_4B_8H_8]$, together with an unstable, purple isomer of this. Aerial oxidation of $CpCr[Et_4C_4B_8H_8]$ gives the yellow, unstable $CpCr[Et_4C_4B_7H_7]$, and a small quantity of a green isomer of this. X-ray diffraction of red $CpCr[Et_4C_4B_8H_8]$ and green $CpCr[Et_4C_4B_7H_7]$ showed that they had 13-vertex and 12-vertex nido-geometries respectively. Each formally has 2n+1 skeletal electrons, appearing to violate Wade's rules (which require 2n+4 for nido-geometry). This problem can be overcome by assuming that the deficiency of 3-electrons is localised at the chromium atom, making it formally a 15-electron system.[66]

The complexes $(PR_3)_2NiCl_2$ react with *nido*-7,8-, *nido*-7,9- or *nido*-2,9-$C_2B_9H_{11}{}^{2-}$ to produce the corresponding icosahedral bis(phosphine)nickelacarbaboranes in good yield. Heating *closo*-3,3-(triarylphosphine)$_2$-3,1,2-$NiC_2B_9H_{11}$ compounds in benzene solution at 80°C gave the corresponding [*closo*-3,8-(triarylphosphine)$_2$-3-H-3,1,2-$NiC_2B_9H_{11}$] *via* interchange of phosphine and hydrido ligands. Several routes were found for the preparation of dimeric [*closo*-{3-(μ-CO)-8-PPh_3-3,1,2-$NiC_2B_9H_{11}$}$_2$]. This was characterised by single-crystal X-ray diffraction, showing that it contains a metal-metal bond (2.477(2)Å) and 2 metal-bridging carbonyl groups.[67]

$[(PEt_3)RhC_2B_9H_{10}]_2$ can be prepared from $(PEt_3)Rh(COD)Cl$ and $Cs_2[7\text{-}(7'\text{-}7',8'\text{-}C_2B_9H_{11})\text{-}7,8\text{-}C_2B_9H_{11}]$ under reflux. The product was shown to contain two icosahedral rhodacarbaborane fragments joined symmetrically at three vertices. The Rh-Rh distance (2.725(1)Å) is in the range expected for a single bond, hence there are 4 bonds between the two icosahedra. N.m.r. parameters were reported for the compound.[68]

$[Ph_3PH]^+$[*closo*-3-Ph_3P-3,3-Br_2-3,1,2-$RhC_2B_9H_{11}$]$^-$ can be prepared from BBr_3 and *closo*-3,3-$(Ph_3P)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$. It forms triclinic crystals, space group $P\bar{1}$. The rhodacarbaborane is approximately octahedral about the rhodium atom.[69]

$RhCl(PPh_3)_3$ and *nido*-$B_{10}H_{12}CNH_3$ in the presence of $Bu^n{}_4NOH$ give $[Bu^n{}_4N]$[*closo*-2,2-$(Ph_3P)_2$-2-H-1-(NH_2)-2,1-$RhCB_{10}H_{10}$]. Heating this in methanol converts it to a new orange compound. X-ray diffraction showed this to be the $Bu^n{}_4N^+$ salt of an NH_2 bridged Rh-H-Rh anion dimer containing two $RhCB_{10}H_{10}$ units.[70]

Closo-1-Me-1,2-$C_2B_{10}H_{11}$ reacts with two equivalents of $Co(PEt_3)_4$ at room temperature in toluene yielding 1-Me-4-(Et_3P)-$\mu_{4\text{ or }6\text{ or }7}$-{$Co(PEt_3)_2$-μ-$(H)_2$}-1,2,4-$C_2CoB_{10}H_{10}$. The polyhedral framework is shown to be that of a distorted docosahedron, with carbon atoms in 4- and 5-, and Co(4) in a 6-connectivity vertex, adjacent to both cage carbon-atoms. The $Co(PEt_3)_2$ unit lies *exo* to the polyhedron, in a bridging position, Co(4)-B(7).[71]

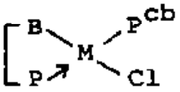
Trans-$[P_2{}^{cb}MCl_2]$, where M = Pd or Pt; P^{cb} = *o*-$HCB_{10}H_{10}CCH_2PPh_2$, readily undergo intramolecular metallation through the B-H bonds of the carbaborane cage to form exocyclic compounds with the unit

$\overset{\longrightarrow}{\text{P-C-C-B-M}}$, i.e. (9a) and (9b), where $\left(\begin{smallmatrix}\text{B}-\\ \text{P}\rightarrow\end{smallmatrix}\right.$ = (10).[72]

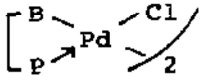
Carbaboranyl derivatives of lanthanides have been prepared from

$$(\text{RCCLi})\text{B}_{10}\text{H}_{10} + \text{LnCl}_3.3\text{THF} \rightarrow [(\text{R-CC-})\text{B}_{10}\text{H}_{10}]_n\text{LnCl}_{3-n}.m\text{THF} \quad \ldots(4)$$

lithium derivatives of carbaboranes and $\text{LnCl}_3.3\text{THF}$, equation (4), where Ln = La, Tm or Yb; n = 1-3; m = 1-5.[73]



(9a)



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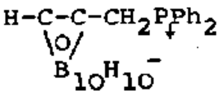


(10)

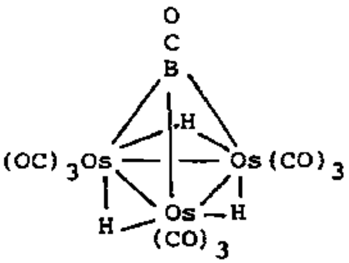
3.1.5 Compounds containing B-C Bonds

The reactivity of borane carbonyl, BH_3CO, has been compared with that of CH_3CO^+. The products are the (carbonyl)trihydroborate anions, $\text{BH}_3\text{C(O)X}^-$, where X = Cl^-, H^-, R^-, OR^-, NR_2^-, O^{2-}. The stabilities of this series are in the order: X = Cl < H < R < OR < NR_2 < O.[74]

The insertion of boron into an Os-CO bond can be achieved by reaction (5), in which both B_2H_6 and $\text{BH}_3.\text{NEt}_3$ must be present.

$$(\mu\text{-H}_2)\text{Os}_3(\text{CO})_{10} + \tfrac{1}{2}\text{B}_2\text{H}_6 \xrightarrow[\text{CHCl}_3]{\text{BH}_3.\text{NEt}_3} (\mu\text{-H})_3(\text{CO})_9\text{Os}_3\text{BCO} + \text{H}_2 \quad \ldots(5)$$

The structure is (11), with approximately C_{3v} symmetry. The BCO group is close to linearity, with a short B-C distance, suggestive of B→CO back-bonding, although this is not reflected in the νCO wavenumber, which is rather high (2120 cm^{-1}).[75]



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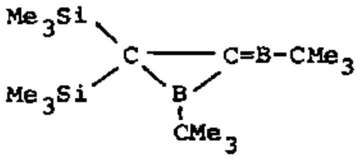


(12)

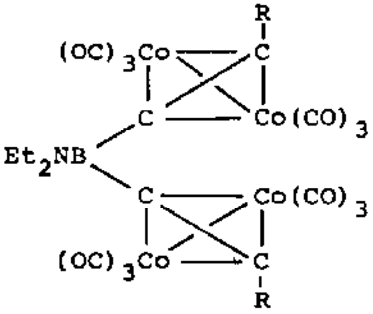
The reaction of 1,1-bis(tert-butylchloroboryl)-2,2-bis(trimethylsilyl)ethene with Na/K alloy in boiling pentane gives a 60%

yield of (12), the first compound containing a B=C double bond. The evidence for this came from n.m.r., especially the chemical shift of the boron atom. In addition, the Raman spectrum contained bands at 1675 cm^{-1} and 1715 cm^{-1}, with an intensity ratio of 4:1, assigned to $\nu(^{11}B{=}C)$ and $\nu(^{10}B{=}C)$ respectively.[76]

$Co_2(CO)_8$ reacts with bis(alkynyl)boranes, forming dicobalthexacarbonyl η^2-alkyne complexes with boryl substituents (13), where R = Me or CMe_3.[77]

Crystals of tetrasodium tetra-μ_3-hydrido-tetrakis(trimethylborate)diethyl ether solvate, $[NaBMe_3H]_4.Et_2O$, are monoclinic, space group $P2_1/m$. The Na and H atoms form a cubane-like structure. Each hydrogen is bonded to the boron of one BMe_3 group, forming a larger tetrahedron of boron atoms.[78]

Compounds containing the very bulky $(Me_3Si)_3C$ (=Tsi) group attached to boron have been prepared, e.g. (Tsi)B$(OMe)_2$ and (14). The latter, with NaOH, gives (Tsi)B$(OH)_2$, while with MeLi, (Tsi)BMe_2 is formed. (Tsi)$AlCl_3$ and (Tsi)Ga(OH)Me were also reported.[79]



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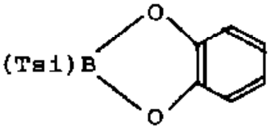


(14)

The compounds BAr_3, where Ar = phenyl, o-tolyl or mesityl, form 1:1 coloured complexes with TCNE. The triarylborane donates π-electrons from the phenyl ring to a vacant antibonding orbital of TCNE.[80]

Correlations of o-, m-, p-, and C(1) carbon resonances in phenylboranes, PhBXY, have been reported. The observed ^{13}C chemical shifts of para-carbons in such compounds show that shielding decreases in the order NHR ~ NR_2 > SR > OR > organyls > halogens. The reverse trend is found for the C(1) ^{13}C chemical shifts.[81]

Borane complexes and arylmagnesium halides react to produce arylborohydrides in good yield. These are readily hydrolysed to aryl boronic acids, (aryl)$B(OH)_2$, where aryl = phenyl or p-X-C_6H_4, (X = Me, MeO, Cl, Br etc.). This constitutes a very convenient synthesis for such compounds.[82]

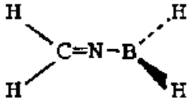
Na[BH_3CN] and HCl in tetrahydrofuran give mainly Na[BH_3CNBH_2CN]. In Me_2S, however, a quantitative yield of "BH_2CN" was produced. The "BH_2CN" in Me_2S exists as monomeric and dimeric adducts, in equilibrium with oligomers. Amines convert these to BH_2CN.amine adducts, while LiCN forms $LiBH_2(CN)_2$.[83]

The ^1H n.m.r. spectra of $[(CH_3C_5H_4)U(\mu\text{-}NCBH_3)]_n$ in non-coordinating solvents such as CH_2Cl_2 can best be explained in terms of temperature-dependent equilibria involving the two rapidly interconverting pseudo-tetrahedral isomers: $(CH_3C_5H_4)_3U(\eta^3\text{-}H_3BCN)$ and $(CH_3C_5H_4)_3U(NCBH_3)$.[84]

The kinetics and mechanism has been investigated for the hydrolysis of several cyano(pyrrolyl-1)borates in aqueous media, e.g. cyanophenyl(pyrrolyl-1)borate, cyano(tripyrrolyl-1)borate and cyanohydro(pyrrolyl-1)borate hydrolyse via two kinds of reaction: (a) a special H^+-catalysed reaction, and (b) an S_N1 mechanism, independent of the concentration of H^+.[85]

3.1.6 Compounds containing B-N, B-P or B-As Bonds

Ab initio calculations on methyleniminoborane, $H_2C{=}N{-}BH_2$, show that a linear, orthogonal form, (15), is preferred over the planar form, (16), by about 50 kJ mol^{-1}. This compares with the isoelectronic $H_2B{-}O{-}BH_2$, for which the planar form is preferred. This shows the importance of B-N π-bonding, since the planar form would have a formally single B-N bond, with a lone pair of electrons localised at the N.[86]



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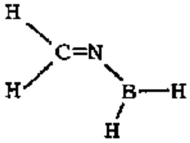
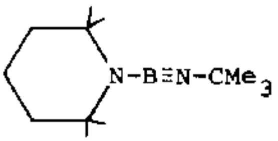
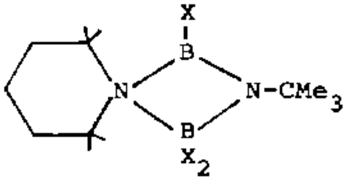


(16)

An amino-imino-borane, (17), can be prepared in good yield by a three-stage reaction. It dimerises quite rapidly, but can be stored as a monomer in solution for several weeks. Addition of BCl_3 or BBr_3 forms four-membered cyclic internal coordination complexes, (<u>18</u>), X = Cl or Br.[87]



(<u>17</u>)

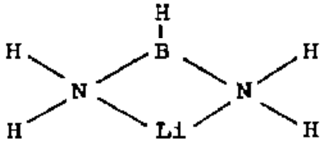


(<u>18</u>)

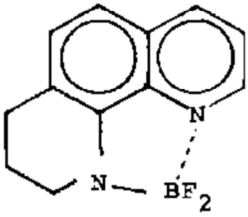
M.o. calculations suggest that $N(BH_2)_3$ is thermodynamically stable, the preferred conformation having two $N(BH_2)$ units coplanar, and the third perpendicular to them. However, dimers would be more stable than the monomer, especially with bridging hydrogen atoms. Calculations on the species $B_6(NH_2)_6$ suggest that a planar B_6 ring should be preferred.[88]

There is some evidence for the formation of boron imides, ArB=NAr (where Ar = Ph, 2-Me-C_6H_4, mesityl or C_6F_5), as intermediates in reactions of the diarylazidoboranes Ar_2BN_3.[89]

Ab initio calculations on $[LiBH(NH_2)_2]^+$ show that the bridged structure (<u>19</u>) should be the most stable.[90]



(<u>19</u>)



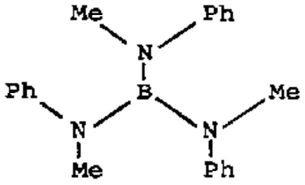
(<u>20</u>)

The u.v. spectrum of (<u>20</u>) confirms the presence of the B...N coordinate bond. X-ray diffraction shows that the B...N distance of 162.9(7) pm is only 8.6% longer than that for the formal single bond also present in the molecule, (150.0(6) pm).[91]

An improved synthesis has been reported for $(H_2NBH_2)_x$ - by the thermal decomposition of ammonia-borane in a pyrolysis tube attached to a commercial sublimer to avoid contamination by $H_3N.BH_3$. The product was characterised by X-ray powder diffraction, ^{11}B F.T. n.m.r. and i.r. spectra.[92]

Natural-abundance ^{15}N n.m.r. measurements on $B(NHMe)_3$ have given an estimate of $^1J(^{15}N^{11}B)$ for this molecule ($\geq$-45±2Hz).[93]

Tris(methylanilido)borane, (<u>21</u>), crystallises in the rhombohedral space group R3. The C_2BN plane is twisted by 37.1° with respect to the BN_3 plane. The B-N bond length (144.8(3) pm) is at the upper limit of BN bond lengths in other triaminoborane systems.[94]



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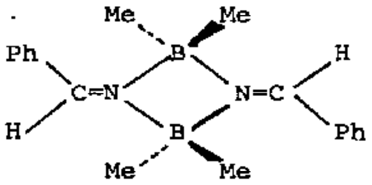
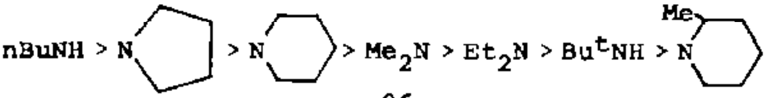


(22)

$B(N=CBu^t_2)_3$ contains "paddle-wheel" shaped monomers, with the $B(NC)_3$ and NCC_2 planes perpendicular to each other, as expected for maximum N$\overset{\ldots}{=}$B π-bonding and minimum Bu^t___Bu^t repulsions. The B-N bond distance is 1.39Å. $(PhCH=NBMe_2)_2$, prepared from benzonitrile and tetramethydiborane (2:1 molar ratio), forms centrosymmetric crystals, containing (22), with a B-N distance of 1.59Å.[95]

Phenyl isocyanate reactions with 27 aminoboranes, $PhB(NR_2)X$, where X = NR_2, NHR, OR, SR or halogen, show that the relative migratory abilities of groups attached to boron are in the order:



; and also RS > RNH > R_2N > OR, Ph or halogen.[96]

^{13}C n.m.r. was used to study the effect of substituents on the free enthalpy of rotation about the B-N bond for the series of compounds $PhB(NMe_2)X$ and $PhB(NPr^i_2)X$ (where X = F, Cl, Br, OMe or SEt). When NR_2 is small - the barrier to rotation is governed mostly by the mesomeric and inductive effect of X. When NR_2 is bulky, the steric effect of X is more important. The rotational barrier decreases with increase in the bulk of NR_2. The rotational barrier results mainly from p_π-p_π N→B bonding, except when NR_2 is very bulky.[97]

The synthesis of $PhB(SEt)NR_2$ has been reported, e.g. equation (6), where R = Me, Pr^i, Bu^s; R_2 = $-CH_2CHMe(CH_2)_3-$ or $-CHMe(CH_2)_4-$.

$$PhB(SEt)_2 + R_2NH \rightarrow PhB(SEt)NR_2 + EtSH \qquad \ldots(6)$$

^{13}C n.m.r. data are consistent with restricted rotation about the

$B{-}NR_2$ bond.[98]

The e.s.r. spectrum of $Et_3N^+{-}\bar{B}H_2{\cdot}$ shows that it is non-planar at the boron atom.[99]

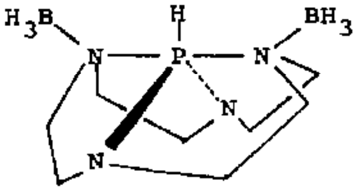
Ab initio calculations have been carried out on $BH_3.NH_3$, using several different basis sets. The electron-correlated Møller-Plesset perturbation method, carried out to the third order (MP3), with double-zeta polarised quality basis sets, gave a computed geometry very close to that recently reported from microwave data. Electron correlation is needed for a proper description of the B-N distance.[100]

The rotational barrier in $BH_3.NH_3$ was calculated by second-order perturbation theory using an ab initio bond-orbital method with experimental geometries, and the Pople STO-3G basis sets, and compared to CH_3CH_3. Despite their very different electronic structures, for both molecules the barrier is due chiefly to vicinal interactions arising from exchange-overlap repulsion between localised bonds having a closed-shell structure.[101]

Charge distributions were calculated for alkylboranes and alkylamines and their adducts with (respectively) NH_3, and BH_3 by four different methods: (i) CNDO-MO-SCF method; (ii) Jolly and Perry procedure; (iii) MNDO method; (iv) modified Sanderson method. All gave reasonable results for the isolated alkyl compounds, but only (iv) gave even fair agreement with experiment for the adducts.[102]

E.s.r. and multinuclear -(^1H, ^{10}B, ^{11}B, ^{14}N) ENDOR spectroscopy were used to identify radical products of single electron transfer from $LiBEt_3H$, e.g. (23).[103]

(23)



(24)

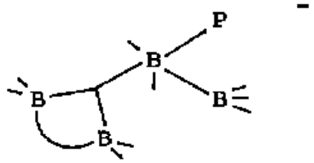
$NaBH_4$ and elemental sulphur in ammonia, primary, secondary and tertiary amines liberate hydrogen gas, and formation of the aminoboranes $R_{3-n}H_nN.BH_3$, where n = 0-3. $NaBH_4$ reacts with carbon disulphide in tertiary amines to form $R_3N.BH_3$.[104]

The bis(borane) adduct of the cyclic phosphorane is shown to have the structure (24). The complex is extremely stable, and it is the first compound for which the pattern $H_3B-N-P-N-BH_3$ has been observed.[105]

Trimethylphosphine and B_4H_{10}, in 1:1 molar ratio, react in THF at -90°C to -70°C, to give $Me_3P.BH_3$, $THF.B_3H_7$ and $[H_2B(THF)_2]^+B_3H_8^-$. Very little $Me_3P.B_3H_7$ was formed. The reaction was then carried out in Me_2O, Et_2O and CH_2Cl_2, and the product distribution patterns compared. The reactions can be rationalised in terms of previous suggestions about the mechanisms of B_4H_{10} cleavage reactions.[106]

A detailed analysis has been given of the infrared and Raman spectra of $CH_3CH_2PH_2.BH_3$, $CH_3CH_2PD_2.BH_3$, $CH_3CH_2PH_2.BD_3$ and $CH_3CH_2PD_2.BD_3$. Both *gauche* and *trans* rotational isomers were seen in fluid states. Bands from the more stable *trans* conformer were assigned in terms of C_s symmetry.[107]

Excess trimethylphosphine and hexaborane(10) form the species "B_6H_{10}". This was shown to consist of a mixture of $B_2H_4.2PMe_3$, $B_4H_6.4PMe_3$ and $B_3H_5.3PMe_3$.[108]



(25)

$B_4H_9.PMe_3^-$ was formed by the reaction of $B_4H_9^-$ and trimethylphosphine in THF. The new anion is stable below 0°C. N.m.r. data suggest a non-rigid trigonal pyramid structure, with the phosphine attached to the apical boron, (25).[109]

$Cp(CO)_2(L)M-AsMe_2$, where M = Mo or W; L = CO or PMe_3, and $BH_3.THF$ form $Cp(CO)_2(L)M-AsMe_2.BH_3$. The products were characterised by ^1H, ^{11}B n.m.r. and infrared spectroscopy.[110]

3.1.7 Compounds containing B-O, B-S or B-Se Bonds

SCF-CI and second-order MBPT calculations were used to study interactions of $B(1s^22s^22p:{}^2P)$ with H_2O. The pathway (7) proceeds with only a small (<12 kcal.mol^{-1}) barrier in the $B.OH_2 \rightarrow HBOH$

$$B + H_2O \rightarrow B.OH_2 \rightarrow HBOH \rightarrow BO(X^2\Sigma) + H_2 \qquad ...(7)$$

step. The formation of BO($A^2\pi$) + H_2 requires much higher barriers.[111] Configuration-interaction calculations were reported for the first 3 doublet states of BO_2. These gave excellent agreement with experimental data, and the position of the $C^2\Sigma_g^+$ state was predicted.[112]

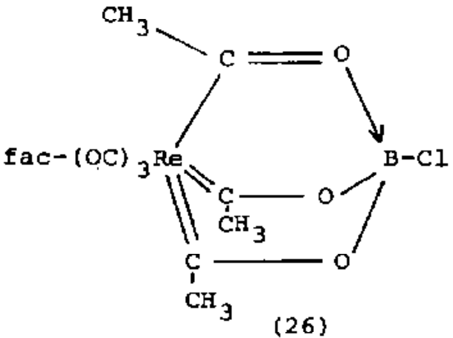
Vertical ionisation potentials for the linear polyatomics X-B=O and X-B=S, where X = H, F, or Cl, have been computed by applying a Rayleigh-Schrödinger perturbation correction to Koopman's theorem. It is believed that the theoretical values will assist in the identification of the, as yet, unobserved photoelectron spectrum of XB=O.[113]

The chemical properties of boron suboxide, B_6O, have been compared with those of α-boron. The greater reactivity of B_6O towards acids is explicable in terms of its crystal structure.[114]

The room-temperature electron-density distribution in $LiBO_2$ has been found by X-ray diffraction. A simple model has been devised for bonding in the "$LiBO_2$ molecule", with polymerisation of these units to form infinite chains of BO_3 triangles held together by electrostatic forces.[115]

Raman spectra of alkaline lithium metaborate solutions in H_2O contain lines assignable to a peroxoborate anion $B(OH)_3(OOH)^-$ (with νO-O at 890 cm^{-1}) in equilibrium with $B(OH)_4^-$ and H_2O. There was no evidence for the formation of peroxoborate acids at low pH values.[116]

Bis(pyrocatecholato)borates, $M[(C_6H_4O_2)_2B]$, where M = Na, K or NH_4, have been prepared and characterised. At 25°C, solubilities of these in water follow the sequence: $Na^+ > NH_4^+ > K^+$.[117] It proved to be possible to isolate potassium bis(4-methylcatecholato)-borate(III), $K[(CH_3C_6H_3O_2)_2B]$, even from solutions with only small concentrations of $(CH_3C_6H_3O_2)_2B^-$. Stability constants for the complex were measured.[118]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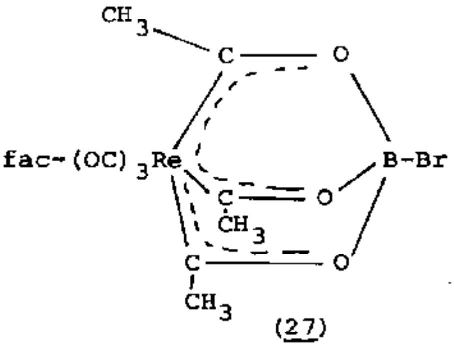

(27)

X-ray molecular structural determinations have been carried out on $[\underline{fac}\text{-}(OC)_3Re(CH_3CO)_3]BX$, where X = Cl or Br. These show that the triacetylrhenato ligand acts as a trioxygen, vicinal bifurcated chelating ligand with approximately C_{3v} symmetry. There are, however, significant differences for X = Cl and Br. The former may be represented as (26), the latter as (27).[119]

Ab initio calculations using extended basis sets (6-31G**, DZ+P) have been reported for diboron trioxide, $O(BO)_2$, and dicyanoether, $O(CN)_2$. Both are calculated to have V-shaped structures (C_{2v} symmetry) at equilibrium. The barrier to inversion at the central oxygen is very low for $O(BO)_2$, ca. 2 kcal.mol^{-1}, however, compared with that for $O(CN)_2$, 20 kcal.mol^{-1}.[120]

Low wavenumber Raman spectra have been obtained for molten and vitreous B_2O_3. Bands in the range 0-300 cm^{-1} are due to motions of large assemblies of atoms, and these do not change significantly when the B_3O_6 ring units break up with increasing temperature, as shown by the decrease in intensity of the B_3O_6 ring mode at ca. 800 cm^{-1}.[121]

The crystal structure of oxybis(dimesitylborane), $(MeS_2B)_2O$, has been obtained. The B-O-B angle is 165.5(12)°, and the B-O bond length 1.36(2)Å. It provided the first confirmation by X-ray diffraction of the "bent-twisted" geometry in $(R_2B)_2O$ systems.[122]

Some tentative assignments have been proposed from the Raman and infrared spectra of $Mg_2B_2O_5$, based on $^{10}B/^{11}B$ isotopic shifts.[123]

The novel, triply-bridged diborate ester: $B(OCH_2C_3H_4CHO)_3B$, was prepared by the reaction of trans-1,2-cyclopropanedicarboxylic acid and BH_3.THF. A single crystal X-ray study shows that it crystallises in the hexagonal system (space group $P6_3$). The molecular symmetry is C_3, with the cyclopropane bridges imposing helicity. Infrared, Raman and vibrational circular dichroism (VCD) spectra of the compound were obtained and correlate with those of previously studied disubstituted cyclopropanes.[124]

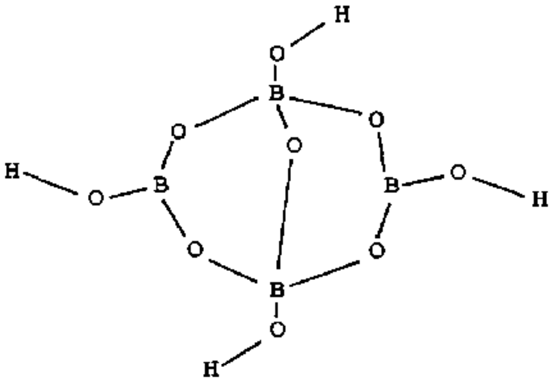
$B_2O_3.SO_3$ and $B_2O_3.2SO_3$ can be obtained by heating B_2O_3 in liquid SO_2.[125] The infrared and ^{11}B n.m.r. spectra of both compounds showed that SO_4 and BO_3 groups were present, as well as distorted BO_4 tetrahedra. The structures are therefore polymeric.[126]

The interaction of boric acid and dimethylamine at 25°C gave the crystalline product $Et_2NH.{}^5/2B_2O_3.3H_2O$. This contains a cyclic anion (not fully characterised) with both 3- and 4-coordinate boron atoms.[127]

$Pb_4O[Pb_2(BO_3)_3Cl]$ forms orthorhombic crystals, space group Pbcm. The structure is built up from Pb_4O tetrahedra, Pb-Pb "dumb-bells", isolated BO_3 planar groups, and Cl^- ions.[128]

Thermal transformations have been elucidated for inderborite, a calcium magnesium hydroxoborate containing the $[B_3O_3(OH)_5]^{2-}$ anion.[129] $Tl[B_3O_4(OH)_2]\cdot 0{\cdot}5H_2O$ forms orthorhombic crystals, space group Pnma. The anion is formed from one tetrahedron and two triangles. These are linked to produce an infinite $[B_3O_4(OH)_2]_n^{n-}$ chain twisted around and along the 2_1 axes. Dehydration and annealing produces TlB_3O_5, with a three-dimensional network built up of B_3O_3 units, formed by one tetrahedron and two triangles.[130]

The interaction of orthoboric acid and diethylene triamine has been studied at 25°C. The compound $[NH(C_2H_4\overset{+}{N}H_3)_2][H_4B_3O_7^-]_2\cdot 4H_2O$ was isolated.[131]



(28)

An X-ray structural determination of $[enH_2][H_4B_4O_9]$ showed that the anion possesses the structure (28).[132]

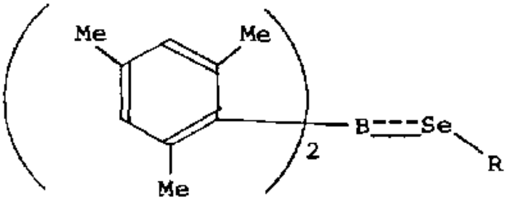
The reaction of excess boric acid and potassium fluoride in aqueous solution gives as final product $K[B_5O_6(OH)_4]\cdot 2H_2O$.[133] Borates of ethylenediamine and hexamethylenetetramine, containing the anion $B_5O_6(OH)_4^-$, decompose to their components in aqueous solution.[134]

127- and 160-MHz ^{11}B n.m.r. spectra have been obtained for aqueous solutions of $KB_5O_8\cdot 4H_2O$, $K_2B_5O_8(OH)\cdot 2H_2O$, $K_2B_4O_7\cdot 4H_2O$ or $NaB_5O_8\cdot 5H_2O$. Separation of all 3 signals in solutions of MB_5O_8 (M = Na or K) enabled formation constants to be calculated for $B(OH)_4^-$, $B_3O_3(OH)_4^-$ and $B_5O_6(OH)_4^-$. $B_4O_5(OH)_4^{2-}$ was not detected. Higher-temperature spectra show that dissociation of polyborate complexes occurs. $B_5O_6(OH)_4^-$ gave a signal due to tetrahedral boron only, as the trigonal boron resonances were not observed.[135]

Crystals of $Na_6Co_3[B_6O_7(OH)_6]_6.26H_2O$ are triclinic, space group $P\bar{1}$. The structure belongs to the class of soroborates - consisting of hexaborate groups, between which the cobalt atoms are octahedrally coordinated.[136] The species $Na_6[Cu_2\{B_{16}O_{24}(OH)_{10}\}].12H_2O$ also forms triclinic crystals (space group $P\bar{1}$). The structure contains the largest known isolated borate anion. Each anion is ring-like, and encloses two Cu^{2+} ions.[137]

A number of papers have appeared which report studies of phase relationships in borate systems. These are as follows: $Li_2B_4O_7$-amide-H_2O (amide = formamide, acetamide or dimethylformamide);[138] $H_3BO_3-CH_3CH_2COOH-H_2O$, $CaB_6O_{10}-CH_3CH_2COOH-H_2O$;[139] $MgB_4O_7-Mg(CH_3CH_2COO)_2-H_2O$, $CaB_6O_{10}-Ca(CH_3CH_2COO)_2-H_2O$;[140] $KBO_2-KCl-K_2MoO_4$;[141] $B_2O_3-Al_2O_3-Li_2O$;[142] $Al_2O_3-B_2O_3-Na_2O$;[143] and $B_2O_3-CdO-Na_2O$.[144]

EHMO calculations on B_8S_{16}, the porphine dianion and Cu^{2+} complexes of both macrocycles have been performed. The results suggest that the Cu^{2+} complex of B_8S_{16} may have some stability, but these conclusions depend <u>both</u> upon inclusion of 3d AO's of sulphur in the basis set and upon the choice of semi-empirical parameters for these AO's.[145]



(<u>29</u>)

Dynamic n.m.r. studies on (<u>29</u>), where R = Me or Ph, provide evidence for B---X π-back-bonding in the sequence $S \gtrsim Se > O$.[146]

3.1.8 <u>Boron Halides</u>

The gas-phase reaction of BF_3 with $Me_3N.MH_3$, where M = Al or Ga, was studied using a combined matrix-isolation i.r. spectrometer/mass spectrometer. The initial reaction products were BF_2H and NMe_3; no MH_3 was detected. The reaction is a halide/hydride exchange, not a Lewis-acid replacement.[147]

The symmetry of BF_3^+ in its nondegenerate ground state is predicted to be lowered by two-mode pseudo-Jahn-Teller interaction with the second excited state.[148]

Ab initio S.C.F. m.o. calculations have been carried out for BF_3^-. The potential minimum occurs for a B-F bond length of 1.442Å. The calculated barrier to inversion is 28 kcal.mol^{-1}.[149]

^{15}N and ^{11}B n.m.r. spectra were reported for NMe_3 adducts of mixed boron trihalides. The values for $J(^{11}B-^{15}N)$ all lie within a narrow range, but they correlate well with $\delta(^1H)$, $\delta(^{13}C)$, $J(^1H-^{11}B)$ and $J(^{11}B-^{19}F)$, although less well with $\Delta\delta(^{11}B)$ (the complexation shift) parameters. $\delta(^{15}N)$ and $\delta(^{11}B)$ are dependent mainly on halogen-induced effects. Species containing fluorine give values falling on a separate curve from the other halogens.[150]

Complexes of 3- or 4-substituted pyridines with BF_3 or BBr_3 have been synthesised, and their infrared and ^{11}B n.m.r. spectral data reported. For a given haloborane the ^{11}B chemical shifts are all very similar, suggesting similar stabilities for the complexes. However, the 3- and 4-cyano-pyridine complexes are slightly less stable than the 3-halo-pyridine adducts.[151]

^1H and ^{19}F n.m.r. studies on $Me_2SO.BF_3$ and $(CD_3)_2SO.BF_3$ show that the two methyl groups are dynamically non-equivalent within the molecule, and re-orient at or above 77K, about their C_3 axes, but with different frequencies. The BF_3 group is rigid at 77K, but above 135K it re-orients about its C_3 axis (activation energy 15.9 kJ.mol^{-1}.[152]

The stability of the hydroperoxofluoroborates, $BF_n(OOH)_{4-n}^-$ (n = 4,3,2 or 1), has been studied by ^1H, ^{11}B, ^{19}F n.m.r. $BF_3(OOH)^-$ is significantly more stable than the di- and tri-hydroperoxo-species.[153]

Solubility was studied in the systems MBF_4-MBH_4-H_2O, where M = Na or K.[154] $RbBF_4$-RbX (X = F, Cl or NO_3) systems have all been shown to be eutectic.[155]

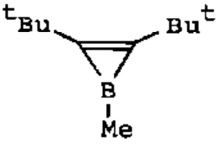
N.m.r. studies of B_2F_4/B_2Cl_4 or B_2Cl_4/B_2Br_4 mixtures show extensive ligand exchange in the latter, but less in the former. It was not possible to assign spectra due to individual mixed halide compounds. BI_3 and B_2Cl_4 react to give an almost quantitative yield of B_2I_4. N.m.r., infrared and mass spectral data were given for the B_2I_4.[156]

^1H, ^{11}B, ^{13}C and ^{31}P n.m.r. data were used to characterise the systems formed between BCl_3 and $R_x(R'O)_{3-x}MO$, where M = N, P or As, i.e. the initial 1:1 adducts and also subsequent condensation products.[157]

Magic-angle rotation suffices to narrow ^{11}B n.m.r. lines for solid tetrahaloborates so that the peaks from different ions could be resolved. It has possible to obtain detailed structural information for a sample containing $[BCl_nBr_{4-n}]^-$, n = 0-4.[158]

3.1.9 Boron-containing Heterocycles

The reaction of C_8K with $MeBBr_2$ and $^tBuC{\equiv}CBu^t$ in benzene gave the borirene (30) both under reflux and at room temperature. At room temperature, however, a species $^tBu_2C_2(BMe)_2$ was also formed. Mass spectral evidence suggested that this is a 1,3-diboretene, probably with the structure (31). The borirene appears to be reasonably stable both under reflux and in mass spectral experiments.[159]



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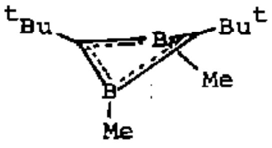
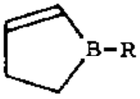


(31)

The first 2-borolenes, (32), where R = NPr^i_2 or Ph, have been prepared by the catalytic isomerisation of the corresponding 3-borolenes, (33), by $[(C_2H_4)_2RhCl]_2$. Larger quantities of the catalyst led to formation of (34).[160]



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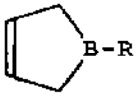

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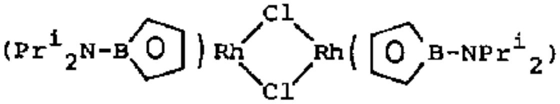
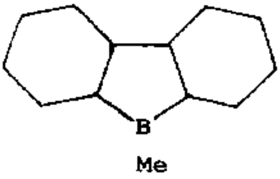


(34)

The system $2C_8K/MeBBr_2$ can be used to generate methylborolene, which is trapped by cyclohexene, to form (35).[161]



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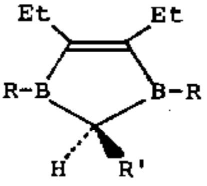
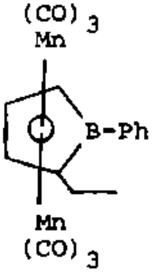


(36)

The compounds (36), where R,R' = Me, Et or H, were used to form triple-decker sandwich complexes related to $CpM(\mu\text{-}C_3B_2H_5)M'Cp$, where MM' = FeCo, CoCo, CoNi, NiNi. The neutral complexes can be oxidised or reduced to form charged species. Several other reactions were reported, including the formation of the quadruple-decker species performed on several of the complexes, and correlated with X-ray results etc.[162]



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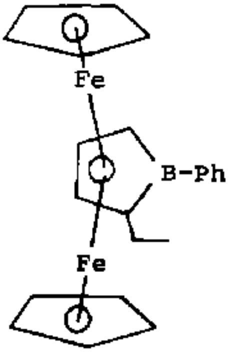

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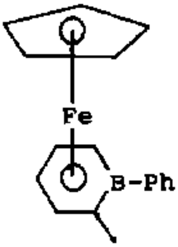
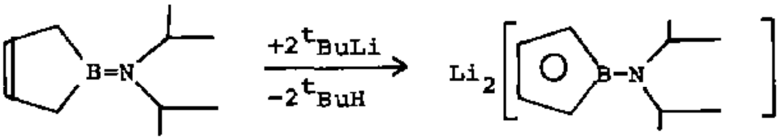


(39)

The thermal reaction of 1-phenyl-4,5-dihydroborepin with $Mn_2(CO)_{10}$ produces (37). The analogous reaction with $[CpFe(CO)_2]_2$ forms, among other products, (38) and (39). The mechanism for the formation of the borabenzene was not elucidated.[163]

The second known example of the six π-electron borole dianion can be prepared by reaction (8). This in turn can form an

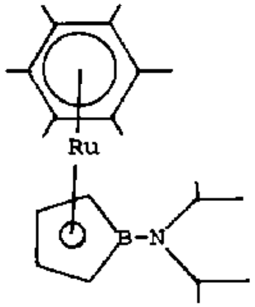


...(8)

eighteen-electron sandwich complex, acting as an η^5-ligand in (40).[164]

The oxidation of crystalline, paramagnetic bis 1-allyl(trimethylsilyl)-2-methyl-η^5-1,2-azaborolinyl cobalt complexes by the ferricenium cation, equation (9), R = Me or CMe_3, leads to the formation of diamagnetic, eighteen-electron cobalticinium cations.[165]

A new general route has been reported for the preparation of



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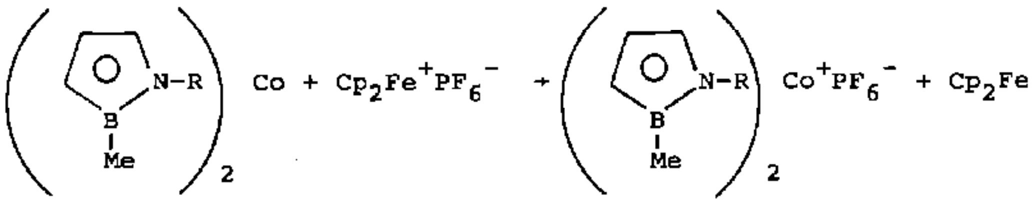
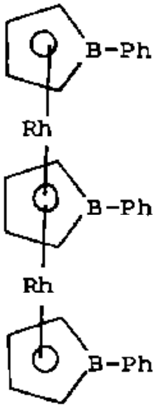


...(9)

(η^5-borole)metal complexes, i.e. B-Ph with $Ru_3(CO)_{12}$, $Ru(C_6H_6)(C_6H_8)$, $Mn_2(CO)_{10}$ or $[(C_2H_4)_2RhCl]_2$. All of the products are shown to contain pentahapto-borole rings (using ^{11}B n.m.r. spectroscopy). The rhodium complex is triple-decked, (41). In this complex the ^{11}B resonance of the central ring is at higher field than that from the outer ligands, and less broadened by nucleus quadrupole relaxation.[166]



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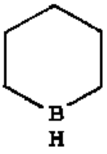
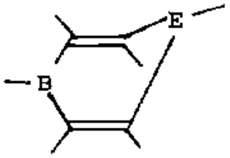


(42)

Borinane, (42), can be prepared conveniently by the hydroboration, using 2 molar equivalents of 9-borabicyclo[3.3.1]-nonane (9-BBN), of 1,4-pentadiene, followed by treatment with

$BH_3.THF$ or $BH_3.SMe_2$.[167]

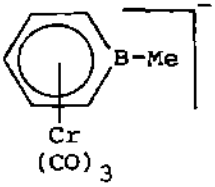


(43)

Radical-initiated hydrophosphination or hydroarsination of diethylaminodialkynylboranes using $PhEH_2$(where E = P or As) produces (43), 1-phospha- or 1-arsa-4-boracyclohexadiene-2,5. The arsenic derivative is reduced by excess $PhAsH_2$ to the dihydro-derivative.[168]

Non-parametrized m.o. calculations have been performed on the borabenzene anion, $C_5H_6B^-$ (BBz^-), and its sandwich complexes $(BBz)_2Fe$, $(BBz)_2Co$. The π-electrons in BBz^- are delocalised. The main bonding interactions between BBz^- and M are similar to those in metallocenes and arenes. Transition metal 4p orbitals contribute significantly to the metal-ring bonding. The sequence of predominantly 3d m.o.'s in both complexes is : $d_\delta(x^2-y^2,xy) < d_\sigma(z^2) \ll d_{\pi\star}(xz,yz)$. The observed "slippage" in the structure (in which Fe is nearer to C than to B) can be rationalised. There was some evidence that the most favoured conformation has trans boron atoms.[169]

$Na[C_5H_5BMe]$ reacts with $Cr(CO)_3(NH_3)_3$ to produce a species containing the anion, (44).[170]



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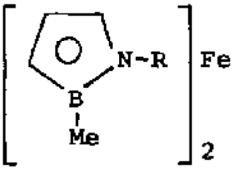
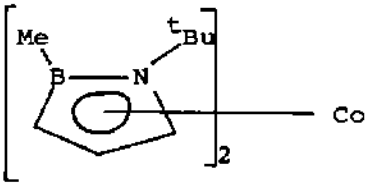


(45)

(Borinato)(cyclobutadiene)cobalt complexes can be prepared from $Co(C_5H_5BR)(1,5\text{-}C_8H_{12})$ and the alkynes $C_2R'_2$, or from $(C_4Me_4)Co(CO)_2I$ and $Tl(C_5H_5BR)$.[171]

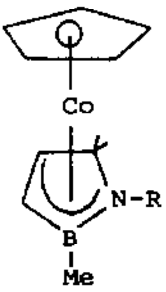
Bis(2-methyl-η-1,2-azaborolinyl)iron and related species, (45), where R = H, Me or Et, are prepared from the $N\text{-}SiMe_3$ precursor via lithiation at nitrogen, followed by treatment with Bu^tOH (for R =

H) or RX (for R = Me or Et).[172]



(46)

Crystal and molecular structures of 2 isomers of (46), [bis(1-*tert*-butyl)-2-methyl-η-1,2-azaborolinyl]cobalt have been determined. One isomer has a clockwise, the other an anti-clockwise conformation of the azaborolinyl rings. In both cases the N-Bu^t groups are staggered. The three ring carbon atoms are closer to the Co than are N or B.[173]



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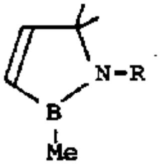

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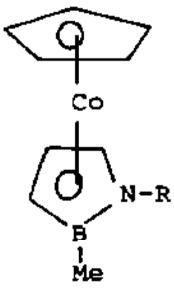
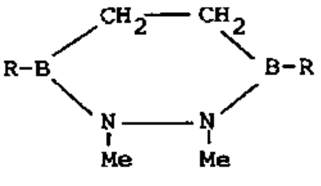


(49)

The substituted 2-methyl-Δ^3-1,2-azaboroline ligands act as four-electron donors in the sandwich complexes (47), where R = CMe_3 or $SiMe_3$, are prepared from (48) and $CpCo(C_2H_4)_2$ at -78°C. Warming to 20-25°C leads to proton loss and formation of η^5-1,2-azaborolinyl complexes, (49).[174]

Diboryl compounds, $R(Cl)B(CH_2)_nB(Cl)R$, where R = Cl or Me, n = 2 or 3, and the silylated or stannylated species $(Me_3Y)_2X$, (Y = Si or Sn; X = S, NMe, O, -NMe-NMe-) can be used in (5+1)- and (4+2)-cyclocondensation reactions. No thiadiborinanes are formed, but varying yields of B/N and B/O heterocycles are formed, e.g. monomeric and dimeric (50).[175]

^{13}C n.m.r. spectra have been assigned for (51), and related borazines. π-Charge densities from LCAO-MO Hückel calculations were in reasonable agreement with experimental chemical shifts.[176]



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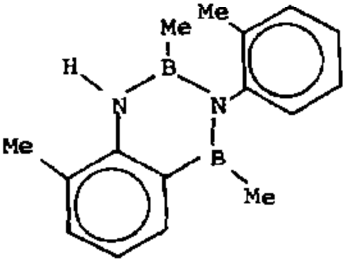
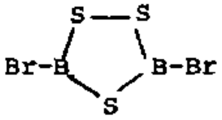


(51)

The reaction of 1,2,4-trithia-3,5-diborolanes with alkynes does not give 1,3,2-dithiaboroles, as previously suggested, but the hitherto unknown 1,2,3-dithiaboroles, e.g. (52), and R-C≡C-R' (where R = R' = Ph, Et etc) produce (53).[177]



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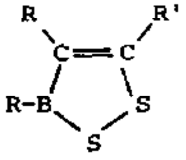
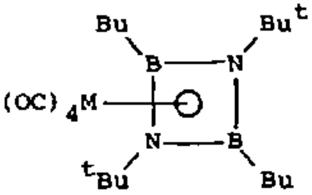


(53)

$M(CO)_5(THF)$, where M = Cr or W, react with Bu-B=N-Bu^t to form (54), in which the non-planar diazaboretidine is acting as a four-electron donor.[178]



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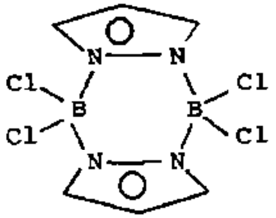
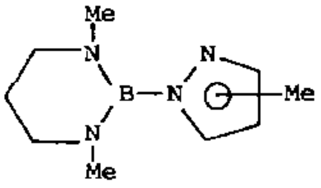


(55)

X-ray structural determinations for the pyrazaboles (55) and related derivatives show that the central B_2N_4 ring can adopt chair, boat or planar conformations - dependent upon the substituents. Thus packing effects determine the ring conformation.[179]

(56) is stereochemically non-rigid at ambient temperature, with the methyl group located at either C(3') or C(5') of the pyrazole



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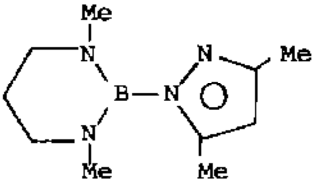
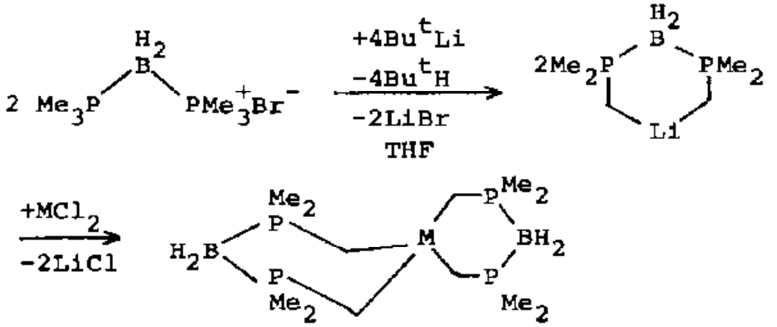


(57)

ring. (57) was also prepared, and characterised by n.m.r.[180]

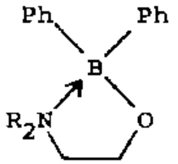
Binary metal ylide complexes can be formed by the sequence (10),



...(10)

where M = Mn or Co. Magnetic measurements show normal high-spin T_d behaviour for the M atom. The i.r. spectra are very different at low wavenumbers from the square-planar d^8 analogues. A single crystal X-ray diffraction for M = Mn confirms the structure shown.[181]

X-ray structural determinations have been performed on (58), where R = H or Me; these confirm that the boron atoms are four-coordinate.[182]



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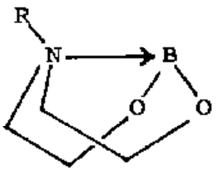
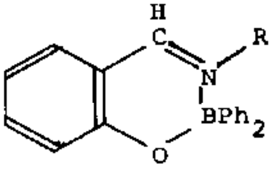


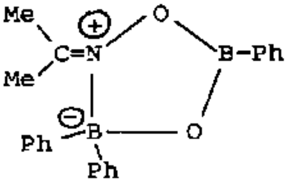
(59)

Intramolecular N-B coordination was demonstrated by dynamic ^1H and ^{11}B n.m.r. data for the thexylboronic esters (59).[183]

The new boron-containing heterocycles (60), where R = $(CH_2)_2OH$, $(CH_2)_3OH$, CH_2COOH etc, can be prepared from salicylaldehyde, the amine component and diphenylboronic anhydride.[184]



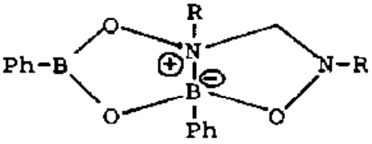
(60)



(61)

The crystal structure of 4-isopropylidene-2,5,5-triphenyl-1,3-dioxa-4-azonia-2-bora-5-boratacyclopentane confirms the structure (61). The five-membered ring is almost planar, containing both trigonal and tetrahedral boron atoms.[185]

Phenylboronic acid, N-alkylhydroxylamines and formaldehyde form bisphenylboronates of N,N'-methylenebis(N-alkylhydroxylamines), (62), where R = Me, Et, Pr^n, Pr^i, C_6H_{11} or CH_2Ph. The presence of the transannular B-N bond was confirmed by infrared and ^1H n.m.r. spectra.[186]



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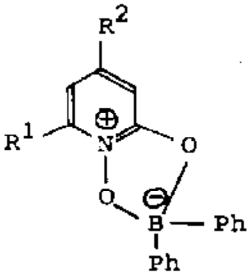
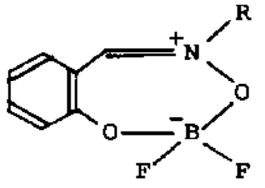


(63)

The crystal structures of (63), where $R^1 = R^2 = H$, or $R^1 = C_6H_{11}$, $R^2 = CH_3$, show that these are the first examples of coordination complexes derived from 2-hydroxypyridine-N-oxide. The tetrahedrally-coordinated boron is in a five-membered OBOCN ring.[187]

Nitrones of salicylaldehyde react as bidentate ligands in forming seven-membered heterocycles with a B,N-betaine structure, e.g. (64), where R = CH_3, CH_2Ph, C_6H_{11}, Ph or $4\text{-}ClC_6H_4$.[188]

Pinacol(trimethylsilyl)methaneboronate, (65), is prepared from (trimethylsilyl)methylmagnesium chloride. It appears to have a very useful synthetic potential.[189]



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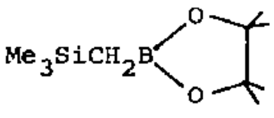
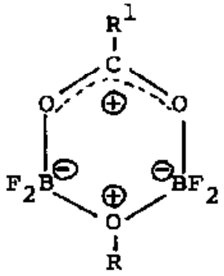


(65)

Trimeric alkoxydifluoroboranes, $(F_2BOR)_3$, react with cyanuric acid anhydrides to form monocyclic acyloxyfluoroboranes such as (66), where R = Me or Et; R^1 = Me, Et or Pr^i. The crystal structure for R = R^1 = Me was determined - this shows that two conformational isomers of the six-membered ring are present i.e. planar and non-planar.[190]



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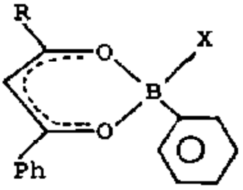

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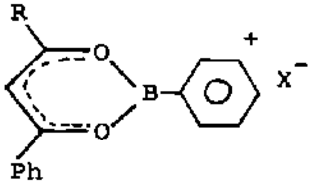
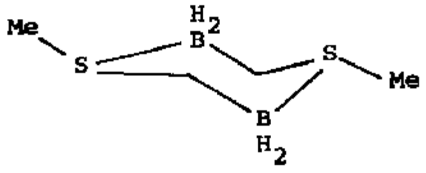


(68)

It has been shown that the previously reported 1,3,2-dioxaborinium cations containing three-coordinate boron are in fact tetracoordinated coordination compounds, i.e. (67), where R = Ph, Me; X = ClO_4 or SO_3CF_3, rather than (68). Thus, n.m.r. spectra show four-coordinate boro , while for X = ClO_4 infrared bands due to a unidentate perchlorato ligand were seen.[191]



(69)

A new boron ring system, 1,4-dimethyl-1,4-dithionia-2,5-diboratacyclohexane, is prepared from $Me_3N.BH_2CH_2SMe$ and methyl iodide, and the subsequent thermal decomposition of the resulting sulphonium salt. X-ray diffraction studies show that in the solid state the conformation is (69), i.e. both the methyl groups are equatorial.[192]

3.1.10 Boron Carbide and Metal Borides

A study of electronic band structures, and density-of-states plots, were used in a discussion of bonding in $B_{13}C_2$. It was suggested that inter-icosahedral bonds are much stronger than intra-icosahedral ones. The B-C bonds lying in the CBC chain show slight multiple-bond character. Calculations for models of $B_{12}C_3$ suggest that a structure in which a carbon atom is substituted into the icosahedron is more stable than the one in which the chain bonding consists of carbon atoms only.[193]

A study has been made of the homogeneity ranges of LaB_6, EuB_6 and SmB_6 with changes in cell dimensions with changing composition.[194]

The charge density distribution in $LiAlB_4$ was investigated by X-ray diffraction. The net charge distribution was found to be $Li^+(Al^{1.7+})_{0.96}(B_{12})^{1.2-}.2B^{0.7-}$ from a population analysis of valence electrons. However, charge integration around the metal atoms gave net charges $Li^{0.7+}$, $Al^{1.5+}$. The results indicate that the $LiAlB_4$ structure is stabilised by charge transfer from the metals to the electron-deficient boron framework.[195]

3.2 ALUMINIUM

3.2.1 Aluminium Hydrides

Calculations on AlH^+ were used in estimating the abundances of aluminium-bearing molecules in interstellar clouds.[196]

AlH_3 reacts with CaH_2 or $NaAlH_4$ and $CaCl_2$ in THF to form $Ca(AlH_4)_2.4THF$ (monoclinic, space group $P2_1/n$). νAl-H is at 1715 cm^{-1}. Desolvation produces $Ca(AlH_4)_2.0{\cdot}3{-}0{\cdot}5THF$ as final product (νAl-H at 1800 cm^{-1}).[197]

X-ray crystal structure determinations have been carried out for $H_{3-n}Al(NMe_2)_n$, (n = 1, 2 or 3). For n = 1, the molecule is trimeric, with a six-membered ring-chair conformation. For n = 2 or 3, dimers are formed, containing planar four-membered rings. Infrared and Raman spectra of the compounds with n = 2 or 3 show that the mutual exclusion rule applies, confirming their centrosymmetric nature in solution. Solid-phase spectra show a breakdown of this rule. Some mode assignments were proposed.[198]

$AlH_3.NEt_3$ reacts with Cp_2YCl in C_6H_6 to give $(Cp_2YCl.AlH_3.NEt_3)_2$. The crystal structure of this shows it to be a Cp_2YCl dimer bonded to the $AlH_3.NEt_3$ group via hydrogen bridges (Y-H-Al), as well as by a weak, "secondary" Al...Cl bond.[199]

A new simple method has been devised for the accurate titration of solutions of $LiAlH_4$ in diethyl ether. It is based on the reaction of benzyl alcohol with the deep-violet complex formed between $LiAlH_4$ and 1,10-phenanthroline in THF, in the presence of Mg^{2+}.[200]

$LiAlH_4$ reacts with CO_2 or $NaHCO_3$ at about 500K to give CH_4 and C_2H_4 as the primary products. These are presumably the explosive products formed by using CO_2 fire-extinguishers on $LiAlH_4$ fires.[201]

Interaction has been studied in the system $Sr(AlH_4)_2$ - di(2-methoxyethyl) ether, in the temperature range -65°C to +100°C. The octasolvate $Sr(AlH_4)_2.8DG$ is formed, which converts to $Sr(AlH_4)_2.4DG$ at 10°C.[202]

$(Cp_2TiCl)_2$ and $LiAlH_4$ in aromatic solvents form a stable compound thought to be a complex consisting of a linear, polynuclear form of Cp_2TiAlH_4, with Cp_2TiH side groups characterised by e.s.r. Small amounts of binuclear species ($Cp_2TiH_2AlCl_2$,$Cp_2TiH_2Al(Cl)H$,$Cp_2TiH_2AlH_2$) are also formed successively.[203]

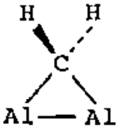
3.2.2 Compounds containing Al-C or Al-Si Bonds

^{27}Al n.m.r. was used to probe the coordination geometry for aluminium atoms in organo-aluminium compounds (with the aluminium in sites of 3-, 4-, 5- and 6-fold coordination). The chemical shift ($\delta(^{27}Al)$) ranges were found to be as follows: 3 C.N., 256-276 ppm; 4 C.N., 146-167 ppm; 5 C.N., 112-126 ppm., 6 C.N., $(Al(acac)_3)$ 0 ppm.[204]

Ab initio calculations on Al^+/CO interaction suggest that both $Al-CO^+$ and $Al-OC^+$ are stable, but that the stabilisation energies are very low (ca. 20 $kJ.mol^{-1}$).[205]

M.O. calculations (using double-zeta (DZ) and DZ + polarisation basis sets, in conjunction with SCF and CI methods) suggest that in Al_2CH_2 the lowest-energy arrangement has a bridging methylene group, and that the CH_2 and Al_2C planes are perpendicular, (70). The calculated bond distances were Al-C, 2.00Å; Al-Al, 3.61Å, with ∠HCH = 105.5°. The terminal structure, $Al-Al-CH_2$, was calculated to be ca. 46 kcal.mol^{-1} higher in energy.[206]

Vapour-pressure data have been collected for Me_2AlCl and $MeAlCl_2$. Ethylaluminium analogues decomposed under comparable conditions.[207] Hydrolysis of R_3Al (where R = Me, Et or Bu^i) in Et_2O takes place in several steps. The first gives a complex $R_3Al.OH_2$. This then gave R_2AlOH. Subsequent stages were dependent on the ratio $R_3Al:H_2O$. If this is 1:1, then R_2AlOH forms stable autoassociates, but if it is 2:1, then R_2AlOH reacts with the excess R_3Al to produce alkylaluminoxanes.[208]



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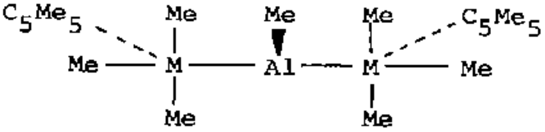


(71)

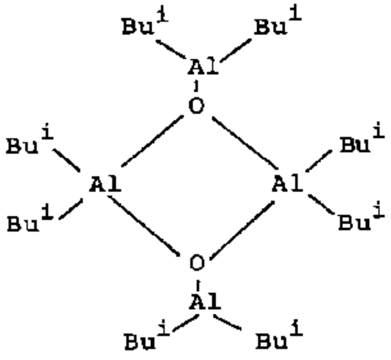
The complexes $(C_5Me_5M)_2Cl_4$, where M = Rh or Ir, react with Al_2Me_6, to form heterotrimetallic species, $(C_5Me_5MMe_3)_2AlMe$, formulated as (71).[209]

The amphoteric ligands $Ph_2PNRAlR'_2$ react with alkylmetal carbonyl complexes, inducing facile migrations. Thus $Ph_2PN\text{-}Bu^tAlEt_2$ and $CpFe(CO)_2Me$ give as main product the chelated acyl complex $Cp(CO)Fe[C(Me)OAlEt_2NBu^tPPh_2]$, as well as a little $Cp(CO)Fe[O(CH{=}CH_2)AlEt_2NBu^tPPh_2]$. An intermediate leading to these was isolated, and X-ray diffraction showed it to be $Cp(CO)Fe[C(Me)OAlEt_2NBu^tPPh_2]$. This consists of a five-membered heterocycle, $C(Me)OAl(Et)_2N(Bu^t)P(Ph)_2$, bounded in an $\eta^2(C,O)$ manner to a $Cp(CO)Fe$ fragment.[210]

$Ph_2PNBu^tAlR_2$ (where R = Me or Et) and $HMn(CO)_5$ form $(OC)_4Mn(CHOAlR_2NBu^tPPh_2)$, in which a net migration of H from Mn to CO has occurred. This migration occurs indirectly, however, via an initial proton transfer from Mn to P. The products react with further starting material (when R = Me) to give $(OC)_3Mn(CHOAlMe_2AlBu^tPPh_2)[PPh_2NBu^tAl(HCH_2)CH_3]$, in which a C-H bond from an Al-Me group is coordinated to manganese.[211]

"R_2Al_2O", where R = H, Me, Et or Bu^i, have structures containing bridging R as well as bridging O groups, except for R = Bu^i. Here the structure is (72). The order of bridging ability is R = H > Me > Et >> Bu^i.[212]

Trimethylaluminium methylates $(AsMe_2O_2)^-$ to form $[AsMe_4]$-



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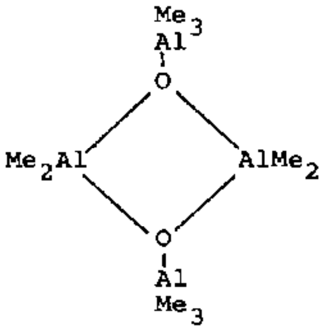


(73)

$[Me_2AlO.AlMe_3]_2$. The aluminoxane anion consists of a planar Al_2O_2 ring, with $AlMe_3$ molecules coordinated to oxygen atoms.[213]

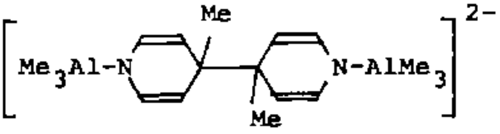
The unusual anion, $[Al_7O_6Me_{16}]^-$, is found in the decomposition of two different high-oxygen content organoaluminium compounds, i.e. $K[Al_2Me_6O_2]$ and $Cs_2[Al_2Me_6O]$. $K[Al_7O_6Me_{16}].C_6H_6$ forms triclinic crystals, space group $P\bar{1}$, while $Cs[Al_7O_6Me_{16}].3C_6H_5Me$ crystals are cubic, space group $P2_13$. The anion consists of an open Al_6O_6 cage, capped by the seventh aluminium atom, which is bonded to three adjacent oxygen atoms in the cage. The six cage aluminium atoms are each bonded to two terminal methyl groups, while the unique Al is bound to only one methyl. Each oxygen atom is three-coordinate, as the oxygens not bound to the unique Al bridge two aluminium atoms and are also coordinated to one methyl group each.[214]

X-ray structural determinations have been carried out on $(Me_3Si)_3Al.OEt_2$, $NaAl(SiMe_3)_4$ and $NaAl(SiMe_3)_4.2C_6H_5Me$. In all three the aluminium atom is tetrahedrally coordinated. The $Al(SiMe_3)_3.OEt_2$ is monomeric (with Al-Si 2.47Å, Al-O 1.95Å), while the tetrakis-compounds form linear chains via contact ion-pair interactions.[215]

3.2.3 Compounds containing Al-N or Al-P Bonds

The reduction of $Me_3Al.NC_5H_4CH_3$ with two equivalents of lithium produces $[Me_3AlNC_5H_4CH_3]_2^{2-}$. N.m.r. data for this are consistent with the formulation (74), while its visible spectrum suggests that there is significant $Al_{d\pi} \leftarrow N_{p\pi}$ bonding.[216]

The crystal structure of the dimer of $(Me_3P)_3CoN_2AlMe_2$ shows the presence of a four-membered Al_2N_2 ring, (75). The ring is planar,



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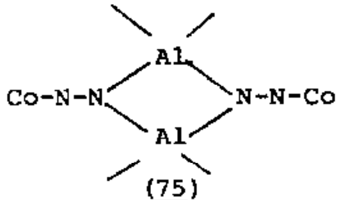
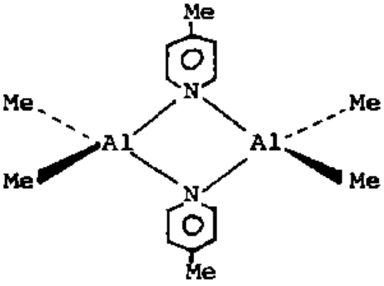


(75)

and centrosymmetric.[217]

Reduction by metallic lithium of $Me_2ClAl.NC_5H_4Me$ forms $(Me_2Al.NC_5H_4Me)_2$, characterised by ^1H, ^{13}C and ^{27}Al n.m.r., and electronic spectroscopy. The suggested structure is (76).[218]



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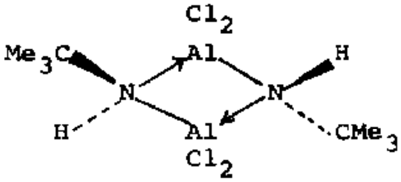


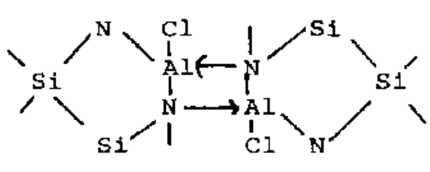
(77)

$(Me_3SiNMe)_2SiFNLiCMe_3$ reacts with aluminium trichloride to give a dimeric silylaminodichloroalane, $[(Me_2SiNMe)_2SiFNCMe_3AlCl_2]_2$. Hydrolysis of this cleaves the Si-N bonds to produce the four-membered ring compound $[Me_3CNHAlCl_2]_2$. The crystal structure of this shows that the four-membered Al_2N_2 ring is planar, with a trans-arrangement of nitrogen substituents, (77).[219]

$\{R_2MN[P(C_6H_5)_2]_2\}_2$, where M = Al or Ga; R = Me or Et, can be prepared from R_3M and $[(C_6H_5)_2P]_2NH$, with evolution of alkane. Spectral data shows that in the aluminium compounds the ligand is unsymmetrically P,N-coordinated, to form AlNPAlNP rings. For gallium the analogous form is present, but also a P,P-coordinated isomer with an eight-membered ring is found in solution. Single crystal X-ray diffraction confirmed the P,N-coordination in $\{Me_2Al[P(C_6H_5)_2\}_2]_2$, with the six-membered ring present in the twist conformation.[220]

The first cycloalumadisiladiazane, $[ClAl(NMeSiMe_2)_2]_2$, has been prepared, from bis(methylamino)tetramethyldisilane and BuLi at -60°C, followed by treatment with $AlCl_3$ in C_6H_6/NMe_3 at -80°C.

The structure was shown to be (78), and n.m.r. and mass spectra show that it persists in the liquid and vapour phases.[221]



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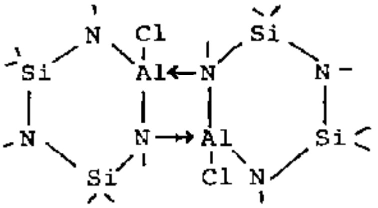
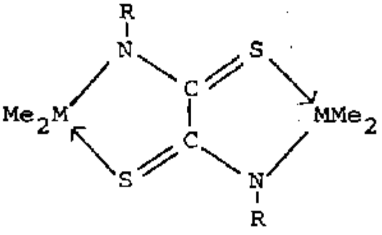


(79)

The analogous disilatriazane system, $[ClAl(NMeSiMe_2)_2NMe]_2$ has also been reported. I.r. and Raman spectra, and also ^1H, ^{13}C, ^{27}Al and ^{29}Si n.m.r. spectra were consistent with the structure (79), which was confirmed by single-crystal X-ray diffraction.[222]

Trimethyl derivatives of Al, Ga or In react with dithio-oxamides, $(HNR\text{-}CS)_2$, where R = H, Me, $SiMe_3$, CMe_3, in a molar ratio of 2:1, to form 2 moles of CH_4 and the monomeric bis(dimethylmetal)dithio-oxamides, (80). ^1H n.m.r., i.r. and Raman spectra show that these exist as two structural isomers, both of which have a planar molecular skeleton of two fused, five-membered rings. They differed in the coordination of the two metal atoms (E- and Z-forms).[223]



(80)

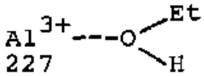
Sodium tetracaprolactamatoaluminate exists primarily as a dimer in benzene solution. Two modes of dimerisation are possible - formation of an eight-membered cyclic caprolactam bridge between two aluminium atoms or the coordination of the caprolactam ligands belonging to two different aluminium atoms to give one sodium atom.[224]

The new amphoteric ligand $(Me_3SiCH_2)_2AlPPh_2$ can be prepared from $Al(CH_2SiMe_3)_3$ or $Al(CH_2SiMe_3)_2H$ and PPh_2H or form $Al(CH_2SiMe_3)_2Br$

and $KPPh_2$. This aluminium phosphide is unique in existing as a monomer/dimer equilibrium in benzene solution.[225]

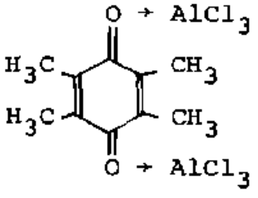
3.2.4 Compounds containing Al-O, Al-S or Al-Se Bonds

Inert matrices containing aluminium atoms and O_2 or O_3 have been studied. Vibrational spectra were analysed using $^{16}O/^{18}O$ isotopic shifts. The results showed that Al and O_2 or O_3 gave unsymmetrical, bent AlOO (of C_s symmetry) in N_2 matrices, with νOO 1337 cm^{-1}, νAl-O 1091 cm^{-1}, but that very little of this species was formed in Ar matrices. In both N_2 and Ar matrices, some ozonides were produced (with bands near 850 cm^{-1}). There was no evidence for metal-superoxide species, such as are found for Ga, In or Tl and O_2.[226]

Twelve complexes of O, N or F bases with Al^{3+} were investigated by *ab initio* m.o. calculations at the 6-31G*/3-21G level. The calculated energies of interaction enable the relative binding energies from gas-phase experiments to be placed on an absolute scale, e.g. for  $Al^{3+}\text{---}O\begin{smallmatrix}\diagup Et\\ \diagdown H\end{smallmatrix}$, the absolute interaction energy is 32±3 kcal mol^{-1}.[227]

A single-crystal X-ray diffraction study has been carried out on $W(\eta^2\text{-}HC{\equiv}COAlCl_3)(CO)(PMe_3)Cl$, from the $AlCl_3$-promoted coupling of CO and $W(CH)(PMe_3)_4Cl$. The Al-O distance was 1.751(3)Å, i.e. there is a significantly stronger Al-O interaction than in other structures containing Al-O (carbonyl; acyl) linkages.[228]

The reactions of $Cr(CO)_5PPh_2K.2(dioxan)$ with AlR_2Br (R = Br, Me, Et or CH_2SiMe_3) give high yields of $Cr(CO)_5[PPh_2(CH_2)_4OAlR_2]$. A crystal structure determination was carried out for R = CH_2SiMe_3, showing that the molecule is dimeric. Each octahedral $(OC)_5CrPPh_2$- fragment is linked by an $-(CH_2)_4O-$ unit to two $Al(CH_2SiMe_3)_2$ fragments. The central AlOAlO ring is planar, with Al-O-Al 100.3(6)Å, O-Al-O 79.7(5)Å.[229]



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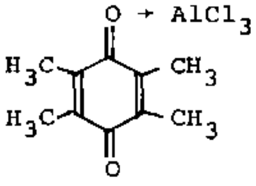


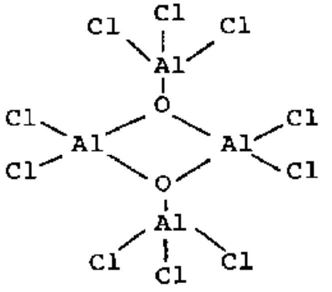
(82)

2,3,5,6-Tetramethyl-p-benzoquinone and Al_2Cl_6 form two stable coordination complexes, identified by i.r. spectroscopy (in the ν(C=O) region) as (81) and (82). The latter gave a band due to the free carbonyl group at 1645 cm^{-1}.[230]

The crystal structure of $Al(NO_3)_3 \cdot 9D_2O$ has been examined by neutron diffraction. The crystals are monoclinic, space group $P2_1/c$, and the asymmetric unit contains octahedral $Al(D_2O)_6^{3+}$, NO_3^- and $3D_2O$ molecules not coordinated to Al^{3+}.[231]

Fluorosulphuric acid reacts with aluminium tris(trifluoroacetate) to form aluminium tris(fluorosulphate). Infrared spectra show this to have a polymeric structure, with bidentate bridging fluorosulphates, and six-coordinate aluminium.[232]

The composition of volatile hydrolysis products of $AlCl_3$ has been studied by mass spectrometry. Thirteen ions of aluminium oxide and hydroxide chlorides were identified.[233]



(83)

Crystals of $Ag_2[Al_4Cl_{10}O_2]$ are orthorhombic, space group Pbca. They are formed in the $AgCl/AlCl_3$ system in the presence of traces of water. The structure contains the isolated ions (83).[234]

Basic aluminium chloride solutions can be prepared from neutral solutions by addition of alkali or by dissolving metallic aluminium. The solutions prepared by both methods contain monomeric, tridecameric and polymeric cations. The formation of tridecameric cations is favoured by low temperature, low basicity and dilute solutions.[235] Kinetic studies were made on basic aluminium chloride solutions of low basicity using ferrone reagent. The rate constant for the reaction of dimeric ions with ferrone was: K = 0.97 0.06 min^{-1}.[236] Reaction of activated alumina with aqueous HCl in sealed tubes, above 100°C, gave basic aluminium chlorides. χ-Al_2O_3 was the best oxide for this preparation.[237] ^{1}H n.m.r. studies of the water molecules in basic aluminium chlorides show that three types of water molecule are present: a) fixed coordination species, b) adsorbed H_2O molecules with possible random motion, and c) H_2O molecules with hindered mobility.[238]

Interactions of Al(III) (as $AlCl_3.6H_2O$) with carbonylated head-groups of potassium dodecanoate contained in a bilayer membrane were studied by n.m.r. Under dilute conditions the aluminium binds very strongly to the carboxylate groups, as the $Al(OH)_4^-$ ion. Partial replacement of K^+ by NMe_3R^+ disrupts this binding.[239]

Redox, hydrolysis and complexation equilibria were studied in the system Al^{3+}-1,2-naphthaquinone-4-sulphonate/1,2-dihydroxy-naphthane-4-sulphonate-OH^-.[240] Equilibria between Al(III), salicylic acid and OH^- were studied at 25°C by potentiometry. Equilibrium constants were determined for AlL^+, AlL_2^-, $Al(OH)L_2^{2-}$ and $Al_2(OH)_2L_2^{3-}$ (where H_2L = salicylic acid).[241] Similar data were determined for Al^{3+} - H_3L - OH^- (H_3L- citric acid). Evidence was found for the mononuclear $[Al(HL)]^+$, AlL, AlL_2^{3-}, as well as a very stable trinuclear complex $[Al_3(OH)_4L_3]^{4-}$.[242]

^{27}Al n.m.r. was used (for 10 mM aqueous solutions) to study interactions of Al(III) with citrate, lactate and EDTA. For lactate, slow exchange phenomena make possible the observation of separate peaks for $Al(H_2O)_6^{3+}$, 1:1 and 1:3 Al-lactate complexes, as well as mixed aquo-lactato and hydroxy-lactato complexes.[243] Complex formation between Al^{3+} and imidazolidine-2-one was also investigated by ^{27}Al n.m.r. Evidence was found for several species with different stoichiometries.[244]

The kinetics of replacement of semithymol Blue (H_4L) by EDTA in AlL^- were studied spectrophotometrically. Two parallel paths (associative and dissociative) were found for the replacement.[245] Equilibrium constants were obtained for Al(III) complexes with methylthymol blue, semimethylthymol blue, xylenol orange and semixylenol orange.[246]

The preparation of hydrated Al_2O_3 from an alkaline solution by carboxylic acid amides has been studied. $Al(OH)_3$ was formed when the solution is slightly supersaturated, as a homogeneous, crystalline precipitate.[247]

The temperature dependence of phase formation has been studied in the systems Al_2O_3 - M_2O_3 (where M = In, V or Ti).[248]

Quadrupolar coupling constants and asymmetry parameters were determined from the ^{27}Al n.m.r. spectra of single β-alumina crystals. The temperature dependence of the spectra gave useful structural information.[249]

Solid-phase ^{27}Al n.m.r., with "magic-angle spinning", was used to probe the environments of aluminium atoms in non-crystalline solids, Al_2O_3-SiO_2 gels, soda glass and mullite precursors. It was possible to obtain quantitative estimates of tetrahedral and octahedral coordination proportions for the aluminium atoms.[250]

^{27}Al n.m.r. and the contribution of Al_2O_3 to molar refractivities show that the aluminium is octahedrally coordinated in α-$LiAlO_2$, but tetrahedrally coordinated in γ-$LiAlO_2$. In β-$LiAlO_2$, contrary to earlier suggestions, only tetrahedral aluminium is present.[251] A similar result was reported from a ^{27}Al n.m.r. study, using magic-angle spinning, of polycrystalline $LiAlO_2$ polymorphs. The symmetry of the aluminium sites was characterised by quadrupole coupling data.[252]

Lithium hydroxocarbonatoaluminate was synthesised by treating $Li_2O.2Al_2O_3.nH_2O$ (where n = 7-11) with CO_2. The product is believed to have a layer structure, based on bayerite, with monoclinic symmetry.[253]

High-resolution ^{27}Al n.m.r. of crystalline aluminium phosphates show that for a wide range of compounds the aluminium is exclusively octahedrally coordinated.[254] I.r., X-ray and thermal analysis data were reported for the crystalline tripolyphosphate, $Na_2AlP_3O_{10}.4H_2O$.[255]

A study of the high-resolution solid-state ^{29}Si and ^{27}Al n.m.r. spectra has been made for the product of treating synthetic zeolite Na-Y with $SiCl_4$ vapour at 560°C. The ^{27}Al n.m.r. spectrum of the dry material showed two peaks, one due to residual lattice aluminium, and one due to $AlCl_4^-$. The washed, dealuminated zeolite Y gives ^{27}Al resonances due to tetrahedral aluminium in the lattice, and octahedral aluminium as cations in the zeolitic channels.[256] Neutron diffraction on zeolites sodium ZK-4 (Si/Al = 1.65) and sodium Y (Si/Al = 2.61) shows that there is no long-range Si-Al ordering, unlike sodium A and X zeolites.[257]

Time-of-flight neutron diffraction data on $NdAlO_3$ show that $NdAlO_3$ crystals are rhombohedral, space group $R\bar{3}c$.[258]

Na_2O and Al_2O_3 react in a closed nickel cylinder at 980K to form colourless single crystals of $Na_{14}Al_4O_{13}$, which are very moisture sensitive. They crystallise in the monoclinic space group $P2_1/c$. The $Al_4O_{13}^{14-}$ anion is built up of four AlO_4 tetrahedra sharing vertices.[259] Basic sodalite, $Na_8Al_6Si_6O_{24}(OH)_2.2H_2O$ forms cubic crystals, space group $P\bar{4}3n$. The 1:1 alumino-silicate framework is completely ordered.[260]

The structure and ionic distribution in the conducting plane of ammonium-hydronium β''-alumina, a solid electrolyte, were determined by single crystal neutron diffraction. The composition is $(NH_4^+)_{1.56}(H_3O^+)_{0.19}Mg_{0.75}Al_{10.25}O_{17}(H_2O)_{0.25}$. The structure comprises spinel blocks of aluminium atoms, either tetrahedrally or octahedrally coordinated to oxygen atoms. One of the two tetrahedrally coordinated Al^{3+} sites is 37% occupied by Mg^{2+} to provide charge compensation in the structure.[261]

Differential calorimetric analysis, ^1H n.m.r. spin-lattice relaxation measurements and X-ray powder diffraction data show that hydration of $CaO.Al_2O_3$ in the temperature range 4-83°C proceeds in three distinct steps.[262]

Reaction of aqueous solutions of $AlCl_3$ and sodium germanate, with subsequent precipitation as the sulphate, gives $[GeO_4Al_{12}(OH)_{24}(H_2O)_{12}](SO_4)_4.xH_2O$. This was characterised by chemical analysis and ^{27}Al n.m.r. The new species was shown to have higher stability than the tridecameric basic aluminium cation.[263]

Solubility, and the composition of solid phases, were studied in the system $Al(NO_3)_3 - Al_2(SO_4)_3 - H_2O$ at 25°C.[264] Phase relationships were established for the systems: $Al^{3+},Ga^{3+} + H^+ \| SO_4^{2-} - H_2O$; $Ga^{3+} + H^+,In^{3+} \| SO_4^{2-} - H_2O$, and $Al^{3+},In^{3+} \| SO_4^{2-} - H_2O$ at 25°C.[265]

$Al_2V_{10}O_{28}.22H_2O$ forms orthorhombic crystals, space group Acmm. Thermal decomposition yields 2:1 mixtures of V_2O_5 and $AlVO_4$.[266] The temperature of peritectic fusion of $AlVO_4$ depends upon the partial pressure of oxygen in the synthesis of the specimens.[267] Phase compositions and equilibria were studied in the system $AlVO_4 - CrVO_4 - FeVO_4 - NaVO_3$. A continuous complex solid solution was formed, involving $NaFeV_2O_7$, $NaCrV_2O_7$ and $NaAlV_2O_7$.[268] Phase diagrams were elucidated for the systems: $Al_2O_3 - SiO_2 - V_2O_5$, $Al_2O_3 - K_2O - V_2O_5$, $Al_2O_3 - K_2O - SiO_2 - V_2O_5$;[269] $Al_2O_3 - Na_2O - V_2O_5$ and $Al_2O_3 - SiO_2 - Na_2O - V_2O_5$.[270] A study of phase composition and equilibrium in the system $FeVO_4 - CrVO_4 - AlVO_4 - KVO_3$ shows that several new pyrovanadates are formed, including $KAlV_2O_7$.[271]

$AlTaO_4$ single crystals can be prepared from Al_2O_3 and Ta_2O_5 at 1800°C. X-ray diffraction shows that the crystals have tetragonal symmetry (space group D_{2h}^{14}-$P4_2/mnm$). The structure is of rutile-type, with a statistical distribution of Al and Ta.[272]

The vibrational spectra of $MAl(MoO_4)_2$, where M = K, Rb or Cs, have been studied, and some assignments proposed.[273] Phase equilibria have been determined in the systems $Bi_2(MoO_4)_3$ - $M_2(MoO_4)_3$, where M = Al or In.[274]

The spinel $ZnAl_2S_4$ has been studied by X-ray diffraction. The lattice constant was 1000.9(1) pm, and the results were explicable in terms of the space group Fd3m. The cation distribution corresponded to the normal spinel structure.[275]

$Al(NR_2)_3$ and $ClAl(NR_2)_2$, where R = Me, insert CS_2 to form the dimethyldithiocarbamates $Al(S_2CNR_2)_3$ and $ClAl(S_2CNR_2)_2$ respectively. The former is monomeric; ^{27}Al n.m.r. suggests six-coordinate aluminium, which is confirmed by X-ray diffraction (the geometry at the aluminium is distorted octahedral). The latter is dimeric, with two bridging chlorine atoms, and six-coordination at each aluminium.[276]

The quasibinary systems $Zn_{1-x}Cd_xAl_2S_4$, $ZnAl_{2(1-x)}Ga_{2x}S_4$, and $ZnAl_2S_{4(1-x)}Se_{4x}$ were investigated by X-ray diffraction and vibrational spectroscopy. In the spinel $ZnAl_2S_4$, up to 20% of the zinc can be replaced by Cd. In the other systems $ZnAl_2S_4$ has no measurable homogeneity range. Thiogallate phases have much broader homogeneity ranges. At 950°C, $ZnAl_2Se_4$ undergoes a reversible phase transition to a wurtzite-type structure.[277]

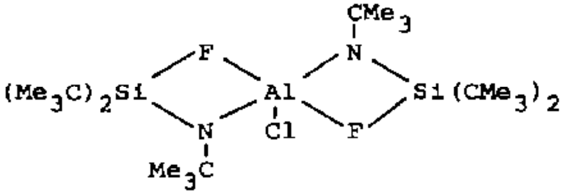
3.2.5 Aluminium Halides

Stability constants have been measured for aluminium fluoro complexes in the system $Al(NO_3)_3$ - NH_4F - NH_4NO_3 - H_2O at 25°C; $K_{AlF^{2+}}$ 2.90 x 10^6; $K_{AlF_2^+}$ 2.76 x 10^{11}; K_{AlF_3} 1.46 x 10^{15}; $K_{AlF_4^-}$ 6.76 x 10^{17}; $K_{AlF_5^{2-}}$ 1.97 x 10^{19}; $K_{AlF_6^{3-}}$ 2.88 x 10^{28}.[278]

Standard extended Hückel techniques, with automatic optimisation, were used to study the structures and energetics of AlX_3 and Al_2X_6 molecules, where X = F, Cl, Br or I. Marked nonrigidity was found for the AlXAlX ring in Al_2X_6.[279]

The interaction of BeF_2 and AlF_3, at temperatures 400-800°C and AlF_3 concentrations of 0-75%, was investigated to give preliminary results on the AlF_3-BeF_2 phase diagram.[280]

The solubilities of $CaCl_2$ and cryolite in aqueous solutions were studied at 60°C and 80°C. The mixed fluoroaluminate $CaNaAlF_6$ was identified.[281] $[C(NH_2)_3]_3MF_6$, where M = Al, Ga or In, were isolated from aqueous solutions of the corresponding fluorides. The compounds are isostructural, space group Pa3.[282] Some phase relationships were elucidated for the system 3Li,3Na‖ AlF_6,3Cl, 3F.[283]



(84)

Silicenium ylides can be stabilised by coordination with aluminium trihalides. A crystal structure determination was carried out for $[(Me_3C)_2SiNCMe_3]_2AlClF_2$,(84).[284]

The nature of ionic species formed by dissolving $AlCl_3$ or $Al(ClO_4)_3$ in anhydrous methanol was studied by ^1H, ^{27}Al and ^{35}Cl n.m.r. For $AlCl_3$, the chief species is $[AlCl_2(MeOH)_4]^+$, with no evidence for monochloro-species. $Al(ClO_4)_3$ solutions give very broad ^{27}Al resonances, probably due to interaction between the anions and hexasolvated Al(III) cations. Addition of H_2O to the $AlCl_3$ solutions leads to the formation of mono- and di-aquodichloro complexes, followed by chloride-free species, with both MeOH and H_2O in the coordination sphere.[285]

I.r. spectra have been obtained for aluminium chloride vapour (Al_2Cl_6, $AlCl_3$), including data on $Al_2{}^{35}Cl_6$ and $Al_2{}^{37}Cl_6$, in the ranges 473-873K and 700-50 cm^{-1}, as well as Raman spectra of Al_2Cl_6 vapour (ca. 500K) and $AlCl_3$ vapour (ca. 1075K), at pressures of 0.3 to 10 atm., including polarisation measurements, and spectra of the ^{35}Cl and ^{37}Cl compounds. Detailed vibrational assignments were therefore possible. The dimer spectra were interpreted in terms of D_{2h} symmetry - all 9 Raman-active and 7 of the infrared-active fundamentals were assigned. All four fundamentals for a D_{3h} monomer were also assigned. Force fields were calculated for both monomer and dimer.[286]

^{27}Al n.m.r. line-widths and ^{13}C n.m.r. chemical shifts have been studied in mixtures of 1-methyl-3-ethylimidazolium chloride and aluminium chloride at room temperature. The ^{13}C shifts were explicable by anion-cation interactions, and the ^{27}Al line widths by the presence of more than one type of chloroaluminate ion. Temperature-dependent ^{27}Al n.m.r. spectra show that chemical exchange takes place between chloroaluminate anions in aluminium chloride-rich molten salts.[287]

$[Al(C_4H_8O_2)Cl_3].C_4H_8O_2$ forms monoclinic crystals, space group $P2_1/m$. The structure contains distorted trigonal planar $AlCl_3$ units bridged by dioxan chairs to form chains parallel to the *b*-axis. The chains are separated by layers of dioxan molecules. The geometry around the five-coordinate aluminium is approximately trigonal-bipyramidal, with some distortion of the equatorial chlorine atoms (angles 115°-123°).[288]

High-resolution ^{1}H and ^{13}C n.m.r. spectra have been obtained for the n-butylpyridinium cation (BP^+) in (BP)Cl-$AlCl_3$ melts. The chemical shifts and proton coupling constants are affected by BP^+-$AlCl_4^-$ association. The ^{7}Li n.m.r. spectra of (BP)Cl-$AlCl_3$-LiCl gave evidence for the formation of $Li^+Al_2Cl_7^-$.[289]

Component interaction was detected in the CuCl-$AlCl_3$ system. The compound $Cu(AlCl_4)_2$ was formed, which melts incongruently at 212°C.[290]

Complexes $YbCl_3$-$(AlCl_3)_n$ have been investigated in the gas phase radiochemically, using tracer ^{169}Yb. ΔH_{298} and ΔS_{298} values were estimated for $YbAlCl_6$, $YbAl_2Cl_9$, $YbAl_3Cl_{12}$ and $YbAl_4Cl_{15}$, from measurements of the equilibrium constants for (11), in the range

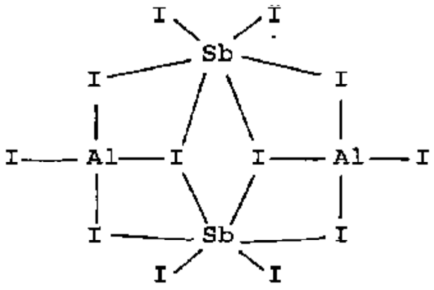
$$YbCl_{3(s)} + n\ Al_2Cl_{6(g)} \rightleftharpoons YbAl_{2n}Cl_{6n+3(g)} \qquad \ldots(11)$$

500-1000K.[291]

The nuclear spins of ^{27}Al, ^{69}Ga or ^{71}Ga in $[MCl_{4-n}Br_n]^-$ and $[M(MeCN)_6]^{3+}$, where M = Al or Ga, relax by means of the second-kind scalar and quadrupole relaxation mechanisms. No exchange processes were found for these ions on the n.m.r. time-scale.[292]

$PI_4^+AlI_4^-$ is produced from PI_3,I_2 and AlI_3 in CS_2 solution. It forms orthorhombic crystals, space group Pna2. The anion is approximately tetrahedral, with an Al-I distance of 251.8 pm. Weak I...I bonds (338.6-345.1 pm) link the anions and cations to form a three-dimensional array.[293] $P_2I_5^+AlI_4^-$ crystals are orthorhombic (space group Pbca), with a mean Al-I bond length of 252.9 pm.[294]

$Al_2Sb_2I_{12}$ is prepared by heating stoichiometric amounts of AlI_3



(85)

and SbI_3 in CS_2. It forms monoclinic crystals, space group C2/m. The $Al_2Sb_2I_{12}$ units are formed by two Sb-I octahedra sharing four common edges with two AlI_4 tetrahedra, (85).[295]

3.2.6 Other Aluminium-containing Species

The electronic absorption spectra have been reported for Al_2, Ga_2 and In_2. The ground state of Al_2 was re-assigned as ${}^1\Sigma_g^+$, not ${}^3\Sigma_g^-$.[296]

The phase diagram has been established for the Ti-Ni-Al-C system at 1100°C. The H-phase Ti_2AlC and the perovskite phase Ti_3AlC are destabilised by even small amounts of Ni.[297]

Aluminium dissolves in $LaNi_5$ to form $LaNi_{5-x}Al_x$ (for x up to 1.5). Hydride phases based on these have been synthesised and characterised. They are more stable than those based on $LaNi_5$ itself.[298]

EXAFS spectra obtained for solid and for flash-melted aluminium films with a single nanosecond pulse of X-rays from a laser-produced plasma. These spectra gave a direct observation of a degree of local order in rapidly-melting aluminium.[299]

3.3 GALLIUM

3.3.1 Compounds containing Ga-C Bonds

The product from the reaction of $Ga(CH_2SiMe_3)_3$ and KH in benzene at 45°C was identified as $KGa(CH_2SiMe_3)_3H$ (by X-ray diffraction, i.r., ^1H n.m.r. spectroscopy, and by its reactions). The compound does not decompose thermally below 200°C. X-ray diffraction shows that the crystals are monoclinic (space group $P2_1/c$). The geometry at gallium was distorted tetrahedral. The infrared spectra of $KGa(CH_2SiMe_3)_3H$, and its Ga-D analogue, showed νGa-D at 1075 cm^{-1}, and hence νGa-H ca. 1500 cm^{-1} - an unusually low value. $In(CH_2SiMe_3)_3$ and KH gave $K[In(CH_2SiMe_3)_3H]$ and $K[In(CH_2SiMe_3)_4]$. The tetrakis-compound formed monoclinic crystals ($P2_1/c$), with In-C distances in the range 2.234(4)-2.251(4)Å.[300]

Chlorogallium(III) porphyrins react with organolithium or Grignard reagents to form new porphyrin species containing a σ-Ga-C bond.[301]

3.3.2 Compounds containing Ga-N or Ga-P Bonds

$Ph_2GaX.L$ (L = py or PPh_3) and $[(Ph_3P)_2N]^+Ph_2GaX_2^-$ (X = Cl or Br) can be prepared from Ph_2GaX. Their vibrational spectra were reported and assigned, e.g. νGaN in the pyridine adduct is at 262 (X = Cl), 248 (X = Br) cm^{-1}; νGaP in the PPh_3 adduct at 310 (X = Cl), 304 (X = Br) cm^{-1}.[302]

A crystal structure determination has been carried out on the gallium(III) complex of the hexadentate ligand ethylenebis[(o-hydroxyphenyl)glycine], EHPG, i.e. $Ga(EHPG)^{2-}$. This complex is a model for the metal-binding site of the human iron-transport protein transferrin. The crystals (monoclinic, space group C2/c) only contain the racemic isomer of EHPG. The gallium is bound to two N atoms, two phenolate O atoms and two carboxylate O atoms.[303]

3.3.3 Compounds Containing Bonds Between Gallium and Group 6 Elements

The alkali metal gallates and indates $MM'O_2$, where M = Li, Na, K, Rb, Cs; M' = Ga; M = Li or Na; M' = In, can be prepared from the corresponding oxides. Infrared and Raman spectra, with some vibrational assignments, were reported.[304]

$K_2Li_3GaO_4$ is prepared from the binary oxides (as a powder) or from $LiGaO_2/KO_{0.48}$ (as single crystals). The crystals are monoclinic, space group $P2_1/c$, while the structure is complex, with all of the gallium atoms four-coordinate (mean Ga-O distance 183 pm).[305] The interaction of lithium molybdate and gallium(III) sulphate produces $Li_3Ga(MoO_4)_3$ and $LiGa(MoO_4)_2$, as well as Li_2SO_4.[306] $CaAGaEO_7$, where A = Ti, Zr, Hf or Sn; E = Sb, Nb or Ta, all have the zirconolite structure.[307]

12-Tungstogallic acid, $H_5[GaW_{12}O_{40}].13H_2O$, and its alkaline-earth metal salts were prepared by ion-exchange from the sodium salt. The compounds were characterised by X-ray powder diffraction, thermogravimetry, i.r. and ^1H n.m.r. spectra, etc.[308]

Infrared and Raman spectra have been reported for the calcium gallium oxides $CaGa_4O_7$, $CaGa_2O_4$, $Ca_3Ga_4O_9$ and $Ca_3Ga_2O_6$. All except the third have gallium only in the tetrahedral coordination state, while the first two have non-centrosymmetric, the last two centrosymmetric structures.[309]

An X-ray diffraction study has been made of the MO_2-$ANbO_4$ systems, where M = Ti, Zr, Hf or Sn; A = Al or Ga. Evidence was found for the new (orthorhombic) compounds $MO_2.4GaNbO_4$ (where M = Ti, Zr, Hf or Sn).[310] Single-crystal X-ray diffraction was used to refine the structural parameters for gadolinium gallium garnet, $Gd_3Ga_5O_{12}$.[311] $Pb_3GeGa_{10}O_{20}$ is isostructural with $Pb_3GeAl_{10}O_{20}$. The structure consists of a framework of six-membered rings of GaO_4 tetrahedra, forming a ribbed plane. These planes are connected by a string of octahedra.[312]

$GaLa_3OS_5$ forms orthorhombic crystals, space group Pnma. The gallium is four-coordinated (by S atoms), with Ga-S distances between 2.215(2) and 2.335(1)Å.[313]

GaX_3 (where X = Cl, Br or I) and the silyl sulphides Me_3SiSR (where R = Me, Et or Ph) react to give the extremely moisture-sensitive $X_2Ga(SR)$, where X = Cl, Br, I; R = Me, Et, Ph, $ClGa(SR)_2$, where R = Me, Et, Ph, $Br_3Ga_2(SR)_3$, where R = Me or Et, and $Ga(SR)_3$, where R = Me, Et or Ph. All were characterised by infrared and ^1H n.m.r. spectroscopy.[314]

Equilibrium diagrams have been established for the systems Ga_2S_3-PbS and Ga_2S_3-Pb.[315] Regions of glass formation have been identified in the systems As_2X_3-GaX (X = S, Se or Te) and related to the equilibrium diagrams in each case.[316]

Crystals of $Ga_2Sn_2S_5$ are orthorhombic (space group $Pna2_1$), containing four-coordinate gallium atoms. The structure is built up from alternating sheets of $[GaS_4]_n$ and $[Sn_2S_{11}]_n$ units. The GaS_4 tetrahedra are linked in pairs, sharing opposite edges.[317] $Ba_4Ga_4S_{10}$ (monoclinic crystals, space group C2/c) contain isolated $Ga_4S_{10}^{8-}$ anions, having the adamantane structure.[318]

The ordered phase of Ga_2Se_3 is monoclinic (space group Bb), with a superstructure of the basic distorted sphalerite-type.[319] X-ray studies of $CuGaX_2$ (X = Se or Te) at high pressure show that there is a transition from the chalcopyrite to the NaCl structure type at 12.5 GPa (X = Se) or 8 GPa (Te).[320]

The new compound $SrGa_2Se_4$ can be prepared from $SrGa_2$ and Se. It forms orthorhombic crystals (space group Cccm), and the structure is a new variant of the TlSe structure-type.[321] $Cs_6Ga_2Se_6$ is produced from Cs_2Ga/Ga_2Se_3 mixtures. The crystals are monoclinic (space group $P2_1/c$), and isolated $Ga_2Se_6^{6-}$ ions are present, with tetrahedral gallium, and two bridging Se atoms. The $GaSe_6$ distances are 238 and 240 pm, the Ga-Se_{br} distances 247 and 250 pm.[322]

GaGeTe crystallises from a melt of the elements. It is a semiconductor, with a novel structural type containing two-dimensional infinite block layers: ${}^2_\infty[\text{Te-Ga-Ge-Ge-Ga-Te}]$, derived from GaSe. The gallium atoms are bonded to 3 tellurium atoms (2.656(3)Å) and one germanium atom (2.440(3)Å).[323]

3.3.4 Gallium Halides

Effective ionic radii have been calculated for the cubic pyrochlores $CsM^{II}GaF_6$, where M^{II} = Mg, Ni, Cu, Zn, Co or Mn.[324]

Chemical equilibria were studied in the HCl-GaP system in the temperature range 800-1100K. Evidence was found for GaCl, $GaCl_2$, $GaCl_3$, HCl, H_2, P_4 and P_2 in the gas phase.[325]

The reaction of gallium and sulphur in chloride melts at ca. 500°C was followed by Raman spectroscopy. The results were consistent with the formation of long-chain chlorosulphides, $(-GaCl_2-S-GaCl_2-S-)$, as well as $GaCl_4^-$ and $Ga_2Cl_7^-$.[326]

It is possible to crystallise a phase $(C_6H_6)_{3.5}Ga_2Cl_4$ from Ga_2Cl_4 solutions in anhydrous benzene. The crystal structure shows that it is made up of cyclic, centrosymmetric $[(C_6H_6)_2Ga^IGa^{III}Cl_4]_2$ units, and isolated benzene molecules. In the bis(benzene)gallium(I) fragment, the two η^6-benzene rings form an interplanar angle of 124.4°.[327]

The formation of gaseous complexes between $NdCl_3$ and $GaCl_3$ was studied by visible absorption spectroscopy in the temperature range 600-1000K, at pressures from 5 to 20 atmospheres. Model thermodynamic calculations suggest that there is a stepwise build up of gaseous complexes: $NdGaCl_6$, $NdGa_2Cl_9$, $NdGa_3Cl_{12}$ and $NdGd_4Cl_{15}$.[328]

GaI_2-$MGaI_4$ (where M = Na, K, Rb or Cs) systems have been studied by thermal analysis. GaI_2 forms continuous solid solutions in the systems with M = Na, K or Rb; with Cs 1:1 and (possibly) 1:3 compounds are formed with $CsGaI_4$.[329]

3.3.5 Other Gallium-containing Species

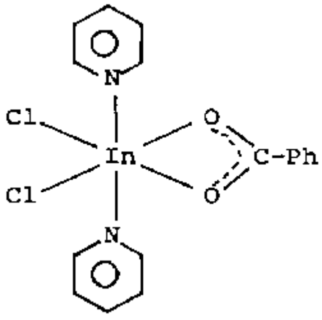
Raman spectra have been obtained for Ga_2, In_2 and Tl_2 molecules in argon and krypton matrices. Resonance progressions gave the following vibrational wavenumbers and anharmonicities: Ga_2:$\omega_e'' = 180\ cm^{-1}$, $\omega_e x_e'' = 1\ cm^{-1}$; In_2: $118\ cm^{-1}$, $0.8\ cm^{-1}$; Tl_2: $80\ cm^{-1}$, $0.5\ cm^{-1}$. The dissociation energies of In_2 and Tl_2 were recalculated as 20 $kcal.mol^{-1}$, 10 $kcal.mol^{-1}$ respectively (±10%).[330]

Crystal structure determinations have been carried out for Ba_8Ga_7, Sr_8Ga_7 and Sr_8Al_7. All are cubic, space group $P2_13$. The structure is characterised by the presence of isolated tetrahedral and triangular clusters of Ga (or Al) atoms inside cages of alkaline-earth atoms.[331]

3.4 INDIUM

3.4.1 Compounds containing In-N, In-P or In-Sb Bonds

Crystals of $Cl_2In(O_2CPh)py_2$ are orthorhombic, space group $Pna2_1$; the structure is (86), with In-Cl, 2.39Å; In-O, 2.25-2.28Å; In-N 2.25-2.30Å. It was suggested that the indium-benzoate bonding involves a three-centre m.o., $In\!-\!\!<^{O}_{O}$ (formally occupying only one coordination site, rather than the conventional form $In\!\lessgtr^{O}_{O}$, occupying two sites.[332]



(86)

A single-crystal X-ray diffraction study of indium(III) dithizonate shows that the crystals are triclinic, space group $P\bar{1}$, and that the asymmetric unit is a monomeric $In(Hdz)_3$ molecule. The indium is five-coordinate (trigonal bipyramidal), with one ligand unidentate and equatorial (via S: In-S = 2.468(3)Å) and the other two bidentate (via N and S), spanning axial and equatorial positions: axial In-N, 2.372(6), 2.334(6)Å, equatorial In-S, 2.477(3), 2.467(3)Å.[333]

The InSb-Tl system was found to be quasibinary, and the solubility of thallium in InSb was studied.[334]

3.4.2 Compounds containing In-O, In-S or In-Te Bonds

A theoretical vibrational analysis has been proposed for $LaInO_3$.[335]

$NH_4[In(C_2O_4)_2].2H_2O$ forms hexagonal crystals, space group $P6_222$. The indium is eight-coordinated by oxygen atoms from four oxalato groups (which are bridging), forming a distorted Archimedean antiprism. There are four In-O bonds at 2.197(4)Å, and four at 2.351(5)Å.[336] The neutral complex $[In_2(C_2O_4)_3(H_2O)_4].2H_2O$ forms monoclinic crystals (space group $P2_1/c$), and the indium is seven-coordinated by oxygens, as a pentagonal bipyramid. These are linked by bridging oxalate groups, forming infinite chains along the [001] direction. The average In-O bond distances are 2.234(16)Å to oxalate, 2.157(2)Å to H_2O molecules.[337]

Phase equilibria have been studied in the $BaO-In_2O_3$ system. The following compounds were found: $Ba_5In_2O_8$, $Ba_3In_2O_6$, $Ba_2In_2O_5$, $\alpha-Ba_4In_6O_{13}$, $\beta-Ba_4In_6O_{13}$ and $BaIn_2O_4$. Lattice parameters, infrared and Raman spectra were obtained for these, and the equilibrium diagram of the $BaO-In_2O_3$ system constructed.[338]

It was found that the systems $LiIn(MoO_4)_2-MIn(MoO_4)_2$ (where M = K or Rb) are eutectic, with regions of liquid immiscibility. No ternary compounds are formed.[339] Complex formation was studied in the In(III)-molybdate system. Heteropoly complexes of the 6-, 9- and 12-series were all formed.[340]

Knudsen cell mass spectrometry was used to study the equilibrium vaporisation of $CuInS_2(s)$ in the temperature range 902-1110K. Evidence was found for the reaction (12), and ΔH°_{298} for this

$$2CuInS_2(s) \rightarrow Cu_2S(s) + In_2S(g) + S_2(g) \qquad \ldots(12)$$

reaction was found to be 630.9±26 kJ mol^{-1}. The enthalpy of formation of $CuInS_2$ was calculated to be, $\Delta H^\circ_{298,s} = -221.7\pm13$ kJ. mol^{-1}.[341]

In_5KS_8 forms monoclinic crystals, space group B2/m. Both four- and six-coordinate indium atoms are present, with In-S distances in the range 2.428-2.749Å.[342] $Pb_{1.6}In_8Bi_4S_{19}$ also forms monoclinic crystals (space group C2/m). Distorted In-S octahedra are present, with bond distances 2.572(6)-2.733(4)Å.[343]

Electrical conductivity, microhardness and lattice parameters were measured in the solid solutions $(In_2Te_3)_x(Hg_3Te_3)_{1-x}$ (for $0 \leqslant x \leqslant 0.1$) at 300K.[344]

3.4.3 Indium Halides

The mechanism of reaction of solid InCl with aqueous nitrate solutions has been investigated. A complex series of processes appears to take place.[345] The effects of adding Cl^- and In(III) on the reaction of solid InCl with aqueous nitrate solutions were also observed. There was some evidence for heterogeneous disproportionation of the InCl.[346]

The quaternary compounds AIn_2X_3Y, where A = Cu or Ag; X = S, Se or Te; Y = Cl, Br or I, can be synthesised at high temperature and pressure. The structures are either of the defect zinc blende or defect NaCl types.[347]

The phase diagram of the In/Cl system has been redetermined in the range 30-50 mole % In. The only mixed valence chlorides detected are In_3Cl_4, In_2Cl_3 and In_5Cl_9. The last compound crystallises with the $Cs_3Tl_2Cl_9$-type of structure, i.e. it contains isolated $In_2^{III}Cl_9{}^{3-}$ anions.[348]

^{81}Br n.q.r. tensors have been determined for $(NH_4)_2InBr_5.H_2O$.[349]

3.5 THALLIUM

3.5.1 Thallium(I) Compounds

N.m.r. spectra have been obtained for Tl^+ in molten binary mixtures of salts. Shifts of $^{205}Tl^+$ increase in the paramagnetic direction with increased temperature and in the diamagnetic direction with decreased size of added foreign cations.[350]

$Tl^I[C_5H_4PPh_2]$ can be prepared from $CpPPh_2$ and Tl(OEt). It is a useful reagent in the synthesis of heterobimetallic Tl-Mn complexes.[351]

^1H n.m.r. data show that at pH values from 7 to 14, Tl(I) is coordinated to β-alanine predominantly <u>via</u> O, to aspartic acid <u>via</u> O and N, although S may participate in coordination. Tl(I) coordinates glycine <u>via</u> N and O, while Tl(III) always coordinates amino-acids <u>via</u> N and O.[352]

$Tl(C_4H_8O_2)^+TlBr_4^-$ forms orthorhombic crystals, space group $Cmc2_1$. The $TlBr_4^-$ anions are tetrahedral, while the Tl^+ cations exist in chains, bridged by 1,4-dioxan molecules. The geometry around the eight-coordinate Tl^+ is a distorted dodecahedron.[353]

^{205}Tl and ^{13}C n.m.r. spectra show that Tl^+ and gramicidin A bind to form a 1:1 complex, with the ligand binding site identified as a carbonyl group.[354]

The cationic conductivity has been measured for thallium hexaniobate, $Tl_2O.6Nb_2O_5$.[355] The Raman spectra of Tl_2CO_3 have been studied at pressures up to ca. 52 kbar, and the infrared spectra to ca. 36 kbar. Phase transitions were detected from the Raman spectra at 13 and 38 kbar.[356]

No fewer than 45 new thallium(I) carboxylates have been synthesised, analysed, and their νCO_2 vibrational wavenumbers assigned.[357] Infrared and Raman spectra of thallium(I) formate, acetate, propionate and acrylate were recorded and assigned. The Tl(I)-carboxylate bond was fractionally completely ionic.[358]

The temperature dependences of ^{205}Tl n.m.r. spectra of thallium(I) formate and acetate were studied. Evidence was found for a number of phase changes not hitherto detected by thermal analysis measurements.[359]

Mass spectra were obtained for RCOOTl, where R = H or aliphatic radical. Tl^+ always had the greatest intensity, while the molecular ion was absent, or very weak. All of the compounds were monomeric in the gas-phase.[360] For RCOOTl, where R = $PhCH_2$, Ph, substituted phenyl or PhCH=CH, the M^+ peak was observed (except for R = Ph). The strongest peak was still always Tl^+. The thallium halogenobenzoates also gave $[TlX]^{+\cdot}$ rearrangement peaks. The intensities of these can be rationalised by using the HSAB principle.[361]

Double molybdates and tungstates, $Tl^{I}Bi(EO_4)_2$, where E = Mo or W, can be prepared by solid-phase reactions of the component oxides. Unit cell parameters and phase transformation temperatures were determined.[362]

Crystals of $Tl_2S_7N_8$ are orthorhombic (space group Pmnb), and consist of Tl^+ cations, $S_3N_3^-$ and $S_4N_5^-$ anions.[363] $TlSbS_2$ forms triclinic crystals, space group $P\bar{1}$. SbS_4 units are linked by weak Tl...S (3.50-3.68Å), Tl...Sb (3.60-3.73Å) and Tl...Tl (3.62Å) interactions.[364] $Tl_2P_2S_6$ crystals are orthorhombic, space group Immm. Tl interacts with ten sulphur atoms, at distances of from 335.0 to 359.3 pm.[365]

The Ge-S-Tl system has been studied by DTA and X-ray diffraction, together with e.m.f., microhardness and saturated vapour pressure measurements. Evidence was found for 5 ternary compounds: $Tl_2Ge_2S_5$, Tl_2GeS_3, $TlGeS_2$, Tl_4GeS_5 and Tl_4GeS_4.[366] Phase diagrams were established, and regions of glass formation observed for the system $TlSe-Tl_4GeS_4-GeSe_2$.[367] Phase diagrams were also constructed for Tl_2S-SiS_2 and $Tl_2Se-SiSe_2$ systems.[368]

Equilibrium diagrams have been determined for the ternary reciprocal systems (13)[369] and (14).[370] Other thallium(I)-

$$HgS + Tl_2Se \rightleftharpoons HgSe + Tl_2S \qquad ...(13)$$

$$HgS + Tl_2Te \rightleftharpoons HgTe + Tl_2S \qquad ...(14)$$

containing systems for which phase diagrams have been studied are: Ag-Se-Tl;[371] $GeSe_2-Tl_2Se$, GeSe-TlSe, $GeSe_2-TlSe$;[372] Hg-Se-Tl;[373] Hg-Te-Tl;[374] and Se-Tl (in the range 33-100% Se).[375]

The solubilities of thallium(I) halides, and their crystallisation from aqueous solutions have been studied. It proved possible to grow large single crystals of high purity.[376]

High-resolution photoelectron spectra were obtained for both valence bands and Tl 5d levels in thallium(I) halides, TlX, where X = Cl, Br or I, in the gas phase. A transition-state Xα-SW calculation on TlCl gave agreement with previous valence band assignments. The ligand field splitting of the 5d Tl level was resolved in all 3 compounds.[377]

$TlCl-LnCl_3$ (Ln = La, Gd or Yb) phase diagrams reveal the existence of $Tl_2Ln_2Cl_7$ (Ln = Gd, Yb); Tl_2LnCl_5 (Ln = La, Gd) and Tl_3LnCl_6 (Ln = Gd, Yb).[378]

Phase equilibria were studied in the systems $PbBr_2-TlBr$ and GeI_2-TlI. The following compounds were found: $TlPbBr_3$, Tl_3PbBr_5, $TlGeI_3$ and Tl_3GeI_5. Single crystals of Tl_3PbBr_5, $TlPb_2Br_5$ and $TlGeI_3$, as well as Tl_3SnI_5 were all obtainable.[379]

The thermodynamics of dissolving thallium(I) iodide in H_2O, and in 0.5M to 4.0M aqueous solutions of $KClO_4$ or KI at 278, 298 and 318K were determined. The observed increase in solubility with increasing temperature and ionic strength were ascribed to an entropy factor.[380]

Solubility, and the composition of the solid phases were established for the system $PbI_2-TlI-H_2O$ at 25°C.[381]

The system $TlI-Tl_2Se$ was investigated by D.T.A., X-ray diffraction and metallography. Two new compounds, Tl_5ISe_2 and Tl_6I_4Se, were formed. The crystal structure of Tl_6Cl_4S, an analogue of the latter, was found. It was based on the TlCl structure, in which $^1/5$ of the Tl or Cl atoms had been regularly replaced by Tl_2S.[382]

3.5.2 Thallium(III) Compounds

The decomposition of $MeTl(OAc)_2$ in methanol, in the presence of amines, e.g. 2-, 3- or 4-picoline, dimethylaniline etc., gave mainly N-methylation.[383]

A very long paper has appeared on the ^{13}C and ^1H n.m.r. parameters for a wide range of mono- and di-organothallium(III) derivatives. The major factor influencing J(Tl-C) and J(Tl-H) is the number of R groups attached to Tl.[384]

Crystal structures of complexes formed by dimethylthallium picrate and two isomers of dicyclohexano-18-crown-6 show that in both there are $[Me_2Tl(crown)]^+$ cations and picrate anions. The complex cations consist of linear Me_2Tl units normal to the plane through the six oxygen atoms of the ligand and the thallium atom.[385]

$TlR_3(diox)$, where R = 2,4,6-$C_6F_3H_2$ or C_6F_5; diox = 1,4-dioxan, are prepared by the reaction of $TlCl_3$ with LiR (for R = $C_6F_3H_2$) or of $[NBu_4][TlR_4]$ with HBF_4 (for R = C_6F_5), with subsequent addition of dioxan. Dioxan can be replaced by neutral or anionic ligands or by metal carbonylates to give e.g. $[TlR_3M]^-$, where M = $CpMo(CO)_3^-$, $Co(CO)_4^-$ or $Mn(CO)_5^-$.[386]

The ternary carbonates $TlLnICO_3)_2$, where Ln = La to Lu or Y, are synthesised at 350°C by dehydration of the carbonates $TlLn(CO_3)_2.xH_2O$, or at 500°C by the reaction of $Tl_2(CO_3)_2$ and $Ln_2(C_2O_4)_3.yH_2O$ under 3000 bar CO_2.[387]

Pentachlorothallates(III) can be prepared by crystallisation from aqueous solutions of $TlCl_3$ and MCl i.e. $K_2TlCl_5.2H_2O$, $M_2TlCl_5.H_2O$ (M = Rb or NH_4). The potassium compound forms monoclinic crystals containing dimeric $Tl_2Cl_{10}{}^{4-}$ anions, formed by edge-sharing octahedra. The monohydrates are orthorhombic.[388] The crystal structure of $(pyH)_2TlCl_5.Me_2SO$ has been determined. There is basic octahedral geometry around the Tl in $[TlCl_5(Me_2SO)]^{2-}$, with Tl-O 2.42(2)Å, and Tl-Cl within the range 2.506(6)Å-2.636(6)Å. The O-coordination of the DMSO confirms spectroscopic results.[389]

$TlBr_3(C_4H_8O_2)$ forms monoclinic crystals, space group C2/c. Distorted planar $TlBr_3$ units are bridged by dioxan chairs forming chains parallel to the c-axis. The overall coordination about the thallium is trigonal-pipyramidal. The Tl-O distance is 2.543(13)Å, with Tl-Br 2.498(3)-2.509(2)Å.[390]

$MTlBr_4$ (where M = K, Rb, Cs or NH_4) are prepared by dehydration of the hydrates or by the reaction of TlBr, MBr and Br_2 in closed glass tubes at 400°C. The K^+ and NH_4^+ salts are both orthorhombic (with the Ga[$GaCl_4$] type of structure).[391]

The previously-suggested space group of [Bu_4^nN][TlI_4], $P2_1$, has been shown to be in fact $P2_1/n$, but this leads to only slight changes in the molecular parameters.[392]

REFERENCES

1 L.Laaksonen, P.Pyykkö and D.Sundholm, Chem. Phys. Lett., 96(1983)1.
2 R.J.Harrison and N.C.Handy, Chem. Phys. Lett., 95(1983)386.
3 D.M.Hirst, Chem. Phys. Lett., 95(1983)591.
4 W.C.Herndon and J.E.Leonard, Inorg. Chem., 22(1983)554.
5 J.B.Casey, W.J.Evans and W.H.Powell, Inorg. Chem., 22(1983)2228.
6 J.B.Casey, W.J.Evans and W.H.Powell, Inorg. Chem., 22(1983)2236.
7 T.Clark, D.Wilhelm, P.v.R.Schleyer, J. Chem. Soc., Chem. Commun., (1983)606.
8 O.D.Kuleshova and A.I.Gorbunov, Russ. J. Inorg. Chem., 28(1983)45.
9 P.C.Keller, R.L.Marks and J.V.Rund, Polyhedron, 2(1983)595.
10 T.Beringhelli, G.Filippini, A.Gavezzotti and M.Simonetta, J. Mol. Struct., 94(1983)51.
11 G.B.Jacobsen, J.H.Morris and D.Reed, J. Chem. Res. (S), (1983)42.
12 R.L.De Kock and C.P.Jasperse, Inorg. Chem., 22(1983)3843.
13 T.Davan, E.W.Corcoran and L.G.Sneddon, Organometallics, 2(1983)1693.
14 J.A.Heppert and D.F.Gaines, Inorg. Chem., 22(1983)3155.
15 E.W.Corcoran and L.G.Sneddon, Inorg. Chem., 22(1983)182.
16 L.G.Hubert-Pfalzgraf and M.Tsunoda, Polyhedron, 2(1983)203.
17 T.P.Fehlner, C.E.Housecroft, W.R.Scheidt and K.S.Wong, Organometallics, 2(1983)825.
18 R.Shinomoto, E.Gamp, N.M.Edelstein, D.H.Templeton and A.Zankin, Inorg. Chem., 22(1983)2351.
19 W.Biffar, H.Nöth and D.Sedlak, Organometallics, 2(1983)579.
20 J.A.Baban, J.C.Brand and B.P.Roberts, J. Chem. Soc., Chem. Commun., (1983)315.
21 L.Ya. Baranov and A.I.Boldyrev, Chem. Phys. Lett., 96(1983)218.
22 M.C.R.Symons, T.Chen and C.Glidewell, J. Chem. Soc., Chem. Commun., (1983)326.
23 R.W.Broach, I.-S.Chang, T.J.Marks and J.M.Williams, Inorg. Chem., 22(1983)1081.
24 D.G.Holah, A.N.Hughes, S.Maciaszek and V.R.Magnuson, J. Chem. Soc., Chem. Commun., (1983)1308.
25 J.C.Bommer and K.W.Morse, Inorg. Chim. Acta, 74(1983)25.
26 C.Bianchini, C.A.Ghilardi, A.Meli, S.Midollini and A.Orlandini, J. Organomet. Chem., 255(1983)C27.
27 M.F.Lappert, A.Singh, J.L.Atwood and W.E. Hunter, J. Chem. Soc., Chem. Commun., (1983)206.
28 U.Mirsaidov, A.Kurbonenkov and M.Khikmatov, Russ. J. Inorg. Chem., 27(1982)1376.
29 V.D.Makhaev, A.P.Borison, B.P.Tarasov and K.N.Semenenko, Russ. J. Inorg. Chem., 28(1983)186.
30 K.Raghavachari, P.v.R.Schleyer and G.W.Spitznagel, J. Am. Chem. Soc., 105(1983)5917.
31 R.L.De Kock, P.Deshmukh, T.P.Fehlner, C.E.Housecroft, J.S.Plotkin and S.G.Shore, J. Am. Chem. Soc., 105(1983)815.
32 A.V.Agafonov, K.A.Solntsev, D.M.Vinitskii and N.T.Kuznetsov, Russ. J. Inorg. Chem., 27(1982)1697.
33 A.S.Rozenberg, G.N.Nechiporenko, L.V.Titov and M.D.Levicheva, Russ. J. Inorg. Chem., 27(1982)1527.
34 J.R.M.Giles, V.P.J.Marti and B.P.Roberts, J. Chem. Soc., Chem. Commun., (1983)696.
35 J.Bould, N.N.Greenwood and J.D.Kennedy, J. Organomet. Chem., 249(1983)11.

36 J.Bould, J.E.Crook, N.N.Greenwood and J.D.Kennedy, J. Chem. Soc., Chem. Commun., (1983)951.
37 D.J.Fuller and D.L.Kepert, Polyhedron, 2(1983)749.
38 P.Brint, J.P.Cronin, E.Seward and T.Whelan, J. Chem. Soc., Dalton Trans., (1983)975.
39 J.E.Crook, N.N.Greenwood, J.D.Kennedy and W.S.McDonald, J. Chem. Soc., Chem. Commun., (1983)83.
40 M.E.O'Neill and K.Wade, Polyhedron, 2(1983)963.
41 D.A.Saulys, N.A.Kutz and J.A.Morrison, Inorg. Chem., 22(1983)1821.
42 J.Bould, J.E.Crook, N.N.Greenwood, J.D.Kennedy and W.S. McDonald, J. Chem. Soc., Chem. Commun., (1983)949.
43 E.H.Wong, L.Prasad, E.J.Gabe and M.G.Gatter, Inorg. Chem., 22(1983)1143.
44 M.A.Beckett, J.E.Crook, N.N.Greenwood and J.D.Kennedy, J. Chem. Soc., Chem. Commun., (1983)1228.
45 J.Bould, N.N. Greenwood and J.D.Kennedy, Polyhedron, 2(1983)1407.
46 W.Jarvis, Z.J.Abdou and T.Onak, Polyhedron, 2(1983)1067.
47 R.J.Asthiemer and L.G.Sneddon, Inorg. Chem., 22(1983)1928.
48 K.Fuller and T.Onak, J. Organomet. Chem., 249(1983)C6.
49 K.Baše, Coll. Czech. Chem. Commun., 48(1983)2593.
50 N.Canter, C.G.Overberger and R.W.Rudolph, Organometallics, 2(1983)569.
51 A.Arafat, G.D.Friessen and L.J.Todd, Inorg. Chem., 22(1983)3721.
52 L.A.Leites, L.E.Vinogradova, J.Belloc and A.Novak, J. Mol. Struct., 100(1983)379.
53 F.Teixidor and R.W.Rudolph, J. Organomet. Chem., 241(1983)301.
54 G.Z.Suleimanov, V.I.Bregadze, N.A.Koval'chuk, Kh.S.Khalilov and I.P.Beletskaya, J. Organomet. Chem., 255(1983)C5.
55 Z.Janoušek, J.Plešek, B.Štibr and S.Heřmanek, Coll. Czech. Chem. Commun., 48(1983)228.
56 D.B.Palladino and T.P.Fehlner, Organometallics, 2(1983)1692.
57 R.G.Swisher, E.Sinn, G.A.Brewer and R.N.Grimes, J. Am. Chem. Soc., 105(1983)2079.
58 R.P.Micciche and L.G.Sneddon, Organometallics, 2(1983)674.
59 R.B.Maynard, R.G.Swisher and R.N.Grimes, Organometallics, 2(1983)500.
60 R.G.Swisher, E.Sinn and R.N.Grimes, Organometallics, 2(1983)506.
61 G.J.Zimmerman and L.G.Sneddon, Acta Crystallogr., C39(1983)856.
62 R.P.Micciche, J.S.Plotkin and L.G.Sneddon, Inorg. Chem., 22(1982)1765.
63 N.W.Alcock, J.G.Taylor and M.G.H.Wallbridge, J. Chem. Soc., Chem. Commun., (1983)1168.
64 G.K.Barker, N.R.Godfrey, M. Green, H.E.Parge, F.G.A.Stone and A.J.Welch, J. Chem. Soc., Chem. Commun., (1983)277.
65 G.K.Barker, M.Green, F.G.A.Stone, W.C.Wolsey and A.J.Welch, J. Chem. Soc., Dalton Trans., (1983)2063.
66 R.B.Maynard, Z.-T.Wang, E.Sinn and R.N.Grimes, Inorg. Chem., 22(1983)873.
67 R.E.King, S.B.Miller, C.B.Knobler and M.F.Hawthorne, Inorg. Chem., 22(1983)3548.
68 P.E.Behnken, C.B.Knobler and M.F.Hawthorne, Angew. Chem., Int. Ed. Engl., 22(1983)722.
69 L.Zheng, R.T.Baker, C.B.Knobler, J.A.Walker and M.F.Hawthorne, Inorg. Chem., 22(1983)3350.
70 J.A.Walker, C.A.O'Con, L.Zheng, C.B.Knobler and M.F.Hawthorne, J. Chem. Soc., Chem. Commun., (1983)803.

71 G.K.Barker, M.P.Garcia, M.Green, F.G.A.Stone and A.J.Welch, J. Chem. Soc., Chem. Commun., (1983)137.

72 V.N.Kalinin, A.V.Usatov, and L.I.Zakharkin, J. Organomet. Chem., 254(1983)127.

73 V.I.Bregadze, N.A.Koval'chuk, N.N.Godovikov, G.Z.Suleimanov and I.P.Beletskaya, J. Organomet. Chem., 241(1983)C13.

74 B.F.Spielvogel, A.T.McPhail, J.A.Knight, C.G.Moreland, C.L.Gatchell and K.W.Morse, Polyhedron, 2(1983)1345.

75 S.G.Shore, D.-Y.Jan, L.-Y.Hsu and W.-L.Hsu, J. Am. Chem. Soc., 105(1983)5923.

76 H.Klusik and A.Berndt, Angew. Chem., Int. Ed. Engl., 22(1983)877.

77 P.Galow, A.Sebald and B.Wrackmeyer, J. Organomet. Chem., 259(1983)253.

78 N.A.Bell, H.M.M.Shearer and C.B.Spencer, Acta Crystallogr., C39(1983)694.

79 C.Eaborn, M.N.El-Kheli, N.Retta and J.D.Smith, J. Organomet. Chem., 249(1983)23.

80 J.E.Frey and E.C.Kitchen, J. Am. Chem. Soc., 105(1983)2175.

81 R.H.Cragg and T.J.Miller, J. Organomet. Chem., 241(1983)289.

82 G.W.Kabalka, U.Sastry, K.A.R.Sastry, F.F.Knapp and P.C.Srivastava, J. Organomet. Chem., 259(1983)269.

83 B.Györi, J.Emri and I.Fehér, J. Organomet. Chem., 255(1983)17.

84 R.D.Fischer and K.Yünlü, Z. Naturforsch., Teil B, 38(1983)1369.

85 J.Emri and B.Györi, Polyhedron, 2(1983)1273.

86 G.Gundersen and S.Saebø, Acta Chem. Scand., Ser. A, 37(1983)277.

87 H.Nöth and S.Weber, Z. Naturforsch., Teil B, 38(1983)1460.

88 A.Neckel, H.Polesak and P.G.Perkins, Inorg. Chem. Acta, 70(1983)255.

89 P.Paetzold and R.Truppat, Chem. Ber., 116(1983)1531.

90 V.Barone, F.Lelj, A.Pastore, P.L.Cristnziano and N.Russo, J. Mol. Struct., 92(1983)103.

91 G.Klebe, K.Hensen and H.Fuess, Chem. Ber., 116(1983)3125.

92 R.Kohm, R.A.Geanangel and R.Liepins, Inorg. Chem., 22(1983)1684.

93 B.Wrackmeyer, J. Magn. Reson., 54(1983)174.

94 H.Nöth, Z. Naturforsch., Teil B, 38(1983)692.

95 J.R.Jennings, R.Snaith, M.M.Mahmoud, S.C.Wallwork, S.J.Bryan, J.Halfpenny, E.A.Petch and K.Wade, J. Organomet. Chem., 249(1983)C1.

96 R.H.Cragg and T.J.Miller, J. Organomet. Chem., 255(1983)143.

97 C.Brown, R.H.Cragg, T.J.Miller and D.O'N.Smith, J. Organomet. Chem., 244(1983)209.

98 R.H.Cragg and T.J.Miller, J. Organomet. Chem., 243(1983)387.

99 J.A.Baban and B.P.Roberts, J. Chem. Soc., Chem. Commun., (1983)1224.

100 J.S.Binkley and L.R.Thorne, J. Chem. Phys., 79(1983)2932.

101 G.F.Musso, G.Figari and V.Magnasco, J. Chem. Soc., Faraday Trans.,2, 79(1983)931.

102 W.Linert, V.Gutmann and P.G.Perkins, Inorg. Chim. Acta, 69(1983)61.

103 W.Kaim and W.Lubitz, Angew. Chem., Int. Ed. Engl., 22(1983)892.

104 H.Binder and W.Diamantikos, Z. Naturforsch., Teil B, 38(1983)203.

105 J.M.Dupart, S.Page and J.G.Riess, J. Am. Chem. Soc., 105(1983)1051.

106 M.Shimoi and G.Kodama, Inorg. Chem., 22(1983)3300.

107 J.D.Odom, P.A.Brletic, S.A.Johnston and J.R.Durig, J. Mol. Struct., 96(1983)247.

108 M.Kameda and G.Kodama, Polyhedron, 2(1983)413.

109 M.Shimoi and G.Kodama, Inorg. Chem., 22(1983)1542.

110 R.Janta, R.Maisch, W.Malisch and E.Schmid, Chem. Ber., 116(1983)395.

111 S.Sakal and K.D.Jordan, J. Phys. Chem., 87(1983)2293.

112 V.Saraswathy, J.J.Diamond and G.A.Segal, J. Phys. Chem., 87(1983)718.

113 D.C.Frost, C.Kirby, W.M.Lau, C.A.McDowell and N.P.C.Westwood, J. Mol. Struct., 100(1983)87.

114 Yu.A.Ugai, N.E.Solov'ev and V.S.Makarov, Russ. J. Inorg. Chem., 28(1983)753.

115 A.Kirfel, G.Will and R.F.Stewart, Acta Crystallogr., B39(1983)175.

116 C.J.Adams and I.E.Clark, Polyhedron, 2(1983)673.

117 V.S.Sagulenko, E.M.Svarcs and V.G.Kalacheva, Russ. J. Inorg. Chem., 28(1983)958.

118 L.Babcock and R.Pizer, Inorg. Chem., 22(1983)174.

119 A.J.Baskar and C.M.Lukehart, J. Organomet. Chem., 254(1983)149.

120 M.T.Nguyen, P.Ruelle and T.-K.Ha, J. Mol. Struct., 104(1983)353.

121 G.E.Walrafen, M.S.Hokmabadi, P.N.Krishnan and S.Guha, J. Chem. Phys., 79(1983)3609.

122 C.J.Cardin, H.E.Parge and J.W.Wilson, J. Chem. Res. (S), (1983)93.

123 Yu.N.Ill'in, V.V.Kravchenko and K.I.Petrov, Russ. J. Inorg. Chem., 28(1983)909.

124 V.J.Heintz, W.A.Freeman and T.A.Keiderling, Inorg. Chem., 22(1983)2319.

125 S.N.Kondrat'ev, S.I.Mel'nikova and A.M.Bondar', Russ. J. Inorg. Chem., 28(1983)487.

126 A.M.Bondar', S.N.Kondrat'ev and S.I.Mel'nikova, Russ. J. Inorg. Chem., 28(1983)483.

127 V.G.Skvortsov, R.S. Tsekhanskii, A.K.Molodkin, V.M.Akimov, O.V.Petrova and V.P.Dolganev, Russ. J. Inorg. Chem., 28(1983)741.

128 H.Behm, Acta Crystallogr., C39(1983)1317.

129 I.G.Saiko, G.N.Kononova, K.I.Petrov and V.N.Agafonov, Russ. J. Incrg. Chem., 27(1983)1374.

130 M.Touboul, C.Bois, D.Mangin and D.Amoussou, Acta Crystallogr., C39(1983)685.

131 V.G.Skvortsov, R.S.Tsekhanskii, A.K.Molodkin, V.P.Dolganev and N.S.Rodionov, Russ. J. Inorg. Chem., 27(1983)1370.

132 E.Uipe-Nava, A.S.Batsanov, Yu.T.Struchkov, V.M.Akimov, A.K.Molodkin, V.G.Skvortsov and N.S.Rodionov, Russ. J. Inorg. Chem., 28(1983)962.

133 J.Emsley and J.S.Lucas, J. Chem. Soc., Dalton Trans., (1983)1811.

134 R.S.Tsekhanskii, V.G.Skvortsov and A.K.Molodkin, Russ. J. Inorg. Chem., 28(1983)486.

135 C.G.Salentine, Inorg. Chem., 22(1983)3920.

136 H.Behm, Acta Crystallogr., C39(1983)1156.

137 H.Behm, Acta Crystallogr., C39(1983)20.

138 R.S.Tsekhanskii, V.G.Skvortsov, A.K.Molodkin and Sh.V.Sadetdinov, Russ. J. Inorg. Chem., 28(1983)441.

139 B.Kh.Khazikhanova, B.A.Beremzhanov, R.F.Savich and V.G.Kalacheva, Russ. J. Inorg. Chem., 28(1983)761.

140 B.Kh.Khazikhanova, B.A.Beremzhanov, R.F.Savich and V.G.Kalacheva, Russ. J. Inorg. Chem., 28(1983)729.

141 Z.L.Khakulov, G.K.Shurdumov and M.V.Mokhosoev, Russ. J. Inorg. Chem., 28(1983)1020.

142 G.K.Abdullaev, P.F.Rza-Zade and Kh.S.Mamedov, Russ. J. Inorg. Chem., 28(1983)428.

143 G.K.Abdullaev, P.F.Rza-Zade and Kh.S.Mamedov, Russ. J. Inorg. Chem., 28(1983)115.

144 G.K.Abdullaev, Kh.S.Mamedov and N.T.Buludov, Russ. J. Inorg. Chem., 27(1982)1671.

145 B.M.Gimarc and J.-K.Zhu, Inorg. Chem., 22(1983)479.

146 R.I.Baxter, R.J.M.Sands and J.W.Wilson, J. Chem. Res. (S), (1983)94.

147 A.E.Shirk and J.S.Shirk, Inorg. Chem., 22(1983)72.

148 E.Haller, H.Köppel, L.S.Cederbaum, W. von Niessen and G.Bieri, J. Chem. Phys., 78(1983)1359.

149 M.A.Benzel, A.M.Maurice, R.L.Belford and C.E.Dykstra, J. Am. Chem. Soc., 105(1983)3802.

150 J.M.Miller, Inorg. Chem., 22(1983)2384.

151 D.R.Martin, J.U.Mondal, R.D.Williams, J.B.Iwamoto, N.C.Massey, D.M.Nuss and P.L.Scott, Inorg. Chim. Acta, 70(1983)47.

152 S.Jurga and J.Depireux, J. Magn. Reson., 55(1983)12.

153 B.N.Chernyshov, G.P.Shchetinina and E.G.Ippolitov, Russ. J. Inorg. Chem., 27(1982)1526.

154 V.I.Saldin, O.V.Brovkina, E.G.Ippolitov and A.P.Popov, Russ. J. Inorg. Chem., 28(1983)273.

155 V.K.Volkova and G.A.Bukhalova, Russ. J. Inorg. Chem., 27(1982)1649.

156 W.Haubold and P.Jacob, Z. Anorg. Allg. Chem., 507(1983)231.

157 R.Bravo and J.-P.Laurent, J. Chem. Res. (S), (1983)6.

158 R.K.Harris, A.Root and K.B.Dillon, Spectrochim. Acta, Part A, 39(1983)309.

159 S.M. van der Kerk, P.H.M.Budzelaar, A. van der Kerk-van Hoof, G.J.M. van der Kerk and P. von R. Schleyer, Angew. Chem., Int. Ed. Engl., 22(1983)48.

160 G.E.Herberich, B.Hessner and D.Söhnen, J. Organomet. Chem., 256(1983)C23.

161 S.M. van der Kerk, J.C.Roos-Venekamp, A.J.M. van Beijnen and G.J.M. van der Kerk, Polyhedron, 2(1983)1337.

162 J.Edwin, M.Bochmann, M.C.Böhm, D.E.Brennan, W.E.Geiger, C.Krüger, J.Pebler, H.Pritzkow, W.Siebert, W.Swiridoff, H.Wadepohl, J.Weiss and U.Zenneck, J. Am. Chem. Soc., 105(1983)2582.

163 G.E.Herberich, J.Hengesbach, G.Huttner, A.Frank and U.Schubert, J. Organomet. Chem., 246(1983)141.

164 G.E.Herberich and H.Ohst, Z. Naturforsch., Teil B, 38(1983)1388.

165 G.Schmid, U.Höhner, D.Kampmann, D.Zaika and R.Boese, J. Organomet. Chem., 256(1983)225.

166 G.E.Herberich, B.Hessner, W.Boveleth, H.Lüthe, R.Saive and L.Zelenka, Angew. Chem., Int. Ed. Engl., 22(1983)996.

167 H.C.Brown and G.G.Pai, J. Organomet. Chem., 250(1983)13.

168 H.-O.Berger and H.Nöth, J. Organomet. Chem., 250(1983)33.

169 N.M.Kostić and R.F.Fenske, Organometallics, 2(1983)1319.

170 G.E.Herberich,and D.Söhnen, J. Organomet. Chem., 254(1983)143.

171 G.E.Herberich and A.K.Naitham, J. Organomet. Chem., 241(1983)1.

172 G.Schmid, U.Höhner, D.Kampmann, D.Zaika and R.Boese, Chem. Ber., 116(1983)951.

173 G.Schmid and R.Boese, Z. Naturforsch., Teil B, 38(1983)485.

174 G.Schmid, U.Höhner and D.Kampmann, Z. Naturforsch., Teil B, 38(1983)1094.

175 W.Haubold, A.Gemmler and U.Kraatz, Z. Anorg. Allg. Chem., 507(1983)222.

176 S.Allaoud, H.Bitar, M.El Mouhtadi and B.Frange, J. Organomet. Chem., 248(1983)123.

177 M.Noltemeyer, G.M.Sheldrick, C.Habben and A.Meller, Z. Naturforsch., Teil B, 38(1983)1182.

178 K.Delpy, D.Schmitz and P.Paetzold, Chem. Ber., 116(1983)2994.

179 K.Niedenzu and H.Nöth, Chem. Ber., 116(1983)1132.

180 F.Alam and K.Niedenzu, J. Organomet. Chem., 243(1983)19.

181 G.Müller, D.Neugebauer, W.Geike, F.H.Köhler, J.Pebler and H.Schmidbaur, Organometallics, 2(1983)257.

182 S.J.Rettig and J.Trotter, Canad. J. Chem., 61(1983)2334.

183 R.Contreras, C.García, T.Mancilla and B.Wrackmeyer, J. Organomet. Chem., 246(1983)213.

184 R.Hohaus, Z. Anorg. Allg. Chem., 506(1983)185.

185 W.Kliegel, D.Nanninga, S.J.Rettig and J.Trotter, Canad. J. Chem., 61(1983)2329.

186 W.Kliegel, J. Organomet. Chem., 253(1983)9.

187 W.Kliegel, D.Nanninga, S.J.Rettig and J.Trotter, Canad. J. Chem., 61(1983)2493.

188 W.Kliegel and D.Nanninga, J. Organomet. Chem., 243(1983)373.

189 D.S.Matteson and D.Majumdar, Organometallics, 2(1983)230.

190 H.Binder, W.Matheis, H.-J.Deiseroth and H.Fu-Son, Z. Naturforsch., Teil B, 38(1983)554.

191 C.K.Narula and H.Nöth, Z. Naturforsch., Teil B, 38(1983)1161.

192 H.Nöth and D.Sedlak, Chem. Ber., 116(1983)1479.

193 D.R.Armstrong, J.Bolland, P.G.Perkins, G.Will and A.Kirfel, Acta Crystallogr., B39(1983)324.

194 Yu.B.Paderno and T.Lundström, Acta Chem. Scand., Ser. A, 37(1983)609.

195 T.Ito and I.Higashi, Acta Crystallogr., B39(1983)239.

196 D.L.Cooper, J.H.Black, M.A.L.Everard and W.G.Richards, J. Chem. Phys., 78(1983)1371.

197 B.M.Bulychev, V.K.Bel'skii, A.V.Golubeva, P.A.Storozhenko and V.B.Polyakova, Russ. J. Inorg. Chem., 28(1983)639.

198 K.Ouzounis, H.Riffel, H.Hess, U.Kohler and J.Weidlein, Z. Anorg. Allg. Chem., 504(1983)67.

199 E.B.Lobkovsky, G.L.Soloveychik, B.M.Bulychev, A.B.Erofeev, A.I.Gusev and N.I.Kirillova, J. Organomet. Chem., 254(1983)167.

200 J.Villieras, M.Rambaud and B.Kirschleger, J. Organomet. Chem., 249(1983)315.

201 B.T.Thompson, T.N.Gallaher and T.C.DeVore, Polyhedron, 2(1983)619.

202 U.Mirsaidov and R.F.Gatina, Russ. J. Inorg. Chem., 28(1983)301.

203 K.Mach and H.Antropiusova, J. Organomet. Chem., 248(1983)287.

204 R.Benn, A.Rufińska, H.Lehmkuhl, E.Janssen and C.Krüger, Angew. Chem., Int. Ed. Engl., 22(1983)779.

205 T.Weller, W.Meiler, H.-J.Köhler, H.Lischka and R.Höller, Chem. Phys. Lett., 98(1983)541.

206 D.J.Fox and H.F.Schaefer, J. Chem. Phys., 78(1983)328.

207 W.Ufnalski and A.Sporzyński, J. Organomet. Chem., 244(1983)1.

208 M.Bolesławski and J.Serwatowski, J. Organomet. Chem., 255(1983)269.

209 A.V.de Miguel, M.Gómez, K.Isobe, B.F.Taylor, B.E.Mann and P.M.Maitlis, Organometallics, 2(1983)1724.

210 J.A.Labinger, J.N.Bonfiglio, D.L.Grimmett, S.T.Masuo, E.Shearin and J.S.Miller, Organometallics, 2(1983)733.

211 D.L.Grimmett, J.A.Labinger, J.N.Bonfiglio, S.T.Masuo, E.Shearin and J.S.Miller, Organometallics, 2(1983)1325.

212 M.Bolesławski and J.Serwatowski, J. Organomet. Chem., 254(1983)159.

213 J.L.Atwood and M.J.Zaworotko, J. Chem. Soc., Chem. Commun., (1983)302.

214 J.L.Atwood, D.C.Hrncir, R.D.Priester and R.D.Rogers, Organometallics, 2(1983)985.

215 L.Rösch, G.Altnau, C.Krüger and Y.H.Tsay, Z. Naturforsch., Teil B, 38(1983)34.

216 W.E. Dorogy and E.P. Schram, Inorg. Chim. Acta, 73(1983)31.

217 H.F. Klein, K. Ellrich and K. Ackermann, J. Chem. Soc., Chem. Commun., (1983)888.

218 W.E. Dorogy and E.P. Schram, Inorg. Chim. Acta, 72(1983)187.

219 W.Clegg, M.Haase, U.Klingebiel, J.Neeman and G.M.Sheldrick, J. Organomet. Chem., 251(1983)281.

220 H.Schmidbaur, S.Lauteschläger and B.Milewski-Mahrla, Chem. Ber., 116(1983)1403.

221 T.Blumenthal, U.Wannagat, D.J.Brauer and A.Bürger, Monatsh. Chem., 114(1983)1271.

222 U.Wannagat, T.Blumenthal, D.J.Brauer and H.Bürger, J. Organomet. Chem., 249(1983)33.

223 T.Halder, W.Schwarz, J.Weidlein and P.Fischer, J. Organomet. Chem., 246(1983)29.

224 O.Kříž, J.Fusek and B.Čásenský, Coll. Czech. Chem. Commun., 48(1983)2728.

225 O.T.Beachley and C.Tessier-Youngs, Organometallics, 2(1983)796.

226 S.M.Sonchik, L.Andrews and K.D.Carlson, J. Phys. Chem., 87(1983)2004.

227 S.F.Smith, J.Chandrasekhar and W.L.Jorgensen, J. Phys. Chem., 87(1983)1898.

228 M.R.Churchill and H.J.Wasserman, Inorg. Chem., 22(1983)41.

229 C.Tessier-Youngs, W.J.Youngs, O.T.Beachley and M.R.Churchill, Organometallics, 2(1983)1128.

230 Z.Florjańczyk and E.Szymańska-Zachara, J. Organomet. Chem., 259(1983)127.

231 K.Hermansson, Acta Crystallogr., C39(1983)925.

232 S.Singh and R.D.Verma, Polyhedron, 2(1983)1209.

233 L.I.Virin, V.N.Galyashin, N.M.Kuz'min, V.G.Lambrev, I.Yu.Popova, I.Ya.Sabaev, A.I.Chernyak and A.V.Shaposhnikov, Russ. J. Inorg. Chem., 28(1983)782.

234 D.Jentsch, P.G.Jones, E.Schwarzmann and G.M.Sheldrick, Acta Crystallogr., C39(1983)1173.

235 S.Schönherr, H.Görz, R.Bertram, D.Müller and W.Gessner, Z. Anorg. Allg. Chem., 502(1983)113.

236 S.Schönherr, R.Bertram and A.Görz, Z. Anorg. Allg. Chem., 503(1983)193.

237 P.Brand and U.Seltmann, Z. Anorg. Allg. Chem., 502(1983)123.

238 P.Brand, U.Seltmann, D.Müller and U.Büchner, Z. Anorg. Allg. Chem., 502(1983)132.

239 A.S.Tracey and T.L.Boivin, J. Am. Chem. Soc., 105(1983)4901.

240 L.-O.Öhman, S.Sjöberg and N.Ingri, Acta Chem. Scand., Ser. A, 37(1983)561.

241 L.-O.Öhman and S.Sjöberg, Acta Chem. Scand., Ser. A, 37(1983)875.

242 L.-O.Öhman and S.Sjöberg, J.Chem. Soc., Dalton Trans., (1983)2513.

243 S.J.Karlik, E.Tarien, G.A.Elgavish and G.L.Eichhorn, Inorg. Chem., 22(1983)525.

244 R.Caminiti, A.Lai, G.Saba and G.Crisponi, Chem. Phys. Lett., 97(1983)180.
245 N.F.Kosenko and I.A.Andriyuk, Russ. J. Inorg. Chem., 27(1982)1568.
246 N.F.Kosenko, Russ. J. Inorg. Chem., 28(1983)71.
247 V.R.Mirolyubov, Russ. J. Inorg. Chem., 28(1983)289.
248 G.A.Korablev, V.T.Ivashinnikov, A.A.Fotiev, V.E.Gladkov and A.S.Zubov, Russ. J. Inorg. Chem., 28(1983)881.
249 M.Villa and J.L.Bjorkstam, J. Magn. Reson., 51(1983)349.
250 J.M.Thomas, J.Klinowski, P.A.Wright and R.Roy, Angew. Chem., Int. Ed. Engl., 22(1983)614.
251 W.Gessner and D.Müller, Z. Anorg. Allg. Chem., 505(1983)195.
252 D.Müller, W.Gessner and G.Scheler, Polyhedron, 2(1983)1195.
253 E.T.Devyatkina, N.P.Kotsupalo, N.P.Tomilov and A.S.Berger, Russ. J. Inorg. Chem., 28(1983)801.
254 D.Müller, I.Grunze, E.Hallas and G.Ladwig, Z. Anorg. Allg. Chem., 800(1983)80.
255 V.A.Lyutsko, M.V.Nikanovich, K.N.Lapko and V.E.Tikavyi, Russ. J. Inorg. Chem., 28(1983)1105.
256 J.Klinowski, J.M.Thomas, C.A.Fyfe, G.C.Gobbi and J.S.Hartman, Inorg. Chem., 22(1983)63.
257 A.K.Cheetham, M.M.Eddy, J.Klinowski and J.M.Thomas, J. Chem. Soc., Chem. Commun., (1983)23.
258 G.Roult, R.Pastuszak, R.Marchand and Y.Laurent, Acta Crystallogr., C39(1983)673.
259 F.Griesfeller, J.Köhler and R.Hoppe, Z. Anorg. Allg. Chem., 507(1983)155.
260 I.Hassan and H.D.Grundy, Acta Crystallogr., C39(1983)3.
261 J.O.Thomas and G.C.Farrington, Acta Crystallogr., B39(1983)227.
262 A.Rettel, W.Gessner, G.Oliew and D.Müller, Z. Anorg. Allg. Chem., 500(1983)89.
263 S.Schönherr and H.Görz, Z. Anorg. Allg. Chem., 503(1983)37.
264 M.R.Petrov, O.N.Roslyakova and T.V.Blau, Russ. J. Inorg. Chem., 27(1982)1534.
265 A.S.Moshinskii, Russ. J. Inorg. Chem., 27(1982)1530.
266 G.Rigotti, A.E.Lavat, M.E.Escobar and E.J.Baran, Z. Anorg. Allg. Chem., 501(1983)184.
267 S.M.Cheshnitskii, A.A.Fotiev and L.L.Surat, Russ. J. Inorg. Chem., 28(1983)758.
268 A.A.Fotiev and L.L.Surat, Russ. J. Inorg. Chem., 27(1982)1800
269 A.A.Fotiev, L.L.Surat and I.P.Kolenko, Russ. J. Inorg. Chem., 28(1983)119.
270 A.A.Fotiev, B.V.Slobodin, L.L.Surat and T.P.Sirina, Russ. J. Inorg. Chem., 28(1983)588.
271 L.L.Surat and A.A.Fotiev, Russ. J. Inorg. Chem., 28(1983)1059
272 B.Jasper-Tönnies and Hk.Müller-Buschbaum, Z. Anorg. Allg. Chem., 504(1983)113.
273 V.V.Fomichev, V.A.Efremov, D.D.Baldanova, O.I.Kondratov and K.I.Petrov, Russ. J. Inorg. Chem., 28(1983)669.
274 E.I.Get'man and V.I.Marchenko, Russ. J. Inorg. Chem., 28(1983)402.
275 H.J.Berthold, K.Köhler and R.Wartchow, Z. Anorg. Allg. Chem., 496(1983)7.
276 H.Nöth and P.Konrad, Chem. Ber., 116(1983)3552.
277 H.Haeuseler and A.Cansiz, Z. Naturforsch., Teil B, 38(1983)311.
278 O.V.Katorinia, V.M.Masalovich and A.S.Korobitsyn, Russ. J. Inorg. Chem., 27(1982)1566.
279 Z.Slanina and S.Beran, J. Mol. Struct., 92(1983)1.

280 B.S.Zakharova and L.P.Reshetnikova, Russ. J. Inorg. Chem., 28(1983)133.

281 V.N.Desyatnik, S.F.Katyshev, K.I.Trifonov and M.M.Nikulina, Russ. J. Inorg. Chem., 28(1983)125.

282 P.Bukoveć, Monatsh. Chem., 114(1983)277.

283 K.V.Gontar', V.N.Derkacheva and L.V.Zolotareva, Russ. J. Inorg. Chem., 27(1983)1358.

284 W.Clegg, U.Klingiebel, J.Neeman and G.M.Sheldrick, J. Organomet. Chem., 249(1983)47.

285 J.W.Akitt, R.H.Duncan and C.Setchell, J. Chem. Soc., Dalton Trans., (1983)2639.

286 T.Tomita, C.E.Sjøgren, P.Klaeboe, G.N.Papatheodorou and E.Rytter, J. Raman Spectrosc., 14(1983)415.

287 J.S.Wilkes, J.S.Frye and G.F.Reynolds, Inorg. Chem., 22(1983)3870.

288 A.Boardman, R.W.H.Small and I.J.Worrall, Acta Crystallogr., C39(1983)433.

289 F.Taulelle and A.I.Popov, Polyhedron, 2(1983)889.

290 V.V.Safonov and V.A.Mireev, Russ. J. Inorg. Chem., 28(1983)460

291 G.Steidl, F.Dienstbach and K.Bächmann, Polyhedron, 2(1983)727.

292 V.P.Tarasov, V.I.Privalov, G.A.Kirakosyan and Yu.A.Busalev, Z. Naturforsch., Teil B, 38(1983)1173.

293 S.Pohl, Z. Anorg. Allg. Chem., 498(1983)15.

294 S.Pohl, Z. Anorg. Allg. Chem., 498(1983)20.

295 S.Pohl, Z. Naturforsch., Teil B, 38(1983)1530.

296 M.A.Douglas, R.H.Hauge and J.L.Margrave, J. Phys. Chem., 87(1983)2945.

297 S.Sridharan, H.Nowotny and S.F.Wayne, Monatsh. Chem., 114(1983)127.

298 K.N.Semenenko, L.A.Petrova and V.V.Burnasheva, Russ. J. Inorg. Chem., 28(1983)107.

299 H.M.Epstein, R.E.Schwerzel, P.J.Mallozzi and B.E.Campbell, J. Am. Chem. Soc., 105(1983)1466.

300 R.B.Hallock, O.T.Beachley, Y.-J.Li, W.M.Sanders, M.R.Churchill W.E.Hunter and J.L.Atwood, Inorg. Chem., 22(1983)3683.

301 A.Coutsolelos and R.Guilard, J. Organomet. Chem., 253(1983)273.

302 B.N.Helliwell and M.J.Taylor, Austral. J. Chem., 36(1983)385.

303 P.E.Riley, V.L.Pecoraro, C.J.Carrano and K.N.Raymond, Inorg. Chem., 22(1983)3096.

304 A.A.Zakharov and I.S.Shaplygin, Russ. J. Inorg. Chem., 28(1983)59.

305 J.Köhler and R.Hoppe, Z. Naturforsch., Teil B, 38(1983)130.

306 F.P.Alekseev, N.M.Kozhevnikova, M.V.Mokhosoev, E.N.N'maeva, and N.N.Smirnyagina, Russ. J. Inorg. Chem., 27(1982)1531.

307 I.N.Belyaev, L.N.Aver'yanova and S.S.Lopatin, Russ. J. Inorg. Chem., 28(1983)517.

308 M.V.Mokhosoev, L.G.Maksimova, L.V.Tumurova and N.A.Suranova, Russ. J. Inorg. Chem., 28(1983)818.

309 N.V.Porotnikov, V.G.Savenko and L.N.Margolin, Russ. J. Inorg. Chem., 28(1983)1098.

310 I.N.Belyaev, L.N.Aver'yanova and S.S.Lopatin, Russ. J. Inorg. Chem., 27(1982)1249.

311 J.Sásvári and P.-E.Werner, Acta Chem. Scand., Ser. A, 37(1983)203.

312 M.C.Cadée, G.C.Verschoor and D.J.W.Ijdo, Acta Crystallogr., C39(1983)921.

313 S.Jaulmes, A.Mazurier and M.Guittard, Acta Crystallogr., C39(1983)1594.

314 G.G.Hoffmann, Chem. Ber., 116(1983)3858.

315 Z.D.Melikova and P.G.Rustamov, Russ. J. Inorg. Chem., 28(1983)919.

316 T.M.Il'yasov and P.G.Rustamov, Russ. J. Inorg. Chem., 27(1982)1500.

317 A.Mazurier, F.Thevet and S.Jaulmes, Acta Crystallogr., C39(1983)814.

318 B.Eisenmann, M.Jakowski and H.Schäfer, Z. Naturforsch., Teil B, 38(1983)1581.

319 G.Ghémard, S.Jaulmes, J.Etienne and J.Flahaut, Acta Crystallogr., C39(1983)968.

320 A.Kraft, G.Kühn and W.Möller, Z. Anorg. Allg. Chem., 504(1983)155.

321 W.Klee and H.Schäfer, Z. Anorg. Allg. Chem., 499(1983)145.

322 H.-J.Deiseroth and H.Fu-son, Z. Naturforsch., Teil B, 38(1983)181.

323 D.Fenske and H.G. von Schnering, Angew. Chem., Int. Ed. Engl., 22(1983)407.

324 D.Babel and F.Binder, Z. Anorg. Allg. Chem., 505(1983)153.

325 V.A.Goliusov, V.A.Voronin and S.K.Churchmarev, Russ. J. Inorg. Chem., 27(1982)1799.

326 R.W.Berg and N.J.Bjerrum, Polyhedron, 2(1983)179.

327 H.Schmidbaur, U.Thewalt and T.Zafiropoulos, Organometallics, 2(1983)1550.

328 T.Foosnaes and H.A.Øye, Inorg. Chem., 22(1983)3873.

329 P.I.Fedorov, N.S.Malova and I.Yu.Rodimtseva, Russ. J. Inorg. Chem., 27(1982)1350.

330 F.W.Froben, W.Schulze and U.Kloss, Chem. Phys. Lett., 99(1983)500.

331 M.L.Fornasini, Acta Crystallogr., C39(1983)943.

332 M.A.Khan, C.Peppe and D.G.Tuck, Acta Crystallogr., C39(1983)1339.

333 J.M.Harrowfield, C.Pakawatchai and A.H.White, J. Chem. Soc., Dalton Trans., (1983)1109.

334 O.V.Sorokina, S.B.Evgen'ev and I.V.Mashchenko, Russ. J. Inorg. Chem., 28(1983)916.

335 N.V.Porotnikov, O.I.Kondratov and K.I.Petrov, Russ. J. Inorg. Chem., 28(1983)1051.

336 N.Bulc, L.Golič and J.Šiftar, Acta Crystallogr., C39(1983)176.

337 N.Bulc and L.Golič, Acta Crystallogr., C39(1983)174.

338 T.A.Kalinina, L.N.Lykova, L.W.Kovba, M.G.Mel'nikova and N.V.Porotnikov, Russ. J. Inorg. Chem., 28(1983)259.

339 N.N.Smirnyagina, N.M.Kozhevnikova, F.P.Alekseev and M.V.Mokhosoev, Russ. J. Inorg. Chem., 28(1983)892.

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

341 H.Wiedemeier and R.Santandrea, Z. Anorg. Allg. Chem., 497(1983)105.

342 D.Carré and M.P.Pardo, Acta Crystallogr., C39(1983)822.

343 V.Krämer, Acta Crystallogr., C39(1983)1328.

344 G.G.Grushka, V.S.Gerasimenko and Z.M.Grushka, Russ. J. Inorg. Chem., 28(1983)1066.

345 A.N.Red'kin and V.A.Smirnov, Russ. J. Inorg. Chem., 28(1983)625.

346 V.A.Smirnov, Russ. J. Inorg. Chem., 28(1983)772.

347 K.-J.Range and H.-J.Hübner, Z. Naturforsch., Teil B, 38(1983)155.

348 G.Meyer and R.Blachnik, Z. Anorg. Allg. Chem., 503(1983)126.

349 K.Yamada, N.Weiden and A.Weiss, J. Mol. Struct., 111(1983)217.

350 Y.Nakamura, Y.Kitazawa, M.Shimoji and S.Shimokawa, J. Phys. Chem., 87(1983)5117.

351 M.D.Rausch, B.H.Edwards, R.D.Rogers and J.L.Atwood, J. Am. Chem. Soc., 105(1983)3882.
352 Yu.B.Yakovlev and V.G.Ushakova, Russ. J. Inorg. Chem., 28(1983)1217.
353 S.E.Jeffs, R.W.H.Small and I.J.Worrall, Acta Crystallogr., C39(1983)1205.
354 G.L.Turner, J.F.Hinton and F.S.Millett, J. Magn. Reson., 51(1983)205.
355 I.N.Belyaev and V.B.Nalbandyan, Russ. J. Inorg. Chem., 28(1983)1224.
356 D.M.Adams, P.D.Hatton and I.D.Taylor, J. Raman Spectrosc., 14(1983)144.
357 T.V.Lysyak, S.L.Rusakov, I.S.Kolomnikov and Yu.Ya.Kharitonov, Russ. J. Inorg. Chem., 28(1983)756.
358 Yu.Ya.Kharitonov, I.I.Oleinik and N.A.Knyazeva, Russ. J. Inorg. Chem., 28(1983)477.
359 J.F.Hinton and K.R.Metz, J. Magn. Reson., 53(1983)117.
360 N.V.Gerbeleu, K.M.Indrichan and G.A.Popovich, Russ. J. Inorg. Chem., 27(1982)1570.
361 K.M.Indrichan, G.A.Popovich and N.V.Gerbeleu, Russ. J. Inorg. Chem., 28(1983)1115.
362 P.V.Klevstsov, A.P.Perepelitsa and R.F.Klevstova, Russ. J. Inorg. Chem., 28(1983)363.
363 H.Martan and J.Weiss, Acta Crystallogr., C39(1983)959.
364 N.Rey, J.C.Jumas, J.Olivier-Fourcade and E.Philippot, Acta Crystallogr., C39(1983)971.
365 C.Wibbelmann, W.Brockner, B.Eisenmann and H.Schäfer, Z. Naturforsch., Teil B, 38(1983)1575.
366 M.Babanly, N.A.Kulieva and I.S.Sattar-Zade, Russ. J. Inorg. Chem., 27(1982)1340.
367 E.Yu.Turkina and G.M.Orlova, Russ. J. Inorg. Chem., 28(1983)1180.
368 V.B.Lazarev, E.Yu.Peresh and V.I.Starosta, Russ. J. Inorg. Chem., 28(1983)1189.
369 M.M.Asadov, Russ. J. Inorg. Chem., 28(1983)1025.
370 M.M.Asadov, Russ. J. Inorg. Chem., 28(1983)1190.
371 M.B.Babanly and A.A.Kuliev, Russ. J. Inorg. Chem., 27(1982)1336.
372 M.B.Babanly and N.A.Kulieva, Russ. J. Inorg. Chem., 28(1983)877.
373 M.M.Asadov, M.B.Babanly and A.A.Kuliev, Russ. J. Inorg. Chem., 27(1982)1793.
374 M.M.Asadov, Russ. J. Inorg. Chem., 28(1983)303.
375 E.Yu.Turkina and G.M.Orlova, Russ. J. Inorg. Chem., 28(1983)764.
376 F.N.Kozlov, G.A.Kitaev and L.V.Zhukova, Russ. J. Inorg. Chem., 28(1983)268.
377 G.M.Bancroft and D.J.Bristow, Canad. J. Chem., 61(1983)2669.
378 R.Blachnik and E.Enninga, Z. Anorg. Allg. Chem., 503(1983)133.
379 V.B.Lazarev, E.Yu.Peresh, V.V.Tsigika, V.M.Chereshnya, V.S.D'ordyai and N.P.Stasyuk, Russ. J. Inorg. Chem., 27(1982)1668.
380 I.D.Isaev, V.A.Fedorov, V.P.Antonova and V.E.Mironov, Russ. J Inorg. Chem., 28(1983)751.
381 R.M.Shklovskaya, S.M.Arkhipov, V.A.Kuzina and T.E.Vdovkina, Russ. J. Inorg. Chem., 28(1983)1058.
382 R.Blachnik, H.A.Dreisbach and B.Engelen, Z. Naturforsch., Teil B, 38(1983)139.
383 U.Knips and F.Huber, Z. Naturforsch., Teil B, 38(1983)434.

384 F.Brady, R.W.Matthews, M.M.Thakur and D.G.Gillies, J. Organomet. Chem., 252(1983)1.
385 D.L.Hughes and M.R.Truter, Acta Crystallogr., B39(1983)329.
386 R.Usón, A.Laguna, J.A.Abad and E. de Jesús, J. Chem. Soc., Dalton Trans., (1983)1127.
387 H.Schweer and H.Seidel, Z. Anorg. Allg. Chem., 498(1983)205.
388 G.Thiele and B.Grunwald, Z. Anorg. Allg. Chem., 498(1983)105.
389 B.D.James, M.B.Millikan and M.F.Mackay, Inorg. Chim. Acta, 77(1983)L251.
390 S.E.Jeffs, R.W.H.Small and I.J.Worrall, Acta Crystallogr., C39(1983)1628.
391 H.W.Rotter and G.Thiele, Z. Anorg. Allg. Chem., 499(1983)175.
392 J.Glaser, P.L.Goggin, M.Sandström and V.Lutsko, Acta Chem. Scand., Ser. A, 37(1983)437.