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NEW PHOSPHANEBORANE CHEMISTRY

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Summary

Following a short account of pertinent literature, recent work on two classes of phosphaneboranes is summarized.

$H_3B(CH_3)_2PCl$ (1) was found to be an excellent precursor for an extended new chemistry of the $H_3B(CH_3)_2P$-group, which is isoelectronic with the $(CH_3)_3Si$-group. Boranatodimethylphosphinic acid $H_3B(CH_3)_2POH$, its anhydride $H_3B(CH_3)_2P—O—P(CH_3)_2BH_3$, salts, complexes, esters and carboxylates have been prepared and identified through analytical and spectroscopic studies. The corresponding sulphur analogues are also available. The amide $H_3B(CH_3)_2PNH_2$ is formed from 1 and NH_3 as a stable crystalline product. It is easily converted into its imide $H_3B(CH_3)_2P—NH—P(CH_3)_2BH_3$ and a variety of organic derivatives. $H_3B(CH_3)_2P—CH_2—P(CH_3)_2BH_3$ has protic hydrogen atoms in the CH_2 bridge and affords a crystalline ylidic Li salt, the crystal structure of which was determined. CH_3 metallation of $(CH_3)_3PBH_3$ leads to similar products useful for derivatisation.

The $(CH_3)_3P—BH_2—P(CH_3)_3^+ X^-$ salts are starting materials for the preparation of the novel $^-CH_2(CH_3)_2PBH_2P(CH_3)_2CH_2^-$ ligand system. Its coordination chemistry, with examples from most groups of the Periodic Table, is reviewed, including both diamagnetic and paramagnetic species. Representative structures were determined by X-ray diffraction, and multi-nuclei NMR and magnetic data were used for further characterisation.

I. Introduction and acknowledgement

Along with other descendents of the Alfred Stock-Egon Wiberg-Max Schmidt school, the author has drawn advantage in his scientific work from use of the Isoelectronic Principle [1]. A typical and very interesting step was made in recent years, when the boundary between phosphanealkylenes ($R_3\overset{+}{P}—\overline{\underline{C}}H_2$) and phosphaneboranes ($R_3\overset{+}{P}—\overline{B}H_3$) was crossed [2,3].

After three years of experimental work it is possible to present some new aspects of a research area which had been largely neglected in the two decades since the classical initial studies. It is hoped that this account will be able to contribute to the popularity of non-transition element chemistry at a time when too many members of the organometallic community have divorced themselves from main group studies and turned fully to the mistress of transition metal chemistry.

It has been pointed out previously that the compounds of the following series are isoelectronic and that certain structural as well as chemical similarities are to be expected (Scheme 1):

Scheme 1:

mononuclear		*binuclear*	
$(CH_3)_3PNH$	$(CH_3)_3SiOH$	$[(CH_3)_3PNP(CH_3)_3]^+$	$(CH_3)_3SiOSi(CH_3)_3$
$(CH_3)_3PCH_2$	$(CH_3)_3SiNH_2$	$[(CH_3)_3PCHP(CH_3)_3]^+$	$(CH_3)_3SiNHSi(CH_3)_3$
$\boxed{(CH_3)_3PBH_3}$	$(CH_3)_4Si$	$\boxed{[(CH_3)_3PBH_2P(CH_3)_3]^+}$	$(CH_3)_3SiCH_2Si(CH_3)_3$

The two phosphaneborane species are by far the least studied members in these series, and it was obvious from a survey of the literature that there was an almost complete lack of information on functional derivatives. Such a functionality can be introduced either by substituents at boron or carbon, or by replacing an organic group as a whole.

After a short survey of pertinent references the present article will show novel examples of each of these possibilities, i.e. introduction of halogen at boron, metallation at carbon, and substitution of an organic group by halogen, hydroxy, alkoxy, amino, thiol and other ligands. The resulting products often have unusual properties, which are still under investigation.

The synthetic, analytical and spectroscopic work was carried out by two enthusiastic coworkers, Gerhard Müller and Erwin Weiss, with the assistance of the service institutions of the new Garching institute. The help of the X-ray laboratory in particular should be gratefully acknowledged. Some of the results have been published in short communications or full papers, as indicated in the text. As coauthorship was not allowed for this special issue, I would like at this stage to thank my colleagues and students for providing fascinating results and for their excellent team-work. We are all looking forward to further interesting joint endeavours.

II. Phosphaneboranes in the literature

As early as 1890, A. Besson synthesized $H_3P—BCl_3$ as the first compound to contain a discrete P—B bond [4], and E.L. Gamble and B. Gilmont reported their fundamental study on H_3PBH_3 in 1948 [5], but it was not until the pioneering work by A.B. Burg and R.I. Wagner in 1953 that phosphaneboranes were recognized as a new important field offering a broad scope [6]. The observation of the unexpected stability of $(CH_3)_3PBH_3$ and its homologues, as well as the unique chemical properties of the cyclic and polymeric phosphaneboranes $(R_2PBH_2)_n$, focussed a rapidly growing interest on compounds with a combination of P—C and P—B bonds. Structural studies subsequently [7—14] showed that phosphaneboranes have straightforward standard structures, closely resembling those of phosphanes, phosphane oxides and phosphonium cations, or of the analogous nitrogen compounds. The peculiar properties, such as the inertness towards oxygen and moisture or sometimes even towards strong acid and base, are thus not a consequence of an unusual structure but must result from the low polarities and polarizibilities of the P—B and B—H bonds [15—19].

This reasoning was used in a large number of preparative and physical studies of compounds with a great variety of substituents at phosphorus and at boron [15,16], and it was shown that the $P—BH_3$ group was indeed greatly influenced by the electronic effects of these substituents. The nature of the X_3PBY_3 compounds thus ranges from labile, sensitive adducts to extremely resistent species, depending on the nature of X and Y. The reduced polarity of the B—H bond and the apparent non-hydridic character of the BH_3 hydrogen atoms have been ascribed to a hyper-conjugative contribution in the valence-bond description [17,18], and to the contributions from linear combinations of phosphorus *d*-orbitals and the BH_3 orbitals in the molecular orbital description [19—22]. Both treatments reach similar conclusions, and an increased $\mathrm{P}\overset{-}{\cdots}\mathrm{B}$ bond order and a transfer of negative charge from hydrogen to boron and phosphorus are deduced, which is consistent with the experimental findings [15,16]. Further experimental evidence is available from high $\mathrm{P}\overset{-}{\cdots}\mathrm{B}$ rotational barriers [9,12], slightly reduced $\mathrm{P}\overset{-}{\cdots}\mathrm{B}$ bond lengths, and compressed CPC bond angles [7—14]. Dipole moment studies [9,12] leave no doubt, however, that phosphaneboranes are molecules of high overall polarity, and this also becomes obvious from other gross physical properties, such as low volatilities and high melting points.

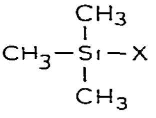
Recent work on phosphaneboranes is oriented towards the thermodynamic characteristics of the compounds, which have also been neglected for many years [23]. There is also considerable activity with regard to the vibrational and nuclear magnetic resonance spectroscopy of phosphaneboranes, mainly in the laboratories of Durig and his collaborators [19,24—28].

The bis-phosphane-boronium salts (see Scheme 1) are of special significance for the chemistry reviewed in the present article. They are closely related to the corresponding nitrogen analogues reported by Parry [29]. Their preparation was first described by Muetterties and coworkers [30], who pointed out many of the peculiar features, but unfortunately very little research was carried out on these compounds in the following years [31,32].

In summary, the literature on phosphaneboranes is surprisingly limited and represents little more than a basic treatment of some fundamental species [33]. Progress was slow after a rapid growth in the 1950s and 1960s, and was advanced by only very few laboratories in recent years. The state of the art is very encouraging, however, and more work appears to be desirable. The above literature coverage is not complete and the reader is referred to the relevant reviews [15,33].

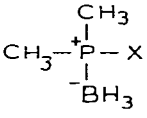
III. The chemistry of the $H_3B(CH_3)_2P$-group

Trimethylsilyl compounds Me_3SiX are of ever growing importance to the synthetic and analytical chemist. The Isoelectronic Principle suggests a related "boranatodimethylphosphinyl" chemistry, as inferred from the two structural formulae I and II (X = functional group):



$(CH_3)_3Si{-}X$

(I)

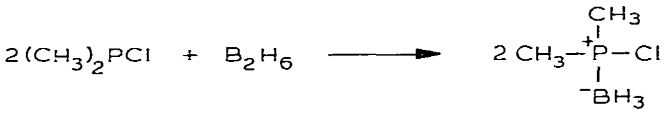


$(CH_3)_2(H_3B^-)P^+{-}X$

(II)

Only very few examples of type II are known (X = H, Cl [6,34]) and their chemical and physical properties are virtually unexplored.

Chlorotrimethylsilane $(CH_3)_3SiCl$ is the most important chemical for silylation reactions. It is commercially available at low cost. We were therefore prompted to base our own studies on chlorodimethylphosphaneborane $H_3B(CH_3)_2PCl$, which had been synthesized earlier by Durig and coworkers [34] from $(CH_3)_2PCl$ and B_2H_6 on a small scale using high vacuum techniques. The compound was carefully characterized by vibrational and NMR spectroscopy.



$$2\,(CH_3)_2PCl + B_2H_6 \longrightarrow 2\,(CH_3)_2(H_3B^-)P^+{-}Cl$$

(1)

In our introductory experiments it was shown that it is accessible on a synthetic scale and with standard laboratory equipment from $(CH_3)_2PCl$ and BH_3 complexes, preferentially $C_4H_8O \cdot BH_3$ (C_4H_8O = tetrahydrofuran), which are readily available at reasonable prices. With the availability of this synthesis (and because $H_3B(CH_3)_2PCl$ is a distillable, rather stable liquid which can be stored in large quantities in the refrigerator) it was possible to begin on a more extensive investigation of $H_3B(CH_3)_2P$ chemistry.

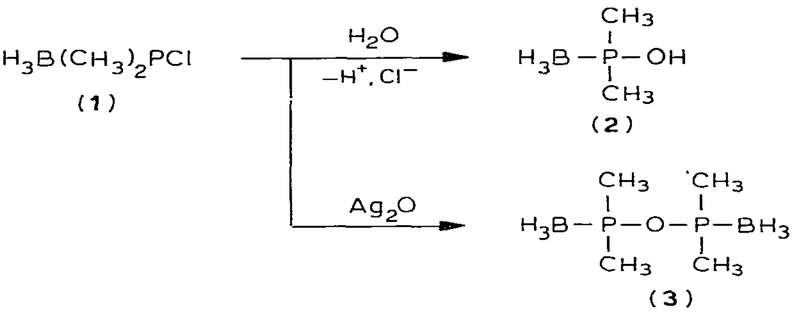
$$(CH_3)_2PCl + C_4H_8O{\cdot}BH_3 \xrightarrow[20\,^\circ C,\ 85\%]{-C_4H_8O} H_3B(CH_3)_2PCl$$

(1)

1. *Boranatodimethylphosphinic acid, anhydride and esters [35]*

Silanols and disiloxanes are the most prominent derivatives of chlorosilanes. They are obtained from the halosilane by hydrolysis. Very unexpectedly, the analogous reactions of **1** lead to the corresponding products **2** and **3**, without any hydrogen evolution or other undesirable side reactions.

Compound **2** is a novel monobasic phosphinic acid, from which salts such as $Na[H_3B(CH_3)_2PO]$, **4** (below), can be derived. The corresponding anhydride **3** is at least somewhat reminiscent of the inert siloxanes in that it is isolated as a very stable crystalline solid, unaffected by air and moisture, easily sublimed, and readily soluble in many polar solvents.



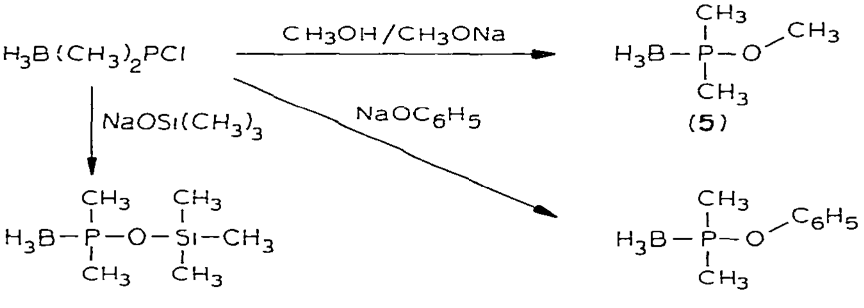
In the reaction of 1 with NaOH in THF a colorless salt 4 is generated, which was identified as the sodium salt of the phosphinic acid 2. It dissolves in water to give a solution of neutral pH:

$$H_3B(CH_3)_2PCl + 2\ NaOH \xrightarrow[-NaCl]{-H_2O} H_3B(CH_3)_2P{-}O^-Na^+$$

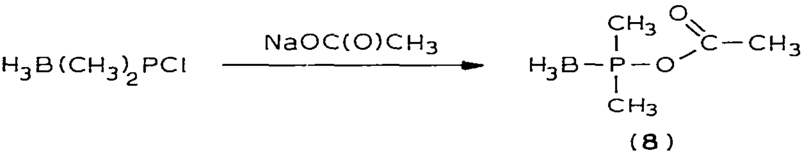
(4)

Compound 4 can be stored at room temperature and is only slowly attacked by air and moisture. It is a versatile reagent for the synthesis of many boranatodimethylphosphinites (below). In this respect it resembles the siloxide ("silanolate") $(CH_3)_3SiO^-Na^+$, which has been used successfully in a wide variety of preparations [36,37].

Alkyl, aryl and silyl esters of the acid 2 could be synthesized either from the halide 1 or the phosphinate 4 in high yields. They are isolated as distillable oily liquids of high thermal stability, miscible with most organic solvents:



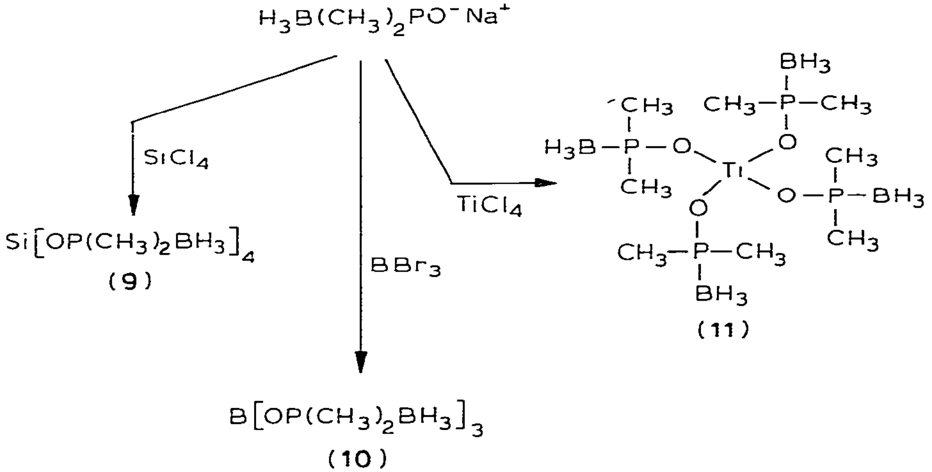
The methyl ester 5 exhibits a camphor-like odor very similar to that of $(CH_3)_3$-$SiOCH_3$ [38]. The silyl ester 7 is an analogue of hexamethyldisiloxane [39]. The esters are important intermediates for the synthesis of other $H_3B(CH_3)_2P$-compounds under strictly neutral conditions. The acetate 8 is available similarly from 1 and $NaOOCCH_3$ in ether. As a mixed anhydride of a carboxylic and a phosphonic acid, it is also a useful synthon for further reactions:



According to spectral data the acetate is bonded to phosphorus through only one oxygen atom. The compound is stable in air and hydrolysed only very slowly. Distillation under reduced pressure yields a pure, undecomposed product.

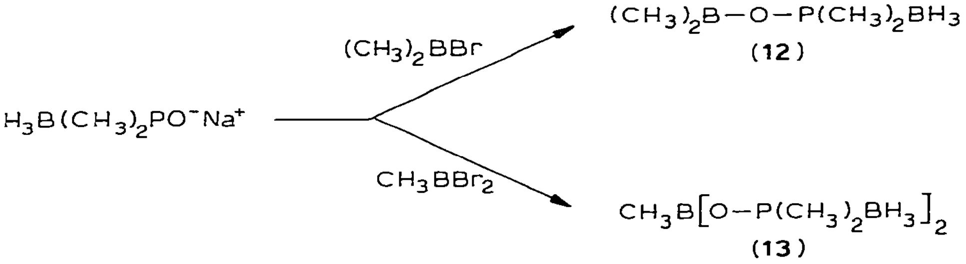
2. *Metal boranatodimethylphosphinates*

Metals both from the main group and the transition series form a plethora of siloxides and disilylamides, which have attracted great interest in the past decade [36,37,40]. In some cases, the metals can be obtained in extremely low coordination numbers [40,41], and often the compounds are characterized by high volatility and good solubility in nonpolar solvents. It is therefore of some significance that the $H_3B(CH_3)_2P$-group can play a similar rôle in metal oxide and amide chemistry. However, the more polar nature of the $H_3B(CH_3)_2P$-group is likely to lead to different ligand properties and thus induce distinctly modified properties. Two typical examples taken from Group IV elements are obtained from $SiCl_4$ and $TiCl_4$ in an inert solvent:



The titanium complex **11** forms colorless crystals (m.p. 94—95° C, dec.), which are soluble in many organic solvents. The silicon compound **9** and the boron compound **10** are mixed anhydrides of the phosphinic acid **2** and boric or silicic acid, respectively. They are important simple model compounds with Si—O—P and B—O—P linkages.

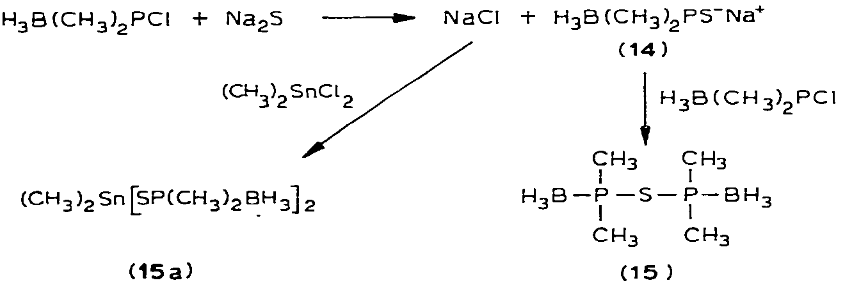
Following the synthesis of the organoboron derivatives **12** and **13** from $(CH_3)_2BBr$ and CH_3BBr_2, the homologous series of compounds $(CH_3)_{3-n}$-$B[OP(CH_3)_2BH_3]_n$ was completed:



Due to the presence of CH_3—B functions these products are very sensitive to oxidation and hydrolysis, whereas the H_3B—P functions are completely inert in all the above compounds.

3. *Boranatodimethylthiophosphinic acid derivatives [42]*

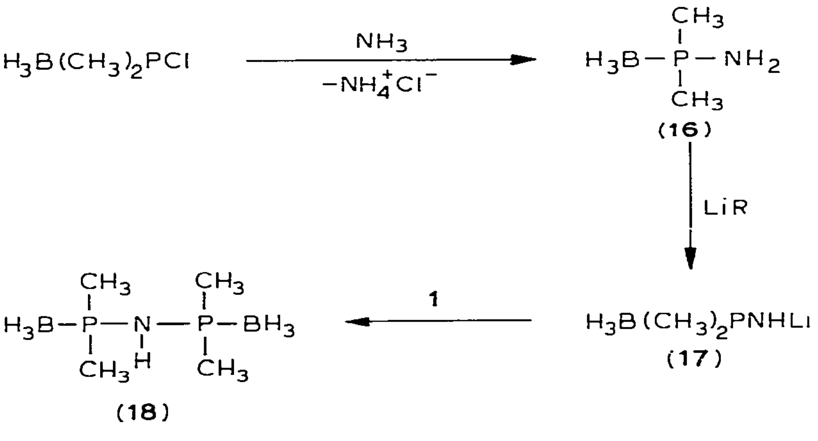
The chloro precursor **1** reacts with Na_2S in THF to form sodium boranatodimethylthiophosphinate **14** in good yield. This salt is an important starting material for other related thiophosphinates. Its reaction with a second equivalent of **1** affords the anhydride **15**, an analogue of hexamethyldisilthian $(CH_3)_3SiSSi(CH_3)_3$:



Compound **15** is a colorless crystalline solid, m.p. 75° C, which readily sublimes in vacuo. Its chemistry is largely unexplored. A tin derivative **15a** is obtained with $(CH_3)_2SnCl_2$.

4. *Boranatodimethylphosphinic amides and imides*

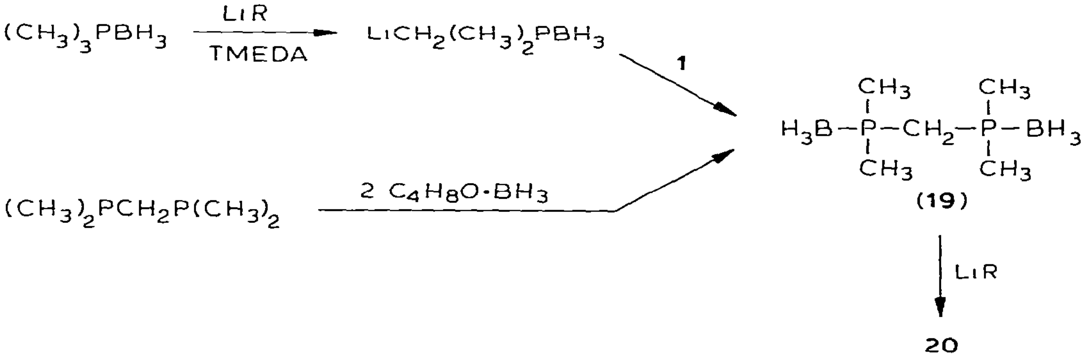
Whereas $(CH_3)_3SiNH_2$ is known to be an extremely unstable compound [43], the corresponding amide in the $H_3B(CH_3)_2P$-system (**16**) turned out to be a stable crystalline material, an analogue of $(CH_3)_3SiNH_2$. (Similar reactions with primary amines yield compounds of the type $H_3B(CH_3)_2P$—NH—R (e.g. R = C_6H_5), which are easy to handle and can be stored indefinitely at ambient temperature.) Synthesis from **1** and NH_3 is straightforward. Metallation with alkyllithium reagents leads to an isolable lithium amide (**17**), which again is a useful starting material for the imide **18** (or $H_3B(CH_3)_2P$—NR—$P(CH_3)_2BH_3$, e.g. R = C_6H_5, m.p. 100—101°C)).



Metallation of the nitrogen in **18** is also possible, but secondary reactions with the product quite often result in complex mixtures. Thus the tertiary compound $[H_3B(CH_3)_2P]_3N$ has not yet been isolated.

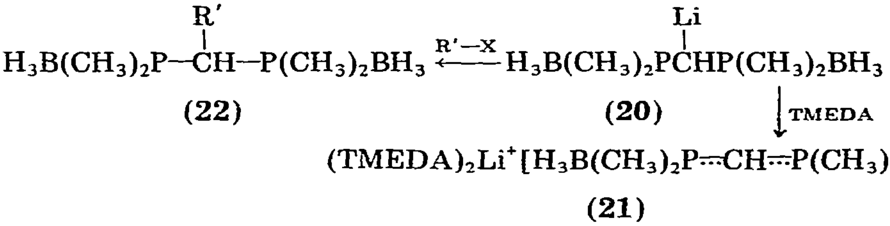
5. *Boranatodimethylphosphinic methanes and methanides [44]*

$(CH_3)_3PBH_3$ can be subjected to metallation at carbon if the more powerful alkyllithium bases such as tert-butyllithium in the presence of tetramethylethylenediamine are employed. The product undergoes a coupling reaction with **1** to yield the dinuclear homologue **19**:



Compound **19** can be more easily obtained from tetramethyldiphosphinomethane and tetrahydrofuranborane and in virtually quantitative yields. It is a colorless, air-stable solid, which crystallizes in thin hexagonal plates. (Attempts to determine the crystal structure failed due to the thinness of the crystals.)

As expected from experiences with phosphane alkylenes [45—46], **19** can be metallated much more readily at its bridging carbon (**20**). The 2 : 1 TMEDA-complex of the product was isolated in pure form and its crystal structure determined (**21**). It is comprised of $(TMEDA)_2Li^+$ cations and $[H_3B(CH_3)_2PCHP(CH_3)_2BH_3]^-$ anions, the dimensions of which give an important clue as to the structure and bonding in $H_3B(CH_3)_2P$ compounds. The bond distances and angles given in Fig. 1 show very clearly the great similarity of P—C and P—B bonds and their close correspondence to Si—C bonds.



$$\underset{(22)}{H_3B(CH_3)_2P{-}\overset{R'}{\overset{|}{C}}H{-}P(CH_3)_2BH_3} \xleftarrow{R'-X} \underset{(20)}{H_3B(CH_3)_2P\overset{Li}{\overset{|}{C}}HP(CH_3)_2BH_3}$$

$$\downarrow \text{TMEDA}$$

$$\underset{(21)}{(TMEDA)_2Li^+[H_3B(CH_3)_2P\overset{\cdots}{=}CH\overset{\cdots}{=}P(CH_3)_2BH_3]^-}$$

The transylidation reaction of $H_3B(CH_3)_2PCl$ with $(CH_3)_3P{=}CH_2$ provides direct access to a boranatodimethylphosphino ylide **23**, which is isoelectronic with the anion in **21**. This compound is more easily made from the phosphino-

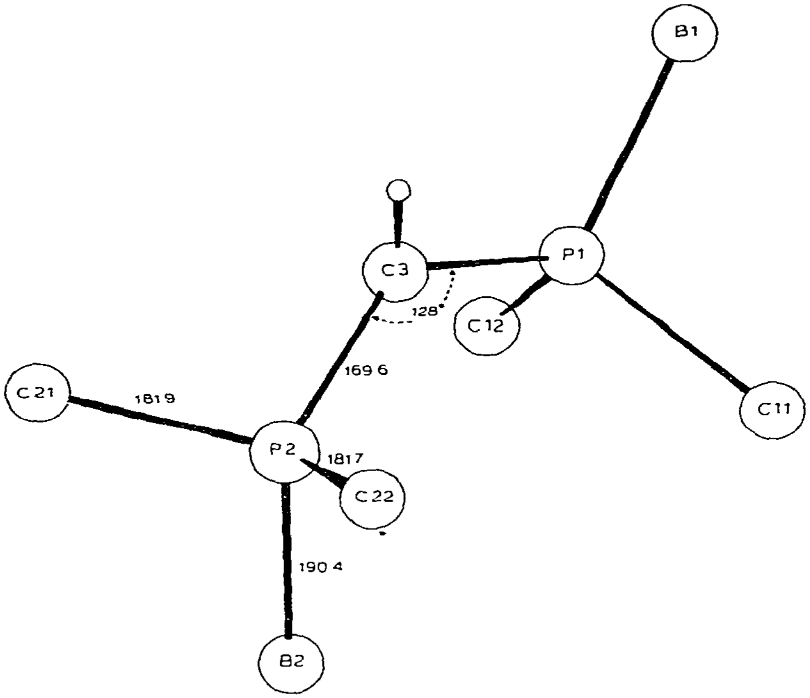
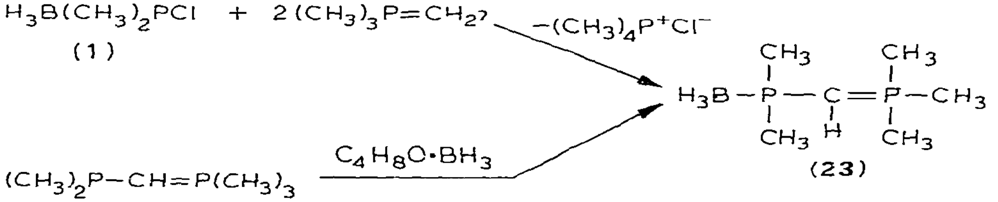


Fig. 1. Structure of the anion $H_3B(CH_3)_2P{-}CH{-}P(CH_3)_2BH_3^-$ as determined by X-ray diffraction of the $Li(Tmeda)_2^+$ salt **21** [44]. (Bond distances in pm.)

ylide and THF · BH_3:



Compound **19** is converted into its organic derivatives **22** through the reaction sequence **19** $\xrightarrow{LiR}$ **20** $\xrightarrow{R'X}$ **22** (R′ = $CH_2C_6H_5$, m.p. 123°C). Compounds of this type (**22**) are again also available from the substituted diphosphinomethane and THF · BH_3: $H_3B(C_6H_5)_2PCH(CH_3)P(C_6H_5)_2BH_3$, m.p. 200°C (dec.).

Bromination of **19** with HBr leads to the introduction of Br at boron. Under mild condition a pure symmetrical dibromide is obtained (**24**, m.p. 131°C):

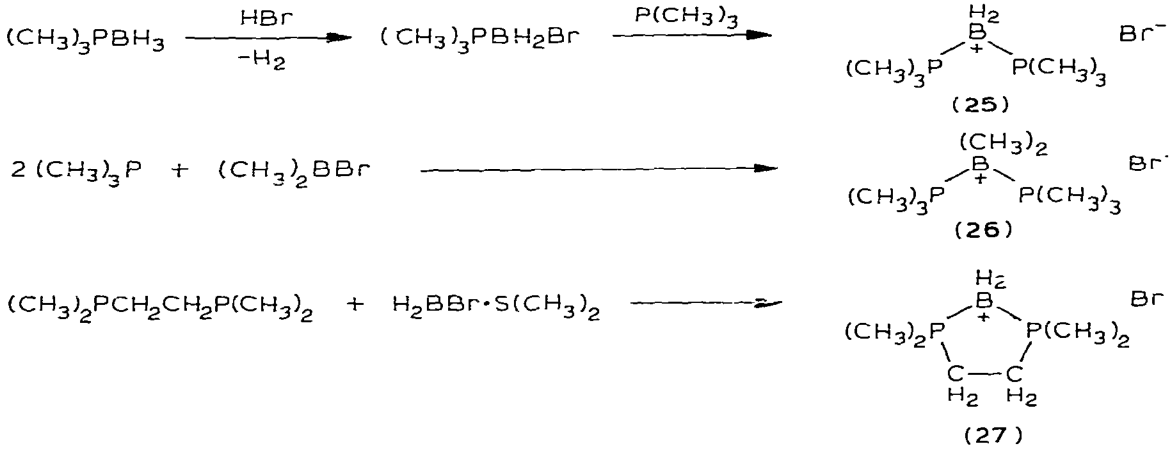
$$\underset{\textbf{(19)}}{H_3B(CH_3)_2P{-}CH_2{-}P(CH_3)_2BH_3} \xrightarrow[-2\,H_2]{2\,HBr} \underset{\textbf{(24)}}{BrBH_2(CH_3)_2P{-}CH_2{-}P(CH_3)_2BH_2Br}$$

All the new $H_3B(CH_3)_2P$ compounds mentioned in the above section were carefully studied by ^1H, ^{11}B, ^{13}C, and ^{31}P NMR spectroscopy, as well as by analysis and by vibrational and mass spectroscopic techniques. Most of the data will be included in the Thesis of E. Weiss and will be published as soon as they are complete.

IV. The chemistry of the $(CH_3)_3PBH_2P(CH_3)_3^+$ cation and its ylides [47]

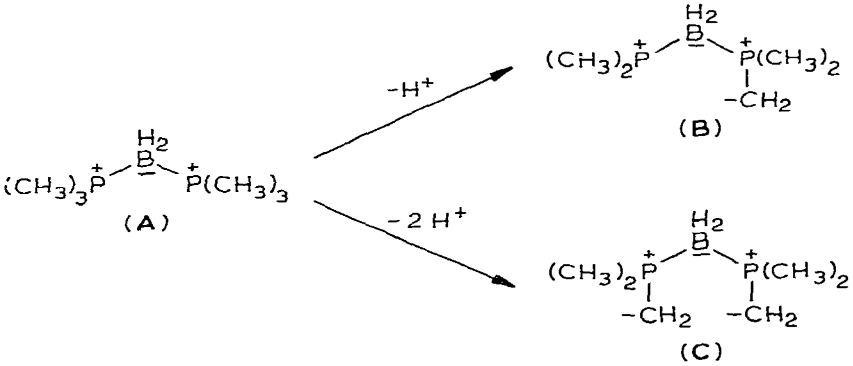
1. Bis-triorganophosphane-boronium salts

The introduction of a second trialkylphosphane moiety at the boron atom in phosphaneboranes R_3PBH_3 leads to symmetrical cations $R_3PBH_2PR_3^+$. These species again show many of the reactions of the mononuclear phosphaneboranes. It is very fortunate that some straightforward high-yield syntheses are available for the starting materials. As depicted in the equations below, open-chain and cyclic types are readily accessible by standard methods. This is true not only for the basic BH_2 compounds but also for the dialkylboronium salts with BR_2 bridges:



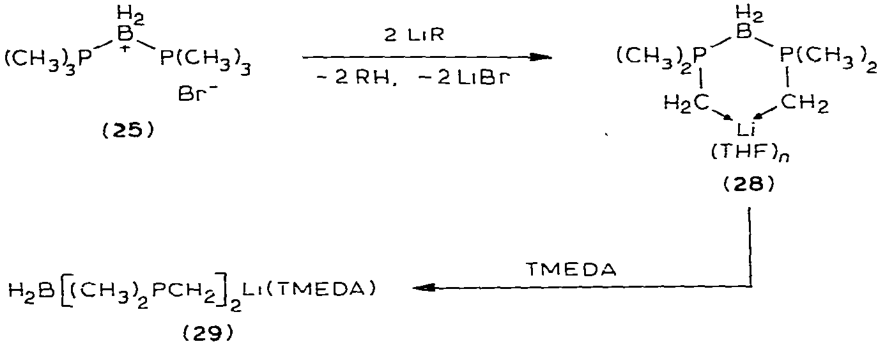
The procedures used in this laboratory are modified versions of the classical syntheses published some twenty years ago [30], and are now carried out as one-pot preparations.

All experiments designed to yield a mono-ylide (B) of the above cations (A) have failed, and only the bis-ylide anions (C) were formed regardless of the ratio of reactants. This observation suggested that the generation of a complete series of alternating charges in the CPBPC chain is extremely favoured, and that this might allow the synthesis of many new systems based on building blocks of this type:



2. *Lithium boranato-bis[dimethylphosphonium-methylides] [48]*

Metallation of $(CH_3)_3PBH_2P(CH_3)_3^+Br^-$, **25**, with an alkyllithium reagent ($R = n\text{-}C_4H_9$, $t\text{-}C_4H_9$) in THF at −20°C yields a clear colourless solution of the lithium complex **28**, which can be separated from the LiBr by-product by treatment with benzene. The NMR spectral data of the product clearly indicate the presence of a solvate of this formula, but its degree of association is not known. Addition of TMEDA to toluene solutions of the THF solvate precipitates a yellowish 1 : 1 complex **29**, which could be characterized by high resolution ^1H, ^{13}C, ^{31}P NMR of benzene solutions, and by broad line ^7Li NMR of the THF-free solid:

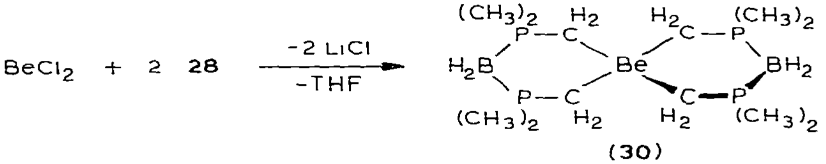


Solutions containing **28** in THF, benzene or toluene were used for metathesis reactions with a variety of metal halides or their complexes, and quite often isolation of the reagent or its separation from LiBr is unnecessary [47].

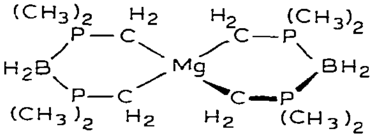
3. *Beryllium and magnesium bis[boranato-bis(dimethylphosphonium-methylides)]*

Organoberyllium chemistry is still a very undeveloped field, and activity in this area is presently decreasing even further since toxicological and environmental problems discourage studies with volatile species in particular [49]. It is therefore very fortunate that with the new ligand C a non-ionic type of organoberyllium compound becomes available, in which a discrete covalent bonding of beryllium to four aliphatic carbon atoms is present (**30**). This type of derivative previously represented a gap in organoberyllium chemistry [49].

As a consequence of the multipolar charges in the six-membered ring, the crystalline compound is not very volatile at room temperature, but sublimes at 75°C under 10^{-3} Torr. The compound, which is synthesized from anhydrous $BeCl_2$ and two equivalents of **28**, is easily characterized by spectroscopic and analytical data. Its crystal structure is being determined:



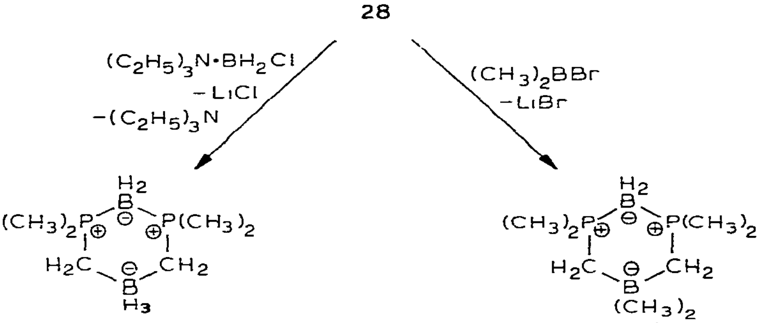
The analogous magnesium compound **31** was also synthesized by the same procedure and purified by sublimation. Its NMR and IR spectra are very similar to that of **30**, and suggest a closely related structure with a tetrahedral array of carbon atoms around the metals [47]:



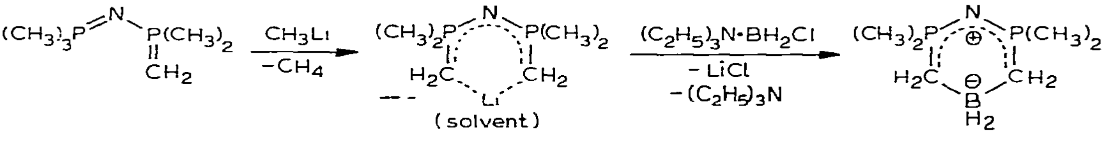
(31)

4. *Boron, aluminium and gallium heterocycles*

If $H_2BCl \cdot N(C_2H_5)_3$ or $(CH_3)_2BBr$ are coupled with the lithium reagent **28**, monocyclic products of the formulae **32** and **33** are obtained in low to moderate yields with polymeric materials as by-products. Both heterocycles form colourless crystals after purification by vacuum sublimation. An analogous phosphonitrilic heterocycle **34** is formed from $(CH_3)_3P{=}N{-}P(CH_3)_2{=}CH_2$ and $H_2BCl \cdot N(C_2H_5)_3$ in a transylidation reaction. The molecular structure of **34** was determined by X-ray diffraction. It was found to have the expected chair conformation, and **32** is expected to be structurally similar (Fig. 2) [50]:

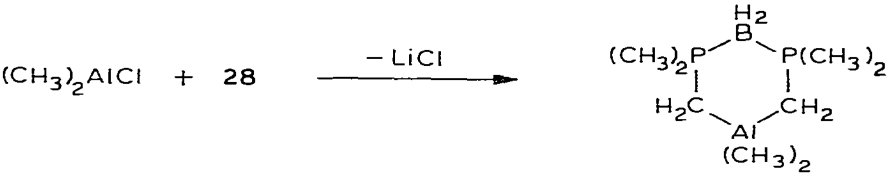


(32) (33)



(34)

The related aluminium and gallium species **35** and **36** can be synthesized either by a similar procedure or directly from the salt precursor **25** and the lithium tetramethylmetallates. In this convenient preparation the two salts are mixed and heated in vacuum to give a sublimate of the pure product. Two equivalents of CH_4 are evolved in the process [47]:



(35)

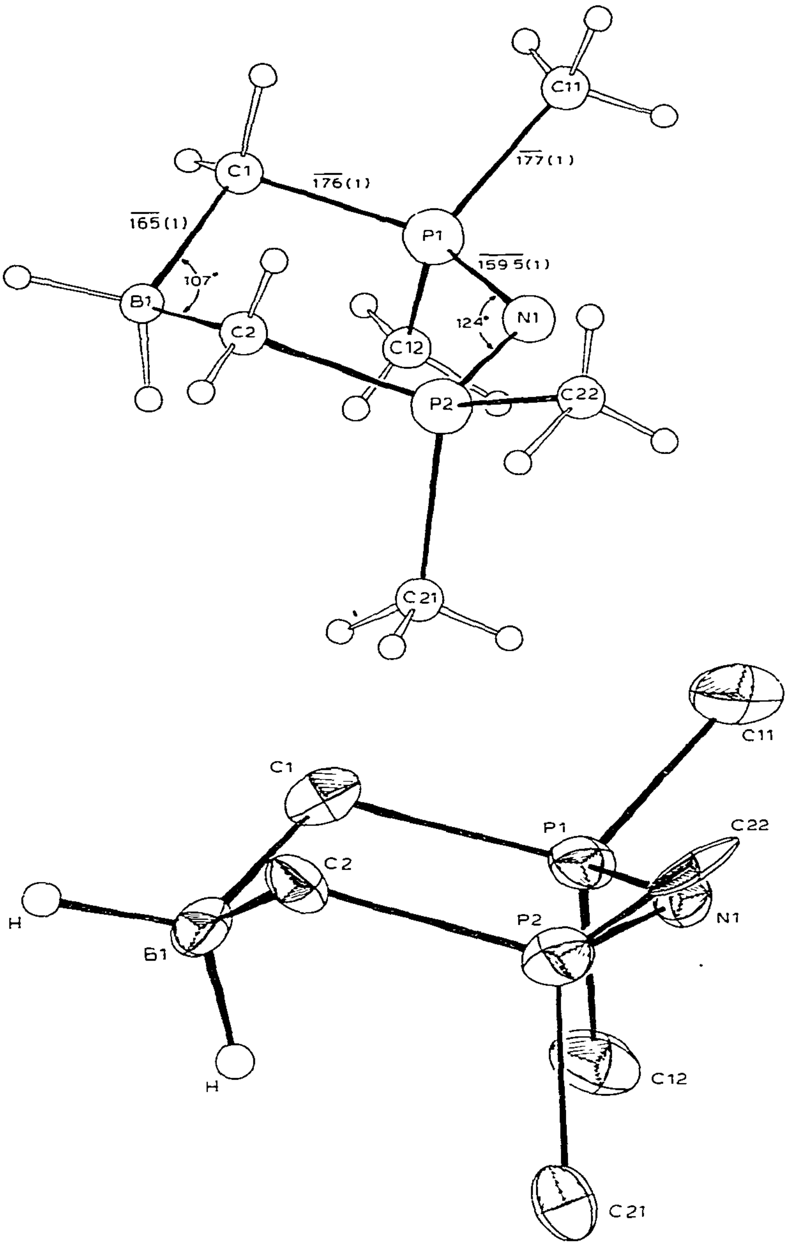
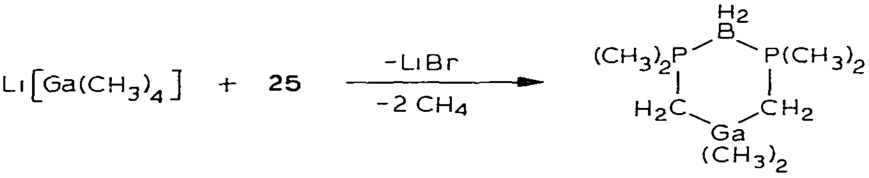


Fig. 2. Molecular structure of the heterocycle 34 as determined by X-ray diffraction [50]. (Bond distances in pm.)



(36)

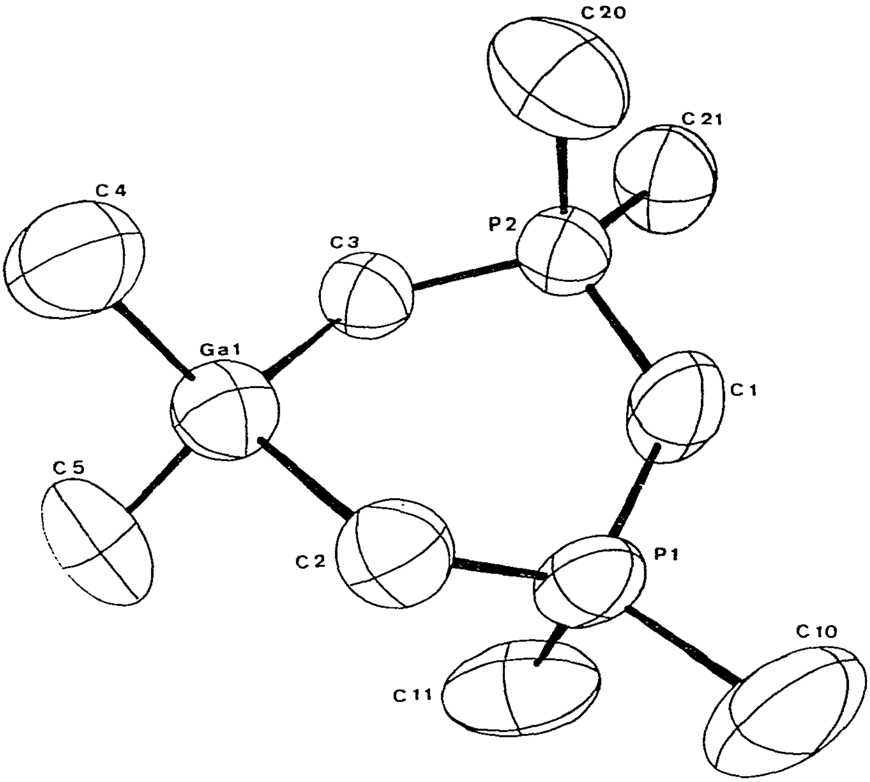
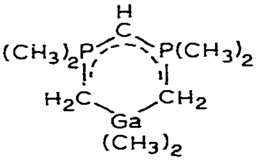


Fig. 3. Molecular structure of the heterocycle 36a as determined by X-ray diffraction [51].

The crystal structure of a related methanide-bis(dimethylphosphonium-methylide) complex (36a) has been determined by X-ray diffraction. Compound 36 is likely to have a very similar chair-form conformation (Fig. 3). The metal atoms are tetrahedrally bonded [51].



(36a)

5. Dimethylgold(III) and gold(I) boranato-bis(dimethylphosphonium)-methylides

The CPBPC ligand is found to be part of a square planar array of ligands in the corresponding dimethylgold(III) complex 37. This molecule was also synthesized from 28 and $[(CH_3)_2AuCl]_2$ and its structure solved by diffraction methods (Fig. 4). The diamagnetic low spin d^8 complex has only aliphatic car-

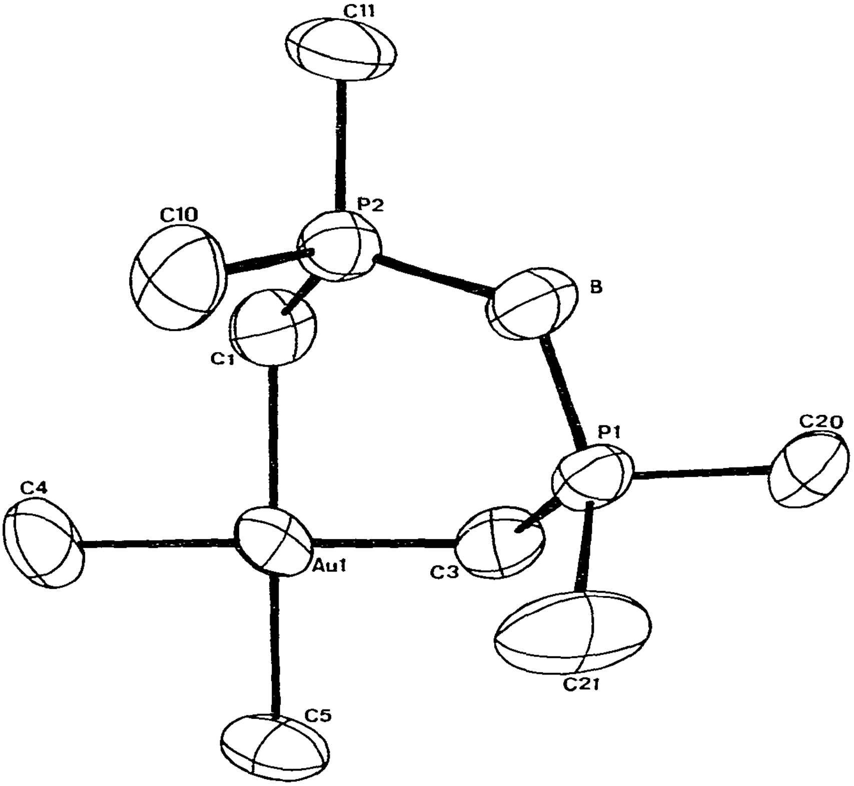
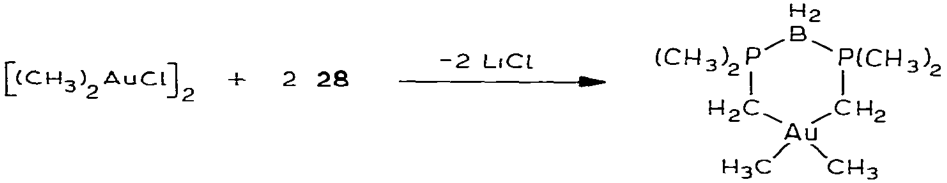


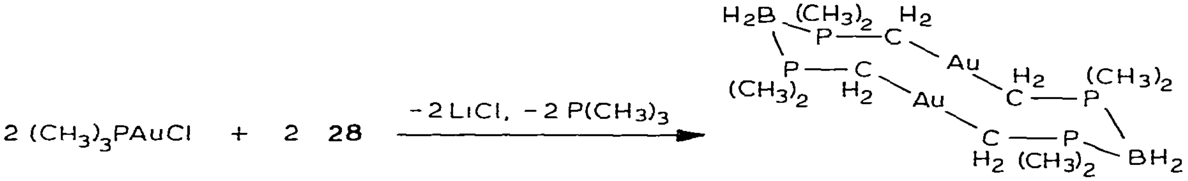
Fig. 4. Molecular model of the gold(III) complex 37 (compare [53,54]).

bon atoms as ligands to the metal. It is stable to air and moisture [52]:



(37)

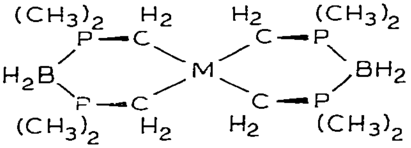
The syntheses and structures of the analogous PNP and PCHP molecules [53,54] have been reported previously. The reaction of 28 with AuCl complexes affords a novel macrocyclic system (38). The preference of gold(I) for the linear two-coordinated state requires dimerisation of the product in order to accommodate the chelating groups in a strain-free metallocycle. A double-chair form is again suggested [55]:



38

6. *Nickel, palladium, and platinum complexes [48,56]*

The strong ligand field of the boranato-bis-ylide ligand gives rise to the analogous d^8 low spin configuration with the metals Ni, Pd and Pt in their oxidation state +2. The *spiro*-chelated complexes **39**—**41** are easily synthesized from **28** and the metal halides in high yields and can be crystallized from pentane in deep yellow (**39**) to colourless needles (**40**,**41**). Chemical and thermal stabilities are found to increase in the sequence Ni < Pd < Pt, and decomposition of **41** is noticeable only above 187° C. Mass spectral studies confirm that monomeric species are present in the gas phase, and the satellite multiplicities in the NMR spectra give the same result. The crystal structure of the nickel complex **39** has been solved by X-ray diffraction. A double-chair conformation is found for the two metallocycles, with a planar NiC_4 geometry (Fig. 5). The close similarity of the IR spectra and the diamagnetism leave no doubt that **40** and **41** have analogous structures.

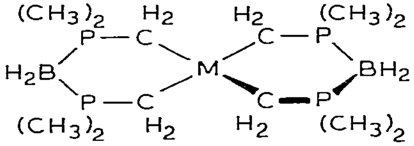


(39, M = Ni
40, M = Pd
41, M = Pt)

The crystal structure of the related PNP complex of nickel has been reported previously, and the P(CH)P complexes are also known [51,53].

7. *Zinc, cadmium, and mercury complexes [47]*

The d^{10} metal ions Zn^{II}, Cd^{II} and Hg^{II} again yield *spiro*-chelating coordination compounds of the general formula:



(42, M = Zn
43, M = Cd
44, M = Hg)

The three permethylated species **42**—**44** are obtained as colourless crystalline materials. The zinc and cadmium complexes can be sublimed in vacuum, but the mercury compound is of very limited stability. Together with the analogous PCHP complex, it is one of the rare cases of tetracoordination of Hg^{II} with four alkyl ligands. In one case this feature has been established by ^{199}Hg resonance studies. For both compounds a complete set of ^1H, ^{13}C, ^{31}P (^{11}B) NMR data is available [57].

8. *A paramagnetic cobalt(II) complex 45 [47]*

The reaction of **28** with anhydrous $CoCl_2$ in THF gives a deep blue mixture.

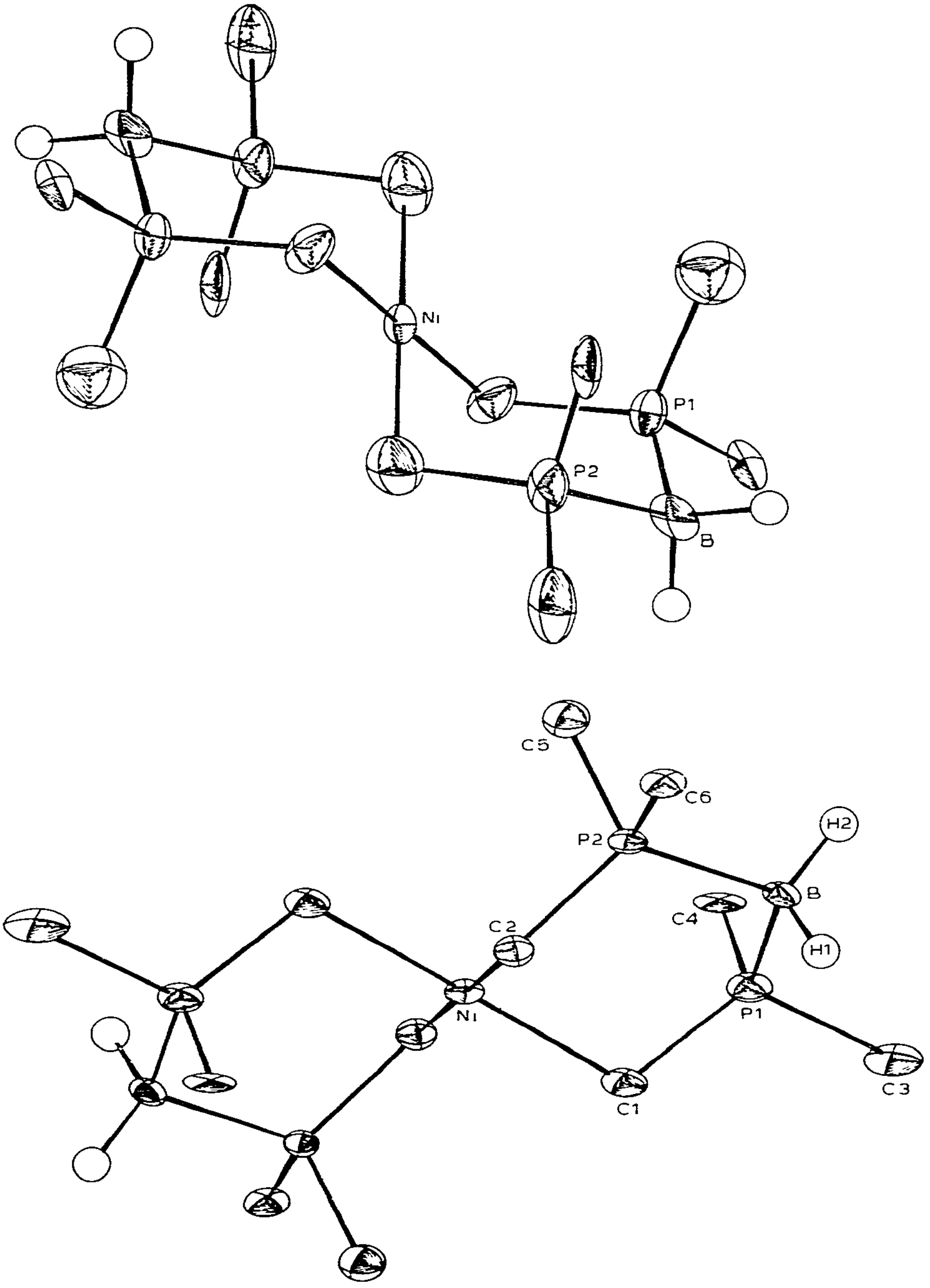


Fig. 5a, b. Molecular structure of the nickel(II) complex 39 as determined by X-ray diffraction [48,56].

Filtration, concentration of the filtrate in vacuo, and crystallisation from pentane at −78°C yield dark blue transparent crystals, which are extremely sensitive to air and moisture.

Elemental analysis and mass spectrometry confirm a formula $C_{12}H_{36}B_2CoP_4$

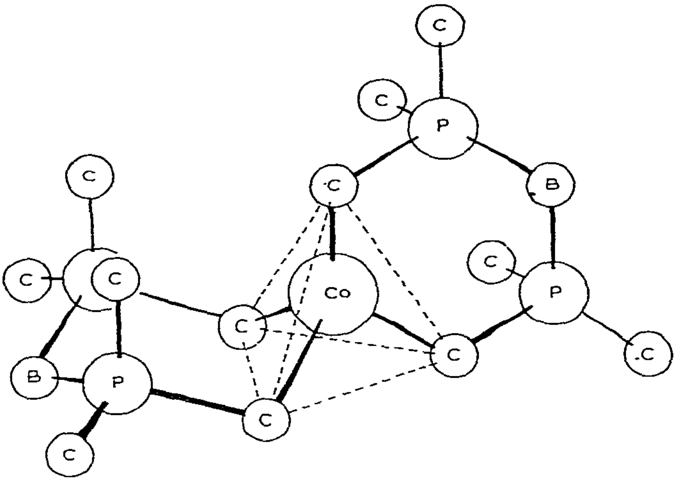


Fig. 6. Molecular model of the tentative structure of the cobalt complex 45.

(M.W. 384.867), and the vibrational spectra suggest a molecular structure similar to that of the above zinc or cadmium complexes (42, 43). Toluene solutions and toluene matrixes at ambient temperature or —196° C, respectively, do not exhibit an ESR signal, but a ^{1}H NMR spectrum with the typical features of a paramagnetic compound was obtained. The spectrum is temperature dependent and the following chemical shifts were determined (in C_6D_6 rel. TMS):

	$T_1 = 287.5$ K	$T_2 = 320$ K
$\delta(CH_3)$ (ppm)	+ 17.47	+ 15.89
$\delta(CH_2)$ (ppm)	+ 258.87	+ 232.57
$\delta(BH_2)$ (ppm)	+ 11.37	+ 10.62

Diamagnetic corrections, based on measurements of the cadmium compound, lead to standardized shifts $\delta(CH_3) = -16.24$ and $\delta(CH_3) = -258.79$ ppm at 20° C. This pattern is direct evidence for unpaired electron density at the metal center with limited delocalization into the ligand system. It therefore confirms the idea of a strictly σ-donating boranato-bis-ylidic chelate *.

Measurements of the magnetic susceptibility of the crystalline solid in the temperature range from 4.2 to 300 K indicated a magnetic moment, $\mu = 4.1$ B.M., which is close to the spin-only value of 3.87 B.M. The Curie-Weiss law was obeyed throughout **.

The cobalt complex is thus tentatively assigned a tetrahedral structure in a d^7 low spin configuration with four strong alkyl σ-donor ligands. The crystal structure remains to be determined. (See Fig. 6 for a drawing of the conformations).

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* We thank Prof. F.H. Köhler for the measurements.

** We thank Prof. K. Dehnicke and Dr. J. Pebler for these measurements.

The situation in complex 45 is quite unique, as other cobalt alkyls in the absence of auxiliary ligands are very unstable and poorly characterized. As in previous examples, this finding again illustrates the exceptional properties of the nitrido, methanido, and boranato-bis-ylide ligands. The steric and inductive effects of two phosphonium centers in positions adjacent to the metal-to-carbon bonds appear to provide a significant stabilisation of organometallic compounds which has not been fully explored.

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