Reactivity of cyclooligophosphanes: synthesis and structural characterisation of *cyclo*-1,4-$(BH_3)_2(P_4Ph_4CH_2)$ and *cyclo*-1,2-$(BH_3)_2(P_5Ph_5)$†

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Received 19th August 2005, Accepted 11th October 2005
First published as an Advance Article on the web 1st November 2005
DOI: 10.1039/b511833f

The borane complexes *cyclo*-1,4-$(BH_3)_2(P_4Ph_4CH_2)$ (**3**) and *cyclo*-1,2-$(BH_3)_2(P_5Ph_5)$ (**4**) were prepared by reaction of *cyclo*-$(P_4Ph_4CH_2)$ and *cyclo*-(P_5Ph_5) with $BH_3(SMe_2)$. Only the 2 : 1 complexes **3** and **4** were isolated, even when an excess of the borane source was used. In solution, **3** exists as a mixture of the two diastereomers (R_P*,S_P*,S_P*,R_P*)-(±)-**3** and (R_P*,R_P*,R_P*,R_P*)-(±)-**3**. However, in the solid state the (R_P*,S_P*,S_P*,R_P*)-(±) diastereomer is the major stereoisomer. Similarly, while only one isomer of **4** is observed in its X-ray structure, NMR spectroscopic investigations reveal that it forms a complex mixture of isomers in solution. **3** may be deprotonated with ^{t}BuLi to give the lithium salt *cyclo*-1,4-$(BH_3)_2(P_4Ph_4CHLi)$ (**3**·Li), though this could not be isolated in pure form.

Introduction

While the chemistry of linear and cyclic oligophosphanes has been an active field of research for many decades, this area has attracted increased attention in recent years. Among other examples, this is illustrated by our investigations of the cyclopentaphosphanide anion *cyclo*-$(P_5{}^tBu_4)^-$, which have unravelled its fascinating coordination chemistry.[1,2] Motivated by these results we also showed that the carbon analogue of this anion, the tetraphosphacyclopentanide anion *cyclo*-$(P_4{}^tBu_4CH)^-$ (**1**), can be prepared by deprotonation of *cyclo*-$(P_4{}^tBu_4CH_2)$ with lithium alkyls.[3] In contrast, ring cleavage is observed in the same reaction with *cyclo*-$(P_4Ph_4CH_2)$ (**2**).

In the context of our ongoing investigations on oligophosphanide chemistry,[1–4] we now report the synthesis and structural characterisation of two BH_3 complexes of cyclooligophosphanes, *cyclo*-1,4-$(BH_3)_2(P_4Ph_4CH_2)$ (**3**) and *cyclo*-1,2-$(BH_3)_2(P_5Ph_5)$ (**4**). The purpose of this study was twofold: first, borane complexes of cyclooligophosphanes are interesting objects of study, as their structures give insights into the reactivity of cyclooligophosphanes and particularly into the relative nucleophilicity of the coordinated and uncoordinated phosphorus atoms. To our knowledge, such complexes have not yet been described in the literature, except for an early report by Cowley and Pinell, who treated cyclooligophosphanes *cyclo*-(P_nR_n) (R = Et, ^{n}Pr, ^{n}Bu, Ph) with boron trihalides.[5] No crystallographic or NMR data were given at the time, and the structural identity of the isolated compounds could not be firmly established. Second, complexation of boranes is often used to modify the properties of tertiary phosphanes.[6] Therefore, we reasoned that the formation of a borane complex of *cyclo*-$(P_4Ph_4CH_2)$ might facilitate the formation of the respective tetraphosphacyclopentanide anion.

Interestingly, while BH_3 complexes of cyclooligophosphanes have remained elusive, Baudler *et al.* reported reactions of the cyclooligophosphanes *cyclo*-$(P_4Ph_4CH_2)$ (**2**) and *cyclo*-(P_5Ph_5) (**5**) with elemental sulfur to give the sulfides *cyclo*-$(S_2P_4Ph_4CH_2)$ (**2**·2S)[7] and *cyclo*-(SP_4Ph_4).[8] While **2**·2S has an intact P_4C ring, the P_4S heterocycle in *cyclo*-(SP_4Ph_4) formally originates from the insertion of a sulfur atom into *cyclo*-(P_4Ph_4). Recently, Burford *et al.* showed that phosphonium cations of cyclooligophosphanes such as [*cyclo*-(P_3tBu_3Me)]OTf, [*cyclo*-$(P_4tBu_3Me_2)$]OTf, [*cyclo*-(P_4Cy_4Me)]OTf and [*cyclo*-(P_5Ph_4RR')]OTf (R, R′ = Me, Ph) can be prepared by reaction of cyclooligosphanes with phosphenium triflates or methyl triflate.[9] These reports are of particular relevance to the present study, as the BH_3 complexes presented here may be regarded as neutral, isoelectronic analogues of these cationic compounds.

Results and discussion

Complexes **3** and **4** were prepared (Scheme 1) by reaction of two equivalents of $BH_3(SMe_2)$ with *cyclo*-$(P_4Ph_4CH_2)$ (**2**) and *cyclo*-(P_5Ph_5) (**5**). Significantly, formation of BH_3 complexes with a larger number of BH_3 groups in the molecule was not observed when an excess of the BH_3 source was used. This was indicated by $^{31}P\{^1H\}$ NMR spectra of the reaction mixtures, which remained practically unchanged, and by the fact that **3** and **4** were isolated in moderate to good yields regardless of whether two or more equivalents of BH_3 were used.

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† Electronic supplementary information (ESI) available: (a) Graphical representations of the experimental and simulated $^{31}P\{^1H,^{11}B\}$ NMR spectra of **3**; (b) graphical representation of the ^{31}P MAS spectrum of **3**; (c) graphical representation of the low-temperature NMR experiment on **3**; (d) graphical representation of the $^{31}P\{^1H\}$–$^{31}P\{^1H\}$ COSY NMR spectrum of **4**; (e) graphical representations of the optimised B3LYP structures of the symmetrical diastereomers of *cyclo*-$(P_4Ph_4CH_2)$ (**2**) and *cyclo*-1,4-$(BH_3)_2(P_4Ph_4CH_2)$ (**3**). See DOI: 10.1039/b511833f

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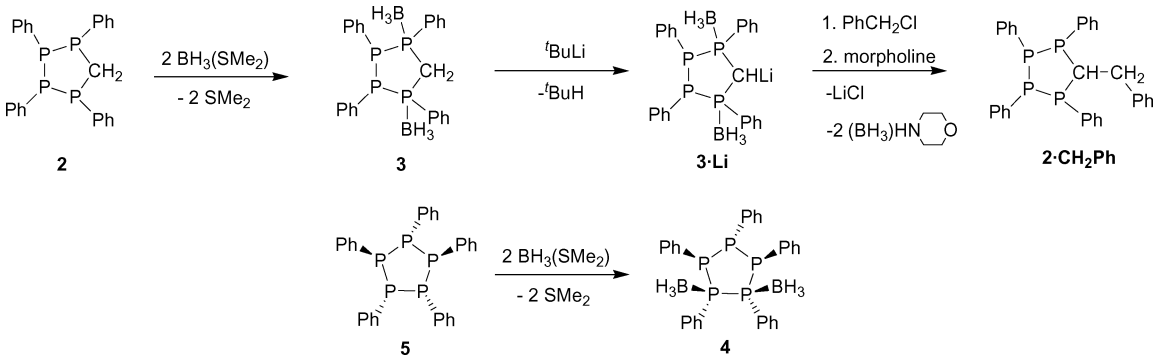


Scheme 1 Synthesis of **3**, **3**·Li, **2**·CH_2Ph and **4**.

Both complexes were studied in detail by multinuclear NMR spectroscopy and X-ray crystallography (Table 1). **3** crystallises in the space group $P\bar{1}$ with two molecules in the unit cell (Fig. 1). The asymmetric unit contains the (S_P,R_P,R_P,S_P) enantiomer, while the opposite enantiomer (R_P,S_P,S_P,R_P)-**3** is generated by the inversion centre, so that the compound exists as a racemate. The four symmetric diastereomers of **3** in which the pairs of borane groups are mutually *cis* or *trans* to one another are depicted in Fig. 2.[10] During refinement, minor, but significant, disorder of the atoms P2 and P3 and their attached phenyl groups was observed. These atoms were refined with occupancy factors of 94.3 : 5.7%. The disorder can be interpreted in terms of an inversion of the respective phosphorus atoms, which corresponds to the presence of a minor amount of the (R_P*,R_P*,R_P*,R_P*)-(±) diastereomer of **3** in the solid state (Fig. 3). Significantly, the same diastereomer is also observed in solutions of **3** (*vide infra*). Due to the presence of this diastereomer in the crystal and partial overlap of the two components, the disorder could not be fully resolved, and the following structural discussion is restricted to the major component (R_P*,S_P*,S_P*,R_P*)-(±)-**3**.

In this isomer, the BH_3 groups are connected in a transoid arrangement to the two phosphorus atoms (P1 and P4) adjacent

Table 1 Crystal data for *cyclo*-1,4-$(BH_3)_2(P_4Ph_4CH_2)$ (**3**), *cyclo*-1,2-$(BH_3)_2(P_5Ph_5)$ (**4**) and [*cyclo*-1,2-$(BH_3)_2(P_5Ph_5)$]·CH_2Cl_2 (**4**·CH_2Cl_2)

	3	**4**	**4**·CH_2Cl_2
Empirical formula	$C_{25}H_{28}B_2P_4$	$C_{30}H_{31}B_2P_5$	$C_{31}H_{33}B_2Cl_2P_5$
M	473.97	568.02	653.00
T/K	223(2)	207(2)	200(2)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$C2/c$
a/Å	10.717(2)	10.775(5)	19.6208(3)
b/Å	10.717(2)	22.123(5)	10.1953(1)
c/Å	12.340(2)	13.275(5)	33.8163(5)
α/°	78.798(3)	90	90
β/°	75.012(3)	108.435(5)	96.7138(6)
γ/°	72.274(3)	90	90
V/Å^3	1293.7(3)	3002.0(19)	6718.2(2)
Z	2	4	8
D_c/Mg m^{-3}	1.217	1.257	1.291
θ_{max}/°	30.80	29.46	25.01
Total data	10634	19111	31775
Unique data (R_{int})	7547 (0.019)	7494 (0.027)	5896 (0.04)
Goodness of fit on F^2	0.996	1.037	1.0432
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0502, 0.1094	0.0382, 0.0900	0.0356, 0.0394
$R1$, $wR2$ (all data)	0.0905, 0.1239	0.0640, 0.1005	0.0686, 0.0582

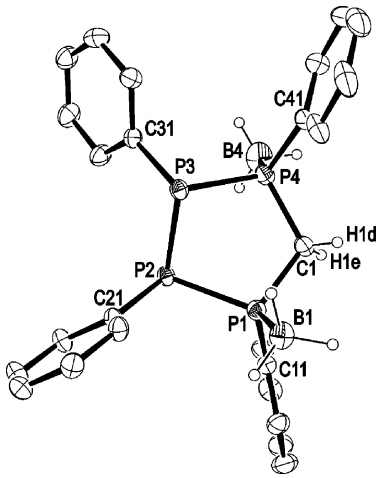


Fig. 1 Solid-state molecular structure of *cyclo*-1,4-$(BH_3)_2(P_4Ph_4CH_2)$ (**3**) (disorder and H atoms except those on C1, B1 and B4 omitted for clarity). Selected bond lengths (Å) and angles (°): P1–P2 2.229(1), P2–P3 2.2184(8), P3–P4 2.2291(9), P1–B1 1.928(3), P4–B4 1.911(3), P1–C1 1.839(2), P4–C1 1.835(2), mean P–C(*ipso*) 1.818; P1–C1–P4 114.6(1), C1–P1–P2 101.74(8), P1–P2–P3 91.73(3), P2–P3–P4 91.23(3), P3–P4–C1 102.83(7), C1–P1–B1 105.9(2), C1–P4–B4 108.3(2), B1–P1–P2 124.3(1), B4–P4–P3 118.8(1), C11–P1–C1 107.0(1), C11–P1–P2 100.85(7), C11–P1–B1 105.9(2), C41–P4–C1 107.8(1), C41–P4–P3 101.91(8), C41–P4–B4 116.0(2), C21–P2–P1 103.25(8), C21–P2–P3 102.00(9), C31–P3–P2 103.15(8), C31–P3–P4 97.64(8).

to the ring carbon atom (C1). The phenyl groups are in an all-*trans* arrangement with respect to each other. The B–P and P–P distances are in the expected ranges [d(P1–B1) = 1.928(3) Å; d(P4–B4) = 1.911(3) Å; d(P1–P2, P2–P3, P3–P4) = 2.218(1)–2.229(1) Å].[11,12] In contrast to the starting material *cyclo*-($P_4Ph_4CH_2$), which has an envelope conformation in the solid state,[13] the P_4C ring in (R_P*,S_P*,S_P*,R_P*)-(±)-**3** has a twist conformation in which the two β-P atoms P2 and P3 are displaced by 0.789 and 0.661 Å, respectively, from the plane formed by P1, P4 and C1. Interestingly, the disufilde **2**·2S shows a very similar arrangement:[13] the sulfur atoms are bound to the two α-P atoms in a transoid fashion and the P_4C heterocycle has a similar twist conformation.

Crystals of complex **4** could be obtained in an unsolvated form (**4**, space group $P2_1/n$) and in a solvated form (**4**·CH_2Cl_2, space group $C2/c$) with one molecule of CH_2Cl_2 per formula unit (Table 1). As the structural features of **4** and **4**·CH_2Cl_2 are rather similar, we restrict our discussion to the unsolvated form **4**. Only

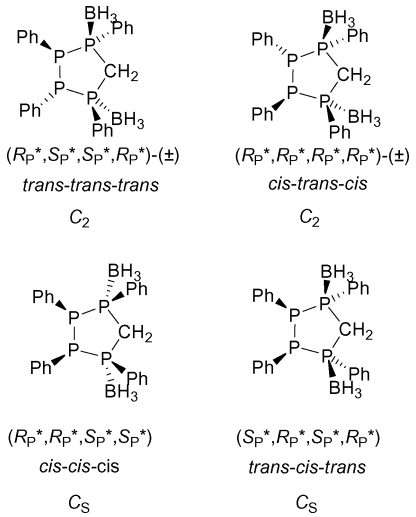


Fig. 2 The four symmetric diastereomers of **3**. Only one enantiomer of the chiral diastereomers is depicted.

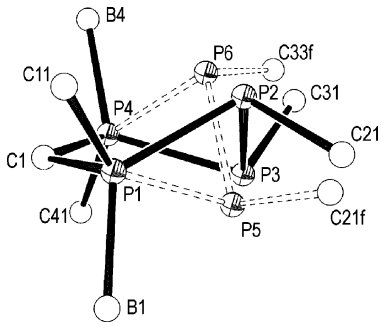


Fig. 3 Core structure of **3** (only P, B and their directly attached carbon atoms are shown; atoms of the minor component are indicated by dashed bonds). Selected bond lengths (Å) and angles (°): P5–P6 2.195(2); P1–P5–P6 84.3(5), P4–P6–P5 84.1(5), C21f–P5–P1 95(1), C21f–P5–P6 109(2), C33f–P6–P4 98(2), C33f–P6–P5 106(2).

one diastereomer of **4** is present in the unit cell, corresponding to two enantiomers related by the crystallographic centre of symmetry (Fig. 4). The two BH_3 groups are coordinated to two adjacent phosphorus atoms of the *cyclo*-(P_5Ph_5) unit. The resulting $P_2Ph_2(BH_3)_2$ moiety is in a *syn* conformation (torsion angle B1–P1–P2–B2: 35.6°). The remaining phenyl substituents display an all-*trans* arrangement. As in **5**,[14] the P_5 ring is in an envelope conformation. The P–P bond lengths are normal [*d*(P1–P2, P2–P3, P3–P4, P4–P5, P5–P1) = 2.206(1)–2.243(1) Å][12] and the B–P bonds compare well with those in **3** [*d*(B1–P1) = 1.941(2), *d*(B2–P2) = 1.956(2) Å].

Multinuclear NMR spectroscopic investigations were carried out on **3** and **4** in solution. Interestingly, the two AA′BB′ spin systems observed in the $^{31}P\{^1H\}$ NMR spectrum of **3** indicate the presence of two symmetric species in a ratio of approximately 1 : 2.5. This situation is also reflected in the ^1H NMR spectrum by two multiplets at 2.80 und 3.02 ppm and by signals in the $^{13}C\{^1H\}$ NMR spectrum at 21.69 and 27.11 ppm corresponding to two distinct methylene groups. This indicates the presence of two separate species in solution. Most likely, these are different stereoisomers of **3**. Of the four possible diastereomers which are in agreement with the symmetry of the ^{31}P NMR spectrum

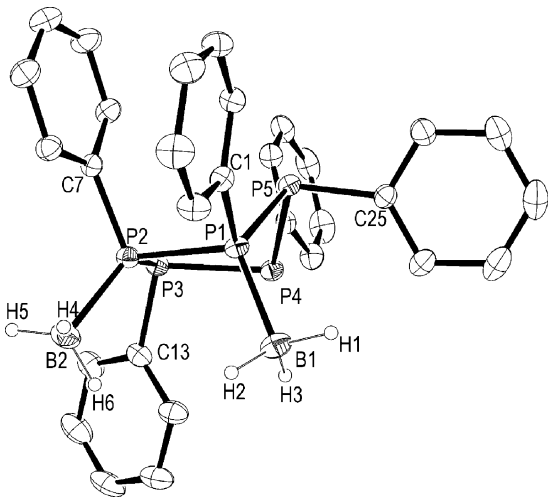


Fig. 4 Solid-state molecular structure of *cyclo*-1,2-(BH_3)$_2$(P_5Ph_5) (**4**) (H atoms except those on B1 and B2 omitted for clarity). Selected bond lengths (Å) and angles (°): P1–P2 2.2221(8), P2–P3 2.2234(8), P3–P4 2.2430(8), P4–P5 2.2207(8), P1–P5 2.206(1), P1–B1 1.941(2), P2–B2 1.956(2), mean P–C(*ipso*) 1.828; P1–P2–P3 103.69(3), P2–P3–P4 101.53(3), P3–P4–P5 96.22(4), P4–P5–P1 92.78(2), C1–P1–B1 114.6(1), C1–P1–P2 104.11(6), C1–P1–P5 105.34(6), B1–P1–P2 111.56(9), B1–P1–P5 120.76(9), C7–P2–B2 114.3(1), C7–P2–P1 101.12(6), C7–P2–P3 105.50(6), B2–P2–P1 111.90(9), B2–P2–P3 118.46(9), C13–P3–P2 101.69(7), C13–P3–P4 99.16(7), C19–P4–P3 98.06(6), C19–P4–P5 99.44(6), C25–P5–P4 102.88(7), C25–P5–P1 100.12(6).

(Fig. 2), the major component presumably corresponds to the energetically favoured all-*trans* diastereomer (R_P*,S_P*,S_P*,R_P*)-(±)-**3**. The second component may be another diastereomer of **3** with a different relative orientation of the phenyl substituents (Fig. 2). The ^{31}P coupling parameters obtained by analysis of the $^{31}P\{^1H,^{11}B\}$ NMR spectra (see Experimental section), differ significantly from those of the related compounds **2** and **2**·2S; in particular, the $^1J_{PP}$ coupling constants are rather small. Another interesting difference is that only one diastereomer is observed in the NMR spectra of **2** and **2**·2S, although the solid-state structure **2**·2S is very similar to that of **3**. Unfortunately, more precise structural information could not be obtained from the ^{31}P NMR parameters of **3**, as more closely related reference compounds are not available for comparison. Attempts to separate the two components by TLC or HPLC failed. Similarly, the ratio of the two isomers remained practically unchanged even after six consecutive recrystallisations of **3** from CH_2Cl_2–*n*-hexane (2 : 1).

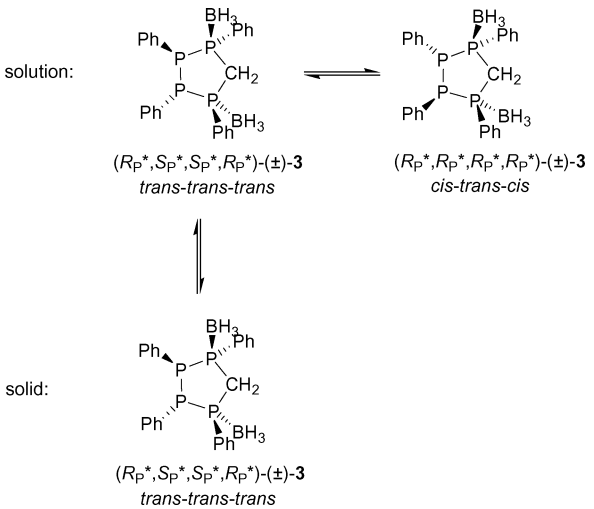
With these observations in mind, quantum chemical calculations were carried out on the four stereoisomers which agree in their symmetry with the $^{31}P\{^1H\}$ NMR spectra, both for **3** and the parent compound **2**. Full geometry optimisations were performed on pre-optimised AM1 geometries at the DFT-B3LYP level with the 6-311G* basis set. Except for minor deviations of the bond lengths, the geometric parameters of the optimised structures of (R_P*,S_P*,S_P*,R_P*)-(±)-**3** and (R_P*,S_P*,S_P*,R_P*)-(±)-**2** correspond well to their solid-state structures (for details see also ESI†). Table 2 contains the relative energies of the different isomers calculated at the B3LYP level and for comparison at the Hartree–Fock level (using the optimised B3LYP geometries). While the stereoisomers of **2** adhere to the expected trend by becoming increasingly energetically disfavoured with increasing

Table 2 Relative energy differences ΔE/kJ mol^{-1} between the stereoisomers of *cyclo*-($P_4Ph_4CH_2$) (**2**) and *cyclo*-1,4-(BH_3)$_2$($P_4Ph_4CH_2$) (**3**) (see Fig. 2) as determined by Hartree–Fock (HF) and DFT calculations (basis set: 6-311G*)

	2		**3**	
Isomer	ΔE_{B3LYP}	ΔE_{HF}	ΔE_{B3LYP}	ΔE_{HF}
cis-cis-cis	51.02	58.33	57.98	71.85
cis-trans-cis	19.25	18.66	5.88	8.53
trans-cis-trans	13.55	11.52	27.79	32.55
trans-trans-trans	0	0	0	0

number of phenyl groups in a *cis* orientation, the same order is not observed for **3**. In this case, the all-*trans* isomer (R_P*,S_P*,S_P*,R_P*)-(±)-**2** is still lowest in energy but, depending on the method employed, the *cis-trans-cis* isomer (R_P*,R_P*,R_P*,R_P*)-(±)-**3** is only 6–8 kJ mol^{-1} higher in energy. Significantly, the energy difference to the *trans-cis-trans* isomer (S_P*,R_P*,S_P*,R_P*)-**3** is several times larger. Hence, it appears that the second isomer in solution is indeed (R_P*,R_P*,R_P*,R_P*)-(±)-**3**. The presence of the all-*trans* and the *cis-trans-cis* isomers in solution also becomes plausible if one considers that both species differ only in the relative configurations of the uncoordinated β-phosphorus atoms. The low inversion barrier of the β-phosphorus atoms would effect the room-temperature interconversion between the two diastereomers. In fact, it is well know that the inversion barriers of catenated phosphorus atoms are often significantly reduced compared to ordinary tertiary phosphanes.[15]

Thus, in solution an equilibrium is assumed between the major component (R_P*,S_P*,S_P*,R_P*)-(±)-**3** and the minor stereoisomer (R_P*,R_P*,R_P*,R_P*)-(±)-**3**. The overwhelming part of the minor isomer is then converted to the all-*trans* form (R_P*,S_P*,S_P*,R_P*)-(±)-**3** on crystallisation in a second-order asymmetric transformation[16] (Scheme 2). The ^{31}P MAS NMR spectrum of the bulk solid confirms the presence of only one isomer (see Experimental section and ESI†) with three resonances in the approximate ratio of 2 : 1 : 1. While the low-field resonance is attributed to the P atoms coordinated to boron, the two peaks at high field are assigned to the β-phosphorus atoms, which have



Scheme 2 Isomerisation of **3** by second-order asymmetric transformation.

different local environments in the crystal. A low-temperature NMR experiment gives additional credence to the suggested mechanism. Thus, the low-temperature $^{31}P\{^1H\}$ NMR spectrum of a freshly prepared sample of **3** showed only the signals of (R_P*,S_P*,S_P*,R_P*)-(±)-**3**. Only after the sample had been warmed to room temperature was the usual picture again observed: the $^{31}P\{^1H\}$ NMR spectrum at −80 °C showed resolved multiplets of both isomers in the usual ratio of approximately 2.5 : 1 (see ESI† for details).

The underlying reason for the small energy gap between the *cis-trans-cis* isomer and the sterically favoured all-*trans* isomer of **3** may be that the repulsion between the phosphorus lone pairs is diminished by the coordinating BH_3 moieties. Preliminary DFT calculations on the related compound **2**·2S reveal that the energies of its symmetric stereoisomers follow the same order as in **3**. However, the energy difference between the all-*trans* isomer (R_P*,S_P*,S_P*,R_P*)-(±)-**2**·2S and the *cis-trans-cis* isomer (R_P*,R_P*,R_P*,R_P*)-(±)-**2**·2S is significantly larger than in **3**.[17] This may explain why a second isomer of **2**·2S was not observed by Baudler and co-workers in solution.[7]

Although the solution behaviour of **3** can certainly not be regarded as trivial, the $^{31}P\{^1H\}$ NMR spectrum of **4** reveals a much more complicated situation (Fig. 5). Numerous multiplets are observed in the regions 0 to +25 ppm and −50 to −20 ppm. Note that the $^{31}P\{^1H\}$ NMR spectrum of **4** is reproducible, and recrystallisation of the product does not lead to a significant alteration of the spectrum. Again, the relative deshielding and the line broadening caused by coupling with the ^{11}B nuclei indicates that the low-field resonances can be attributed to the P atoms coordinated to BH_3. Interestingly, integration of inversely decoupled $^{31}P\{^1H\}$ NMR gives a ratio of 1 : 2.1 between the low-field and the high-field signals, whereas a ratio of 2 : 3 would be expected for **4**. Unfortunately, individual spin systems could not be identified due to severe signal overlap. Therefore, a highly resolved $^{31}P\{^1H\}$ $^{31}P\{^1H\}$ COSY spectrum was recorded. Although it would be inappropriate to identify individual spin systems solely on the basis of this spectrum, it is interesting to note the presence of only two rather weak cross-peaks in the low-field region of the spectrum (corresponding to the phosphorus atoms with coordinated BH_3). The observation of seven diagonal peaks between 0 and +25 ppm therefore seems to indicate the presence of at least six distinct species in solution (see ESI†). Obviously, complex isomerisation processes are taking place in

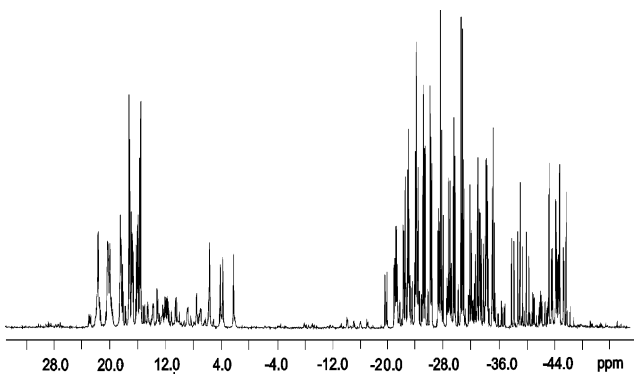


Fig. 5 $^{31}P\{^1H\}$ NMR spectrum of *cyclo*-1,2-(BH_3)$_2$(P_5Ph_5) (**4**) ($CDCl_3$, 161.98 MHz).

solution. These may possibly result in different configurations, constitutions (different positions of the BH_3 groups in the ring), different ring sizes (as observed for the parent compound **5**, which is in equilibrium with the cyclotetra- and cyclohexaphosphane) or even loss of BH_3 moieties.

The deprotonation of **3** was systematically studied with a variety of bases [*e.g.* ^{n}BuLi, lithium diisopropylamide (LDA), $Na\{N(SiMe_3)_2\}$] with the aim of converting it to a tetraphosphacyclopentanide anion (Scheme 1). In most cases, intractable mixtures of products were obtained from these reactions. However, the heterogeneous reaction of **3** with ^{t}BuLi in *n*-pentane initially appeared to be quite promising. An orange, extremely air-sensitive powder was isolated which showed four symmetric multiplets in the $^{31}P\{^1H\}$ NMR spectrum, corresponding to two symmetric AA′BB′ spin systems in the expected ratio of approximately 2 : 1 (Fig. 6). Such a spectrum would indeed be expected for the target compound *cyclo*-1,4-$(BH_3)_2(P_4Ph_4CHLi)$ (**3**·Li) provided that inversion of the β-phosphorus atoms is slow on the ^{31}P NMR timescale and rapid inversion of the anionic ring carbon atom occurs [as observed in the related compound $[Li(thf)_3\{cyclo\text{-}(P_4{}^tBu_4CH)\}]$ (**1**)].[3] However, in subsequent experiments it was found that the synthesis of **3**·Li was only poorly reproducible, additional signals in the $^{31}P\{^1H\}$ NMR spectrum of the product indicating the presence of significant impurities. Moreover, attempts to purify the compound by crystallisation failed to give pure **3**·Li. To confirm its identity, a relatively pure sample of **3**·Li was treated with benzyl chloride (Scheme 1). After removal of the BH_3 groups with morpholine the $^{31}P\{^1H\}$ NMR spectrum showed the presence of an ABCD spin system as major product. This may indicate the formation of the C-substituted species *cyclo*-$\{P_4Ph_4CH(CH_2Ph)\}$ (**2**·CH_2Ph). However, this compound could also not be isolated in pure form. Thus, although in principle the deprotonation of **3** is feasible, it remains of limited synthetic value at present.

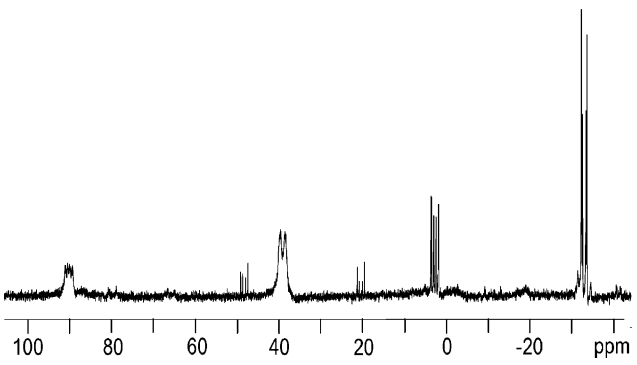


Fig. 6 Section of the $^{31}P\{^1H\}$ NMR spectrum (C_7D_8–THF) of the product isolated from the reaction of ^{t}BuLi with *cyclo*-1,4-$(BH_3)_2(P_4Ph_4CH_2)$ (**3**).

Conclusions

The synthesis of the borane complexes *cyclo*-1,4-$(BH_3)_2$-$(P_4Ph_4CH_2)$ (**3**) and *cyclo*-1,2-$(BH_3)_2(P_5Ph_5)$ (**4**) demonstrates that the cyclooligophosphanes **2** and **5** readily form 2 : 1 adducts with BH_3, whereas the formation of adducts with a higher ratio of BH_3 per molecule appears to be disfavoured. The position of the BH_3 moieties in the cyclophosphane rings of **3** and **4** indicates that the respective P atoms possess a relatively high nucleophilicity. In solution, **3** forms a mixture of two diastereomers related by inversion of the uncoordinated phosphorus atoms, while a complex mixture of isomers is observed in the case of **4**. Attempts to deprotonate **3** so far have failed to generate the desired tetraphosphacyclopentanide anion *cyclo*-1,4-$(BH_3)_2(P_4Ph_4CH)^-$ in a clean manner.

Experimental

General methods

All procedures were performed under an inert atmosphere of pure nitrogen or argon with rigorous exclusion of air and moisture. The solvents were dried by distillation over sodium/benzophenone or $LiAlH_4$ and saturated with argon prior to use. *cyclo*-$(P_4Ph_4CH_2)$ (**2**)[7,18] and *cyclo*-(P_5Ph_5) (**5**)[19] were prepared by literature methods. All other reagents were obtained from commercial sources.

The NMR spectra were recorded with a Bruker AVANCE DRX 400 spectrometer (^1H NMR, 400.13 MHz, internal standard solvent, external standard TMS; ^{13}C NMR: 100.16 MHz, internal standard solvent, external standard TMS; ^{31}P NMR: 161.9 MHz, external standard 85% H_3PO_4; ^{11}B NMR: 128.4 MHz, external standard $BF_3(OEt_2)$; ^7Li NMR: 155.50 MHz, external standard 1 M LiCl in MeOH). The $^{31}P\{^1H,^{11}B\}$ NMR spectra were recorded with a Bruker AMX 300 NMR spectrometer (^1H NMR: 300.13 MHz; ^{31}P NMR: 121.50 MHz; ^{11}B NMR: 96.29 MHz). The $^{31}P\{^1H\}$ $^{31}P\{^1H\}$ COSY spectrum was recorded at 283.43 MHz on a Bruker AVANCE 700 MHz spectrometer equipped with a 5 mm tbi probe. The ^{31}P MAS spectrum was recorded on a Bruker MSL 500 spectrometer at 202.45 MHz. Elemental analyses were performed by staff members of the Research School of Chemistry at the ANU, Canberra. The melting points were determined in sealed capillaries under argon and are uncorrected.

Quantum chemical calculations

All calculations were carried out with the Gaussian98 program package.[20] Full geometry optimisation was performed at the DFT-B3LYP level using the standard triple-ζ 6-311G* basis set. For comparison, single-point Hartree–Fock energies were calculated as well.

Data collection and structure refinement of 3, 4 and 4·CH_2Cl_2

Data [λ(Mo-Kα) = 0.71073 Å] were collected with a Siemens CCD (SMART) diffractometer (for **3**, **4**) or on a Nonius Kappa CCD (for **4**·CH_2Cl_2). All observed reflections were used for refinement of the unit-cell parameters. Empirical absorption corrections were applied to the data of **3** and **4** (SADABS)[21] and analytical absorption corrections were applied for **4**·CH_2Cl_2 (NUMABS).[22] The structures were solved by direct methods (**3**, **4**: SHELXTL PLUS,[23] **4**·CH_2Cl_2: SIR92[24]). Refinement was on F^2 for **3** and **4** (SHELXTL[23]) and on F for **4**·CH_2Cl_2 (CRYSTALS[25]). P, B and C atoms were refined anisotropically; some C atoms of disordered parts (P atoms, phenyl groups in **3**) were refined isotropically; H atoms were located by difference maps and refined isotropically. Table 1 lists crystallographic details. The thermal ellipsoids of the molecular structures in Fig. 1–4 are shown at the 30% probability level.

CCDC reference numbers 280235 (**3**), 280236 (**4**) and 280237 (**4**·CH_2Cl_2).

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b511833f

Synthesis of 3

1.0 ml (10 mmol) of $BH_3(SMe_2)$ was added to a solution of 1.92 g (4.3 mmol) of **2** in 40 ml of toluene. The solution was heated to reflux briefly and stirred overnight. 120 ml of *n*-hexane was added very quickly and the slightly turbid mixture was stored at room temperature. Large, colourless crystals formed within a few days, which were isolated and dried *in vacuo*. Yield: 1.22–1.73 g (60–84%). Melting point: 153–155 °C. $^1H\{^{31}P,^{11}B\}$ NMR (300.13 MHz, C_6D_6), δ 1.76 [s, BH_3 of (R_P*,S_P*,S_P*,R_P*)-(±)-**3**], 2.08 [s, BH_3 of (R_P*,R_P*,R_P*,R_P*)-(±)-**3**], 2.79 [s, CH_2 of (R_P*,S_P*,S_P*,R_P*)-(±)-**3**], 3.01 [s, CH_2 of (R_P*,R_P*,R_P*,R_P*)-(±)-**3**], 6.7–8.3 (m, Ph); $^{13}C\{^1H\}$ NMR (100.16 MHz, C_6D_6), δ 21.69 [tt, $^1J_{PC}$ = 18.6 Hz, $^2J_{PC}$ = 5.4 Hz, CH_2 of (R_P*,R_P*,R_P*,R_P*)-(±)-**3**], 27.11 [tt, $^1J_{PC}$ = *ca.* 17.8 Hz, $^2J_{PC}$ = *ca.* 3.3 Hz, CH_2 of (R_P*,S_P*,S_P*,R_P*)-(±)-**3**], 125–135 (several s and m, Ph); $^{31}P\{^1H,^{11}B\}$ NMR (121.50 MHz, C_6D_6), (R_P*,S_P*,S_P*,R_P*)-(±)-**3**: $\delta_{A,A'}$ = +25.13(1) (m), $\delta_{B,B'}$ = −35.08(1) (m), $^1J_{AB}$ = $^1J_{A'B'}$ = −188.5(3) Hz, $^1J_{BB'}$ = −146.5(2) Hz, $^2J_{AB'}$ = $^2J_{A'B}$ = +35.1(1) Hz, $^2J_{AA'}$ = −15.3(2) Hz, (R_P*,R_P*,R_P*,R_P*)-(±)-**3**: $\delta_{A,A'}$ = +33.65(1) (m), $\delta_{B,B'}$ = −38.99(1) (m), $^1J_{AB}$ = $^1J_{A'B'}$ = −266.6(2) Hz, $^1J_{BB'}$ = −172.6(2) Hz, $^2J_{AB'}$ = $^2J_{A'B}$ = +1.8(1) Hz, $^2J_{AA'}$ = −32.0(2) Hz; $^{11}B\{^1H\}$ (96.29 MHz, C_6D_6), δ 35.3 (br s, BH_3); ^{31}P MAS NMR (202.45 MHz): δ +21.3 (br, 2P, *P*–BH_3), −23.1 [br, 1P, *P*–P(BH_3)], −39.0 [br, 1P, *P*–P(BH_3)]. EI-MS, *m*/*z* (%): 473.9 (0.3) $[M]^+$, 459.9 (0.7) $[M - BH_3]^+$, 368.8 (20) $[M - 2BH_3 - Ph]^+$, 229.9 (27) $[M - 2BH_3 - P_2Ph_2]^+$, 215.9 (7) $[(P_2Ph_2)]^+$. Elemental analysis: found: C 63.35, H 5.95, P 27.00; calc.: C 63.04; H 6.23; P 26.14%.

Synthesis of 3·Li

1.47 ml (1.7 mmol) of ^{t}BuLi (1.14 M in *n*-hexane) was added to 0.79 g (1.7 mmol) of **3** in 40 ml of *n*-pentane. Then the mixture was refluxed for 3.5 h. The resulting yellow–orange suspension was filtered. The residue was dried *in vacuo*. The orange, very air-sensitive powder was insoluble in hydrocarbons, but soluble in THF. It was investigated by NMR spectroscopy. ^1H NMR (400.13 MHz, C_7D_8–THF), δ 0.5–2.2 (br m, BH_3), 2.51 (br m, CH), 6.3–8.5 (m, Ph); $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6–THF), δ +90.2 [br m, $P_{A,A'}$ of (R_P*,R_P*,R_P*,R_P*)-(±)-**3**·Li], +39.1 [br m, $P_{A,A'}$ of (R_P*,S_P*,S_P*,R_P*)-(±)-**3**·Li], +2.7 [m, $P_{B,B'}$ of (R_P*,R_P*,R_P*,R_P*)-(±)-**3**·Li], −32.9 [m, $P_{B,B'}$ of (R_P*,S_P*,S_P*,R_P*)-(±)-**3**·Li], further components: δ +47.6 (m, $P_{A,A'}$ of **2**), +19.9 (m, $P_{B,B'}$ of **2**), −3.8 (m, **5**), −48.2 [s, *cyclo*-(P_4Ph_4)], −62.1 (br s, unidentified species); ^7Li NMR (155.50 MHz, C_7D_8–THF), δ 0.02 (s).

Synthesis of 2·CH_2Ph

0.53 ml (4.6 mmol) of benzyl chloride was added to a clear, ice-cooled solution of **3**·Li (freshly prepared from **3** and ^{t}BuLi according to the above procedure) in 15 ml toluene which contained a few drops of THF in order to dissolve the lithium salt. The solution turned pale and slightly turbid on addition and was stirred overnight. The solvent was removed *in vacuo* and 5 ml of morpholine was added. This mixture was stirred for 3 days. After the morpholine had been removed *in vacuo* 25 ml of degassed MeOH–H_2O (1 : 3) was added, and the mixture heated briefly to reflux and stirred for two days. Subsequently, the mixture was filtered, dissolved in CH_2Cl_2 and the solution dried with molecular sieves. The solvent was removed completely and the colourless residue extracted into 10 ml of diethyl ether. A colourless powder was obtained on storage of the solution at −20 °C for several weeks. This was isolated and contained **2**·CH_2Ph as a major product according to ^{31}P NMR spectroscopy. Attempts to purify the crude product by recrystallisation failed. $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6), ABCD spin system: δ_A = +34.81(1) (m), δ_B = +29.15(1) (m), δ_C = −2.65(1) (m), δ_D = −8.22 (m), $^1J_{AC}$ = ±232.2(2) Hz, $^1J_{BD}$ = ±250.8(2) Hz, $^1J_{CD}$ = ±260.4(2) Hz, $^2J_{AD}$ = ±13.5(2) Hz, $^2J_{AB}$ = ±19.1(2) Hz, $^2J_{BC}$ = ±17.8(2) Hz.

Synthesis of 4

0.95 ml (9.5 mmol) of $BH_3(SMe_2)$ was added to a solution of 2.63 g (4.9 mmol) of **5** in 50 ml of toluene. The mixture was heated to reflux briefly and stirred for 1.5 h. Subsequently, the solvent was removed completely, and the remaining colourless solid dissolved in 10 ml of CH_2Cl_2. 20 ml of *n*-hexane was added quickly, and the slightly turbid mixture was stored at −20 °C for several days. Colourless crystals formed and were isolated and dried *in vacuo*. The crystals contained approximately one molecule of CH_2Cl_2 per formula unit according to ^1H NMR and elemental analysis. Yield: 1.40 g (44% ref. to **4**·CH_2Cl_2 and the amount of **5** supplied). Melting point: >180 °C (decomp.). ^1H NMR (400.13 MHz, $CDCl_3$), δ 0.4–1.7 (br, 6H, BH_3), 6.6–8.2 (m, 25H, Ph); $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$), δ 2–23 (overlapping m, *P*–BH_3), −19 to −46 [overlapping m, *P*–P(BH_3) or *P*–P–P(BH_3)]; $^{11}B\{^1H\}$ (128.4 MHz, $CDCl_3$), +35 (br m, BH_3). Elemental analysis: found: C 56.96; H 5.07; P 24.84. calc.: C 57.02; H 5.10; P 23.72%.

Acknowledgements

We thank Dr Eberhard Matern (Karlsruhe University) for recording the ^{11}B-decoupled NMR spectra and valuable discussions. Dr Winfried Böhlmann is thanked for solid-state NMR measurements, Dr Christina Thiele for recording the 2D ^{31}P NMR spectrum and Prof. Dr Stefan Berger for valuable discussions and spectrometer time on the Bruker AVANCE 700 MHz spectrometer (all University of Leipzig). Dr Alison J. Edwards (ANU, Canberra) is thanked for assistance with the X-ray measurements of **3**. Support from the DAAD (PPP, DAAD/ARC, project number 313-ARC-XIV-00/37) and the Studienstiftung des Deutschen Volkes (PhD grant for R. W.) is gratefully acknowledged.

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