ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 592 (1999) 22–28

Journal of Organometallic Chemistry

Contribution of the *o*-carboranyl fragment to the chemical stability and the ^{31}P-NMR chemical shift in *closo*-carboranylphosphines. Crystal structure of bis(1-yl-2-methyl-1,2-dicarba-*closo*-dodecaborane)phenylphosphine

Rosario Núñez [a], Clara Viñas [a,*], Francesc Teixidor [a], Reijo Sillanpää [b], Raikko Kivekäs [c]

[a] *Institut de Ciència de Materials de Barcelona, Campus de la UAB, E-08193 Bellaterra, Spain*
[b] *Department of Chemistry, University of Turku, FIN-20014 Turku, Finland*
[c] *Department of Chemistry, University of Helsinki, PO Box 55, FIN-00014 Helsinki, Finland*

Received 16 May 1999; accepted 3 August 1999

This article is dedicated to Professor Stanislav Hermánek on the occasion of his 70th birthday in recognition of his contribution to boron and carborane chemistry, and NMR spectroscopy. His points of view on chemistry have been both very rewarding and stimulating.

Abstract

Closo-carboranylphosphines behave differently from *closo*-monothiocarboranes or other organophosphorus compounds. They tend to lose one boron by reacting with a nucleophile such as OH^- with hydrolysis of the C–P bond. On the other hand, they are less basic than similar organophosphorus compounds, and less reactive both towards oxygen and some metal ions. Many or all of these characteristics can be attributed to the carborane cluster. Its influence on the phosphorus has been revealed by studying the ^{31}P chemical shifts of a series of $P(L)R_2$ and $P(L)_2R$ phosphines, where L are different carboranyl fragments. If the series $P(L)Ph_2$ is considered, where a phosphorus atom is surrounded by two phenyl groups and one *o*-carboranyl moiety carbon bonded to the phosphorus, it is observed that the capacity to shift the ^{31}P-NMR resonances of $P(L)Ph_2$ to lower field follows the trend: 1-yl-1,2-dicarba-*closo*-dodecaborane > 1-yl-2-phenyl-1,2-dicarba-*closo*-dodecaborane > 1-yl-2-methyl-1,2-dicarba-*closo*-dodecaborane. These trends are valid for any $P(L)R_2$ series tested so far. It is also found that the absolute value of the ^1J(P–C(1)) coupling constants, where C(1) is the cluster carbon bonded to P atom, also displays the same trend. The molecular structure of bis(1-yl-2-methyl-1,2-dicarba-*closo*-dodecaborane)phenylphosphine is presented in this paper. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Carboranes; Phosphorus; Carboranylphosphines; ^{31}P-NMR

1. Introduction

The synthesis of new *o*-carborane-derived materials such as asymmetric macrocycles [1], compounds for boron-neutron capture therapy, and asymmetric catalysts, requires monosubstituted precursors as the starting material. Our group has been concerned with the synthesis of cluster compounds containing *exo*-cluster atoms with lone pairs, such as S or P, due to their tendency to coordinate to metals and their potential catalytic activity. Previously, we have reported the synthesis and structural characterization of several monosubstituted 1,2-dicarba-*closo*-dodecaborane derivatives which contain sulfur or phosphorus bonded to cluster carbon atom [2,3].

The electronic structures of icosahedral *closo* carboranes have been described as 3D aromatic [4] systems and the implications of the electronic interactions with substituents have received particular interest ever since the first studies of these compounds were made 30 years ago. The carborane clusters have been largely studied by ^{11}B-NMR spectroscopy and trends with electronic

---

* Corresponding author.

PII: S0022-328X(99)00472-6

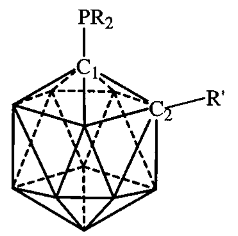
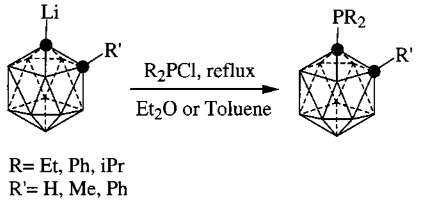


Fig. 1. Schematic representation of the *closo*-carboranylphosphines.



Scheme 1. General reaction for preparing *closo*-carboranylphosphines using the monolithium salt of the *o*-carborane derived.

densities have been described by Hermanek [5] and us [6], among others [7]. The ab initio IGLO/NMR and GIAO/NMR programs have proven to be very useful in estimating quite precisely the ^{11}B chemical shifts, as it has been shown for many examples [8] of boron compounds. However, this is not so straightforward for ^{31}P chemical shifts [9]. Nevertheless, the ^{31}P-NMR technique is relevant to define the molecular structure, to study reaction mechanisms, for the determination of diastereometry or the optical purity of a variety of substances [10].

We report here some results on the properties of the carborane clusters, especially on the contribution of the cluster to the ^{31}P chemical shift in the NMR spectra. In this context, we have studied a family of *closo*-carboranylphosphines 1-PR$_2$-2-R′-C$_2$B$_{10}$H$_{10}$ (R′ = H, Me, Ph; R = Ph, Et, ^{i}Pr) (Fig. 1) reported earlier [3] and others that we describe for the first time. The crystal structure of bis(1-yl-2-methyl-1,2-dicarba-*closo*-dodecaborane)-phenylphosphine is also reported.

2. Results and discussion

2.1. Synthesis of *closo*-carboranylphosphines

The reaction of the monolithium salt of the *o*-carborane derivatives 1-R′-1,2-C$_2$B$_{10}$H$_{11}$ (R′ = H, Me, Ph) with halophosphines such as PClPh$_2$, PClEt$_2$, PCl(^{i}Pr)$_2$ in a 1:1 ratio in diethyl ether or toluene gave the respective *closo*-carboranylphosphines [3,11]. The general reaction is given in Scheme 1.

In this paper, we report the synthesis of three new *closo*-carboranylphosphines: 1-diethylphosphino-2-phenyl-1,2-dicarba-*closo*-dodecaborane (**1**), 1-diethylphosphino-1,2-dicarba-*closo*-dodecaborane (**2**) and 1-diisopropylphosphino-1,2-dicarba-*closo*-dodecaborane (**3**), using the same general method outlined in Scheme 1. The starting reagents are the phenyl-*o*-carborane and *o*-carborane, respectively. Compounds were characterized by elemental analysis and NMR spectroscopy, corroborating the formation of the expected compounds.

All these *closo*-carboranylphosphines studied belong to one of two types of tertiary phosphines, P(L)R$_2$ or P(L)$_2$R (see Fig. 1), where the phosphorus atom is bonded to R (alkyl or aryl groups), and L (a *closo* carborane cluster). The L group is 1-yl-2-R′-1,2-C$_2$B$_{10}$H$_{10}$, being R′ = H, Ph or Me. The phosphines studied and their abbreviations are listed in Table 1.

The interest to obtain chiral compounds with bulky groups for their application in asymmetric catalysis led us to prepare ligands which carry the chiral center at the phosphorus atom. Thus it was planned to have three distinct substituents at P. The intermediate compound required to have a reactive P–Cl bond as a possible group on P. The first compound we aimed at was 1-PClPh-2-Ph-1,2-C$_2$B$_{10}$H$_{10}$ (**4**). The reaction of 1-Li-2-Ph-1,2-C$_2$B$_{10}$H$_{11}$ with PCl$_2$Ph in a 1:1 molar ratio permitted the isolation of this product [12]. Spectroscopic data, elemental analysis and mass spectra showed the presence of a chlorine atom in the molecule, the formula of which corresponded to compound **4**. When a similar reaction was carried out using 1-Li-2-Me-1,2-C$_2$B$_{10}$H$_{11}$ with PCl$_2$Ph in a 1:1 molar ratio, 1-PClPh-2-Me-1,2-C$_2$B$_{10}$H$_{10}$ (**5**) was obtained, as expected [12a]; however, a larger quantity of a second product was also obtained. The formation of **5** was corroborated by a

Table 1
Complete formulae and abbreviations for the *closo*-carboranylphosphines, and ^{31}P chemical shifts (ppm) for the *closo*-carboranylphosphines

Ligands	Compound abbreviation	$\delta(^{31}P)$
1-PPh$_2$-1,2-C$_2$B$_{10}$H$_{11}$	P(L1)Ph$_2$ [a]	25.6
1-PEt$_2$-1,2-C$_2$B$_{10}$H$_{11}$	P(L1)Et$_2$	23.7
1-P(^{i}Pr)$_2$-1,2-C$_2$B$_{10}$H$_{11}$	P(L1)(^{i}Pr)$_2$	54.2
1-PPh$_2$-2-Ph-1,2-C$_2$B$_{10}$H$_{10}$	P(L2)Ph$_2$ [b]	13.4
1-PEt$_2$-2-Ph-1,2-C$_2$B$_{10}$H$_{10}$	P(L2)Et$_2$	9.9
1-P(^{i}Pr)$_2$-2-Ph-1,2-C$_2$B$_{10}$H$_{10}$	P(L2)(^{i}Pr)$_2$	38.5
1-PPh$_2$-2-Me-1,2-C$_2$B$_{10}$H$_{10}$	P(L3)Ph$_2$ [c]	11.0
1-Et$_2$-2-Me-1,2-C$_2$B$_{10}$H$_{10}$	P(L3)Et$_2$	5.4
1-P(^{i}Pr)$_2$-2-Me-1,2-C$_2$B$_{10}$H$_{10}$	P(L3)(^{i}Pr)$_2$	33.8
1-PPh(L3)-2-Me-1,2-C$_2$B$_{10}$H$_{10}$	P(L3)$_2$Ph	29.5

[a] L1 = 1-yl-1,2-dicarba-*closo*-dodecaborane.
[b] L2 = 1-yl-2-phenyl-1,2-dicarba-*closo*-dodecaborane.
[c] L3 = 1-yl-2-methyl-1,2-dicarba-*closo*-dodecaborane.

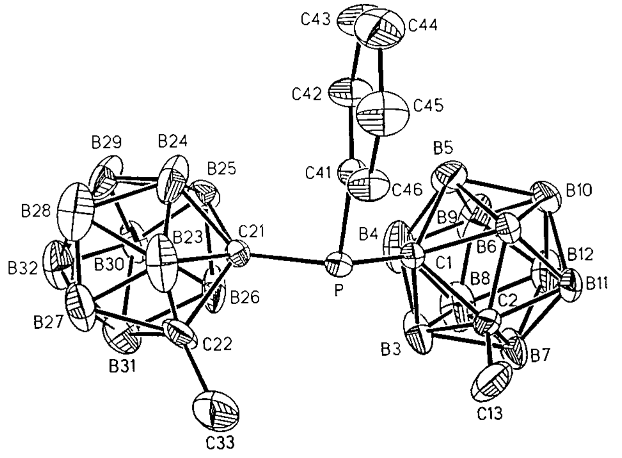


Fig. 2. Perspective drawing of bis[1-yl-(2-methyl-1,2-dicarba-*closo*-dodecaborane)]phenylphosphine (**6**). Displacement ellipsoids are drawn at the 20% probability.

resonance at 82.3 ppm, and the major product showed a resonance at 29.5 ppm in the $^{31}P\{^1H\}$-NMR spectrum. This compound corresponded to the previously described bis(1-yl-2-methyl-1,2-dicarba-*closo*-dodecaborane)phenylphosphine (**6**) [3d]. The molecular structure of **6** has been confirmed by X-ray diffraction (Fig. 2) and is described in the following section.

To produce a fully substituted *o*-carboranylphosphine similar to PPh_3, the reaction of 1-Li-2-Me-1,2-C_2B_{10}H10 with PCl_3 was performed. The result was, however, not the expected one, probably due to the larger steric effect of the methyl-*o*-carboranyl versus the phenyl moiety.

2.2. Molecular structure of bis(1-yl-2-methyl-1,2-dicarba-closo-dodecaborane)phenylphosphine (6)

A single-crystal structure analysis of bis(1-yl-2-methyl-1,2-dicarba-*closo*-dodecaborane)phenylphosphine (**6**) confirmed that the phosphorus atom is connected to two carborane cages through cage carbons, and one phenyl group. Rotations of the cages around the P–C(cage) bonds with respect to the phenyl group are mutually different, and thus the molecule has a *C*1 symmetry. The P–C(phenyl) and P–C(cage) distances are close to the corresponding values normally observed and sum of the bond angles at P is 318.4°. Selected bond lengths and angles for compound **6** are listed in Table 4.

2.3. The cluster influence on the chemical behavior and ^{31}P-NMR chemical shifts in closo-carboranylphosphine series

The behavior of the *closo*-carboranylphosphines towards partial degradation, their chemical stability and the difficulty to coordinate to metal evidenced notable influence of the *closo* cluster on the P atom.

1. An attempt to produce partial degradation of the *closo*-carboranylphosphines using the well-established procedure [13] with alkoxide did not produce the expected new *nido* species, but yielded 7,8-dicarba-*nido*-undecaborate(1-) by C–P bond cleavage. On the other hand, (i) the reaction carried out in refluxing ethanol yielded the *closo*-carboranylphosphines unaltered, and (ii) the degradation process with piperidine–toluene [14] using a 1:4 ratio of *closo*-carboranylphosphines to piperidine at 20°C did not produce the expected *nido*-carboranylphosphines; instead the unattacked *closo* species were recovered. Boron removal (partial degradation) with C–P bond retention was successfully obtained in the reaction of 1-PPh_2-2-Me-1,2-$C_2B_{10}H_{10}$ with piperidine in toluene in a 1:50 ratio. The yield was 99% [3d].
2. In contrast to other common phosphines, *closo*-carboranylphosphine derivatives present a high stability both in solid state and in solution, in the presence of oxygen, alcohols and acids.
3. The *closo*-carboranylphosphines do not react in ethanol at reflux with some transition-metal phosphine complexes, such as Pd(II), Cu(I), Au(I), Rh(I) and Ru(II), as *nido*-carboranylphosphines do [15].

These facts indicated that the nature of the *closo* cluster must influence the chemical behavior of the compounds, and this might also be reflected in the ^{31}P chemical shifts.

Table 1 shows the ^{31}P chemical shift of these compounds which appear in the region between δ $+5$ and $+55$. The chemical shifts in the $^{31}P\{^1H\}$-NMR spectra are related to shielding (σ) by the electron cloud around the phosphorus nucleus [16]. Usually the contributions to σ for a nucleus are considered only for the electrons immediately neighboring that nucleus. The magnitude of σ_p (the paramagnetic contribution) is determined by factors such as bond angles and bond order. The ^{31}P chemical shift will thus be affected by changes in bond overlap and hybridization, changes in atomic charges, as well as changes in ΔE (energy separation between ground and relevant excited states of the molecule). So, for small molecules in solution, shifts are determined by the bond geometry, the electronegativity of the substituents and the relative amount of π bonding of the phosphorus atom [17].

For primary, secondary and tertiary phosphines, Grim and McFarlane [18a], Maier [19], and Fluck and Lorenz [20] succeeded in producing empirical equations that allow calculation of the chemical shifts to within 1–2 ppm. The ^{31}P chemical shifts (δ_P) for tertiary phosphines (PR_3, PR_2R' or $PRR'R''$) are given in Eq. (1):

$$\delta_P = -62 + \Sigma(\sigma_P)_R \tag{1}$$

$(\sigma_P)_R$ is a constant that represents the contribution to the ^{31}P chemical shift of each substituent bonded to the phosphorus atom and are assigned to and characteristic of the various ligands. Some of the additive constants $(\sigma_p)_R$ are given in Table 2. In such composite additive constants, electronegativity, bond angle (including α-, β- and γ-effect parameters), and even π-electron overlap effects cannot be separated.

According to Eq. (1), the phosphorus chemical shift can be calculated if $(\sigma_p)_R$ values of the three substituents in the tertiary phosphines are known.

Once the experimental δ_P for each *closo*-carboranylphosphine ligand is known, it is possible to calculate the empirical $(\sigma_p)_L$ contribution by applying Eq. (1) and the tabulated data.

Table 2 contains the contribution values found for the 1-yl-1,2-dicarba-*closo*-dodecaborane (L1), 1-yl-2-phenyl-1,2-dicarba-*closo*-dodecaborane (L2) and 1-yl-2-methyl-1,2-dicarba-*closo*-dodecaborane (L3) in their different *closo*-carboranylphosphine derivatives along with the average $(\sigma_p)_L$ value obtained. These results indicate that the L1 group displays the higher contribution to the ^{31}P chemical shift (+ 57.2 ppm), followed by the L2 (+43.3 ppm) and finally the L3 moieties (+38.7 ppm). This would agree with the strong electron-acceptor character of *closo*-carborane clusters [21].

Table 3 presents the ^{31}P chemical shift for the three $P(L)Ph_2$ tertiary phosphines. In all compounds the ^{31}P resonances appear at higher frequency with respect to that of the PPh_3. This indicates that a *closo o*-carboranyl group displays stronger electron-acceptor character than a phenyl group and that the substituent group at the second cluster carbon tunes the $^{31}P\{^1H\}$ chemical shift. Furthermore, the $^{31}P\{^1H\}$ chemical shift is affected by the bond geometry and the relative amount of π bonding around the phosphorus atom. This should influence on the distance between the cluster carbon and the phosphorous atom. The calculated values $(\sigma_P)_L$ for the *o*-carborane derivatives indicate that π bonding character around the phosphorus atom decreases when the H on the cluster's second carbon is replaced by a phenyl group and decreases even more when the H is replaced by a methyl group. These results are in accord with the observed $C_{cluster}$–P distances: 1.871(6) when R = H [22], 1.876(5) when R = Ph [23] and 1.884(4) when R = Me [24].

Table 2
Calculated values of the *closo*-carborane cluster contribution ($(\sigma_P)_L$) to the ^{31}P chemical shift (δ (^{31}P), in ppm)

Compound	R	$(\sigma_P)_R$	δ (^{31}P)	$(\sigma_P)_L$	$(\sigma_P)_L$ average
$P(L1)Ph_2$	Ph	18	25.6	51.6	
$P(L1)Et_2$	Et	14	23.7	57.7	
$P(L1)(^iPr)_2$	^iPr	27	54.2	62.2	
					57.2
$P(L2)Ph_2$	Ph	18	13.4	39.4	
$P(L2)Et_2$	Et	14	9.9	43.9	
$P(L2)(^iPr)_2$	^iPr	27	38.5	46.5	
					43.3
$P(L3)Ph_2$	Ph	18	11.0	37.0	
$P(L3)Et_2$	Et	14	5.4	39.4	
$P(L3)(^iPr)_2$	^iPr	27	33.8	41.8	
$P(L3)_2Ph$	Ph	18	29.5	36.8	
					38.7

Table 3
^{31}P Chemical shifts (in ppm), distances between the cluster carbon C(1) atom and the *exo*-cluster P atom (in Å) and coupling constants, in absolute values, between the P and C(1) atoms (in Hz)

Compound	$\delta(^{31}P)$	$(\sigma_P)_L$	d(C1–P)	^1J(P, C(1))
$P(L1)Ph_2$	25.6	57.1	1.871(6)	76.3
$P(L2)Ph_2$	13.4	43.3	1.876(5)	73.0
$P(L3)Ph_2$	11.0	38.7	1.884(4)	34.9
PPh_3	−8	18	1.834(2)	11.1

When one of the substituents at the phosphorus becomes more electron-withdrawing, such as the *o*-carborane cluster, it causes back-donation of the lone pair of electrons on P to the cluster through the carbon atom. The data in Table 3 agree very well with the former explanation, with the exception of the short C(1)–P distances observed in PPh_3. In this case the lower steric volume of the aryl group could account for this singularity.

To conclude, the cluster influence on the phosphorus atom causes changes in both the chemical shift and the chemical properties, as it was indicated before. This accounts for the high stability in solid state and solu-

Table 4
Selected bond lengths (Å) and angles (°) for compound **6** with estimated S.D.s in parentheses

Bond lengths			
P–C41	1.801(5)	C2–C13	1.537(9)
P–C21	1.865(5)	C21–C22	1.675(7)
P–C1	1.879(5)	C22–C33	1.491(10)
C1–C2	1.716(7)		
Bond angles			
C41–P–C21	103.8(2)	B25–C21–P	133.2(4)
C41–P–C1	106.0(2)	C22–C21–P	113.8(3)
C21–P–C1	108.6(2)	B26–C21–P	125.4(4)
B4–C1–P	132.6(4)	B24–C21–P	121.5(4)
B3–C1–P	114.7(4)	B23–C21–P	109.0(4)
B5–C1–P	129.2(4)	C33–C22–B23	115.1(7)
C2–C1–P	109.9(3)	C33–C22–C21	117.3(6)
B6–C1–P	112.2(3)	C33–C22–B27	123.0(6)
C13–C2–B7	121.5(5)	C33–C22–B31	121.7(7)
C13–C2–B3	118.7(5)	C33–C22–B26	122.0(6)
C13–C2–B6	113.5(5)	C42–C41–P	128.5(4)
C13–C2–B11	118.7(5)	C46–C41–P	114.1(4)
C13–C2–C1	118.4(4)		

tion, even under air. The electron-acceptor character of the cluster induces lower charge density at the phosphorus atom, its ^{31}P resonance is shifted to lower field in the NMR spectra, and in turn, decreases the pK_a, which leads to a lower coordinating ability towards transition metals, as it has been shown in these *closo*-carboranylphosphines [25].

3. Experimental

3.1. Instrumentation

Microanalyses were performed in our analytical laboratory using a Carlo Erba EA1108 microanalyser. IR spectra (ν, cm^{-1}; KBr pellets) were obtained on a Nicolet 710-FT spectrophotometer. The ^{1}H-NMR (300.13 MHz), ^{11}B-NMR (96.29 MHz), ^{31}P{^{1}H}-NMR (121.4 MHz) and ^{13}C{^{1}H}(75.47 MHz) spectra were obtained on a Bruker ARX 300 instrument. All NMR measurements were performed in deuterated solvents at 22°C. The ^{11}B-NMR shifts are referenced to external $BF_3·O(Et)_2$, while the δ ^{1}H and δ ^{13}C data are referenced to TMS and the δ ^{31}P data to the 85% H_3PO_4, positive values of the shifts, according to the IUPAC convention, are due to high frequency.

3.2. Materials

Before use, 1-methyl-*o*-carborane, *o*-carborane and decaborane (Katchem Ltd., Prague) were sublimed under high vacuum. Phenyl-*o*-carborane [26] was prepared from decaborane according to the method reported previously. 1-Diphenylphosphino-1,2-dicarba-*closo*-dodecaborane [22], 1-diphenylphosphino-2-methyl-1,2-dicarba-*closo*-dodecaborane [24], 1-diisopropylphosphino-2-methyl-2-dicarba-*closo*-dodecaborane [27], 1-diethylphosphino-2-methyl-1,2-dicarba-*closo*-dodecaborane and bis[2-μ-(1-methyl-1,2-dicarba-*closo*-dodecaborane(12))]phenylphosphine [3d], were prepared according to the literature. 1-Diisopropylphosphino-2-phenyl-1,2-dicarba-*closo*-dodecaborane [28] and 1-diphenylphosphino-2-phenyl-1,2-dicarba-*closo*-dodecaborane [29] were prepared from phenyl-*o*-carborane. A 1.6 M solution of *n*-butyllithium in hexane from Fluka, chlorodiphenylphosphine, chlorodiisopropylphosphine, chlorodiethylphosphine, and dichlorophenylphosphine from Aldrich were used as purchased. Unless mentioned elsewhere, the reactions are carried out under N_2 atmosphere and used solvents were oxygen free and dry.

3.3. Synthesis of 1-diethylphosphino-2-phenyl-1,2-dicarba-closo-dodecaborane (**1**)

To a three-necked round-bottom flask (250 ml) containing diethyl ether (50 ml) was added phenyl-*o*-carborane (1.0 g, 4.5 mmol). The mixture was cooled (ice-water) during the addition (10 min) of *n*-butyllithium (3 ml, 4.5 mmol). After stirring for 1 h at the ice-water temperature, chlorodiethylphosphine (0.55 ml, 4.5 mmol) was added dropwise over a 30 min period. The mixture was refluxed for 2 h and stirred for a further 4 days at room temperature (r.t.). The solution was quenched with water (40 ml) and transferred to a separating funnel. The layers were separated and the aqueous layer was extracted with ethyl ether. The combined organic layers were then dried over anhydrous $MgSO_4$ and concentrated in vacuum. The residue was extracted with petroleum ether (15 ml). Evaporation of the solvent yields a white solid (1.15 g, 82%). Anal. Calc. for $C_{12}H_{25}B_{10}P$ (%): C, 46.73; H, 8.17. Found: C, 47.46; H, 7.93. IR, ν (cm^{-1}): 2966, 2931, 2875 (C–H); 2600, 2572 (B–H). ^{1}H-NMR ($(CD_3)_2CO$, δ, ppm): 0.98 (dt, 6 H, CH_3, ^3J(P, H) = 17 Hz, ^3J(H, H) = 8 Hz); 1.64 (m, 4 H, CH_2); 7.40–7.67 (m, 5 H, C_6H_5). ^{11}B-NMR ($(CD_3)_2CO$, δ, ppm): −0.6 (d, 1 B, ^1J(B, H) = 147 Hz); −3.9 (d, 1 B, ^1J(B, H) = 147 Hz); −9.2 (d, 4 B, ^1J(B, H) = 167 Hz); −10.8 (d, 2 B, ^1J(B, H) = 189 Hz); −11.9 (d, 2 B, ^1J(B, H) = 158 Hz). ^{31}P{^{1}H}-NMR ($(CD_3)_2CO$, δ, ppm): 9.9 (s, $P(Et)_2$). ^{13}C{^{1}H}-NMR ($(CD_3)_2CO$, δ, ppm): 10.6 (d, CH_3, ^2J(P, C) = 21 Hz); 21.5 (d, CH_2, ^1J(P, C) = 18 Hz); 84.5 (d, Cc, ^1J(P, C) = 74 Hz); 129.4, (d, ^3J(P, C) = 4 Hz); 131.5; 131.9; 132.4 (C_6H_5).

3.4. Synthesis of 1-diethylphosphino-1,2-dicarba-closo-dodecaborane (**2**)

To a three-necked round-bottom flask (250 ml) containing a 1:1 mixture of toluene–monoglime (60 ml) was added *o*-carborane (1.5 g, 10.4 mmol). The mixture was cooled (ice-water) during the addition (10 min) of *n*-butyllithium (6.5 ml, 10.4 mmol). After stirring for 15 min at the ice-water temperature, chlorodiethylphosphine (1.30 g, 10.4 mmol) was added dropwise within 30 min. The mixture was stirred for 30 min at 0°C, then 2 h at r.t. and refluxed for 2 h. The solvent was removed under vacuum, and the residue was extracted with petroleum ether (15 ml). Evaporation of the solvent yielded a colorless oil which solidified at −10°C (1.3 g, 54%). Anal. Calc. for $C_6H_{21}B_{10}P$ (%): C, 31.04; H, 9.05. Found: C, 30.97; H, 9.10. IR, ν (cm^{-1}): 2966, 2931, 2875 (C–H); 2572 (B–H). ^{1}H-NMR ($CDCl_3$, δ, ppm): 1.16 (dt, 6 H, CH_3, ^3J(P, H) = 17 Hz, ^3J(H, H) = 7 Hz); 1.67 (m, 4 H, CH_2); 3.56 (s, 1 H, Cc–H). ^{11}B{^{1}H}-NMR ($CDCl_3$, δ, ppm): −3.7 (s, 2 B); −9.5 (s, 2 B); −14.4 (s, 6 B). ^{31}P{^{1}H}-NMR ($CDCl_3$, δ, ppm): 23.7 (s, $P(Et)_2$. ^{13}C{^{1}H}-NMR ($CDCl_3$, δ, ppm): 10.4 (d, CH_3, ^2J(P, C) = 20 Hz); 21.2 (d, CH_2,

^1J(P, C) = 17 Hz); 65.1 (d, Cc, ^2J(C, P) = 22 Hz); 73.8 (d, Cc, ^1J(P, C) = 66 Hz).

3.5. Synthesis of 1-diisopropylphosphino-1,2-dicarba-closo-dodecaborane (**3**)

The same procedure was used as before, using 1.5 g (10.4 mmol) of *o*-carborane, 6.5 ml (10.4 mmol) of *n*-butyllithium and chlorodiisopropylphosphine (1.7 ml, 10.4 mmol). The mixture was stirred for 30 min at 0°C, and a further 3 days at r.t. The solvent was removed under vacuum and the residue was extracted with petroleum ether (15 ml). Evaporation of the solvent gave a colorless oil which solidified at −10°C (1.6 g, 42%). Anal. Calc. for $C_8H_{25}B_{10}P$ (%): C, 36.93; H, 9.62. Found: C, 37.02; H, 9.59. IR, ν (cm^{-1}): 2952, 2924, 2868 (C–H); 2579 (B–H). ^{1}H-NMR (CDCl$_3$, δ, ppm): 1.24 (dd, 6 H, CH$_3$, ^3J(P, H) = 17 Hz, ^3J(H, H) = 7 Hz); 1.29 (dd, 6 H, CH$_3$, ^3J(P, H) = 23 Hz, ^3J(H, H) = 7 Hz), 2.16 (m, 2 H, CH); 3.56 (s, 1 H, Cc–H). ^{11}B-NMR (CDCl$_3$, δ, ppm): −1.7 (d, 2 B, ^1J(B, H) = 149 Hz); −8.1 (d, 2 B, ^1J(B, H) = 149 Hz); −10.9 (d, 2 B, ^1J(B, H) = 153 Hz); −12.7 (d, 4 B, ^1J(B, H) = 171 Hz). ^{31}P{^{1}H}-NMR (CDCl$_3$, δ, ppm): 54.2 (s, P(^{i}Pr)$_2$). ^{13}C{^{1}H}-NMR (CDCl$_3$, δ, ppm): 19.2 (d, CH$_3$, ^2J(P, C) = 9 Hz); 22.6 (d, CH$_3$, ^1J(P, C) = 24 Hz); 26.6 (d, CH, ^1J(P, C) = 22 Hz); 65.1 (d, (Cc), ^2J(P, C) = 22 Hz); 74.3 d, (Cc), ^1J(P, C) = 80 Hz.

3.6. Synthesis of 1-chlorophenylphosphino-2-phenyl-1,2-dicarba-closo-dodecaborane (**4**)

To a three-necked round-bottom flask (250 ml) containing diethyl ether (30 ml) was added phenyl-*o*-carborane (0.5 g, 2.3 mmol). The mixture was cooled (ice-water) during the addition of *n*-butyllithium (1.4 ml, 2.3 mmol). After stirring for 30 min at the ice-water temperature, dichlorophenylphosphine (0.15 ml, 1.3 mmol) was added dropwise for 30 min. The mixture was stirred for 1 h at that temperature, 15 min at r.t., refluxed for 2 h and stirred for a further 11 h at r.t. The solution was quenched with water (30 ml) and transferred to a separator funnel. The layers were separated and the aqueous layer was extracted with additional ethyl ether. The combined filtrates were then dried over anhydrous MgSO$_4$ and concentrated in vacuum. The residue was extracted with petroleum ether (15 ml) to yield a white solid (120 mg, 15%). Anal. Calc. for $C_{14}H_{20}B_{10}ClP$ (%): C, 46.34; H, 5.56. Found: C, 46.00; H, 5.95. IR, ν (cm^{-1}): 2657, 2621, 2600, 2572 (B–H). ^{1}H-NMR (CDCl$_3$, δ, ppm): 7.28–7.69 (m, C$_6$H$_5$). ^{11}B-NMR (CDCl$_3$, δ, ppm): −0.7 (d, 1 B, ^1J(B, H) = 146 Hz); −3.3 (d, 1 B, ^1J(B, H) = 148 Hz); −8.9 (d, 6 B, ^1J(B, H) = 151 Hz); −11.4 (d, 2 B, ^1J(B, H) = 169 Hz). ^{31}P{^{1}H}-NMR (CDCl$_3$, δ, ppm): 80.9 (s, P(ClPh)). ^{13}C{^{1}H}-NMR (CDCl$_3$, δ, ppm): 84.5, (Cc), 86.2 (Cc), 128.3–132.5 (C$_6$H$_5$). MS: *m*/*z* 362 (100%, M$^+$).

3.7. X-ray studies

Several attempts to obtain good single crystals were made, but without success. Data were collected at 193 and 293 K, and because the latter data were slightly better, the present results are based on those. As reflection power was poor only limited data were collected at high reflection angles.

Crystal data, data collection and refinement. $C_{12}H_{31}B_{20}P$, $M_r = 422.54$, monoclinic, space group $P2_1/c$ (no. 14), $a = 11.716(7)$, $b = 14.306(7)$, $c = 15.183(5)$ Å, $\beta = 94.11(3)°$, $V = 2538(2)$ Å^3, $Z = 4$, $D_{calc} = 1.106$ g cm^{-3}, $F(000) = 872$. A colorless transparent crystal of dimensions 0.36 × 0.30 × 0.16 mm (grown from a 1:1 mixture of ethyl ether–petroleum ether (v:v) by slow evaporation) was measured at 293 K on a Rigaku AFC5S diffractometer using monochromatized Mo–K$_\alpha$ radiation ($\lambda = 0.71069$ Å). The cell parameters were determined from 25 reflections in the range 10.2–14.5° θ range. The intensities of reflections were measured by the ω–2θ scan (h = 0–12; k = 0–15; l = −16–16); $\sin\theta/\lambda_{max} = 0.541$ Å^{-1}. A total of 3504 reflections were measured, giving 3314 unique reflections ($R_{int} = 0.0919$) and of those 1556 had $I > 2\sigma(I)$. The data were corrected for Lorentz and polarization effects. An absorption correction based on 3ψ ($T = 0.9614$–0.9826) was also applied. Three standard reflections monitored after every 150 reflections did not show any significant variation. The data reduction was done using TEXSAN [30].

The structure was solved and refined with the SHELX-97 program package [31]. Non-hydrogen atoms were refined with anisotropic displacement parameters, but for methyl carbons and some atoms of the carborane cages ISOR restraint was used. Hydrogen atoms were included in the calculations at fixed distances from their host atoms and treated as riding atoms using the SHELX-97 default parameters. The structure was refined against F^2 to $R_1 = 0.1011$ and $wR_2 = 0.2515$; 300 parameters; $S = 1.098$. Minimum and maximum residual electron densities were −0.335 and 0.850 e Å^{-3}, respectively.

4. Supplementary material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Data Centre as supplementary publication no. CCDC-113901. Copies of the data can be obtained free of charge on application to CCDC, e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

This work was supported by CIRIT/Project QFN95-4721 and by DGICYT/Project PB94-0226.

References

[1] M.F. Hawthorne, Pure Appl. Chem. 63 (1991) 327 and refs. cited therein.

[2] (a) F. Teixidor, A.M. Romerosa, J. Rius, C. Miravitlles, J. Casabó, C. Viñas, E. Sanchez, J. Chem. Soc. Dalton Trans. (1990) 525. (b) F. Teixidor, C. Viñas, J. Rius, C. Miravitlles, J. Casabó, Inorg. Chem. 29 (1990) 149.

[3] (a) L.I. Zakharkin, M.N. Zhubekova, A.V. Kazantsev, Zh. Obshch. Khim. 42 (1972) 1024. (b) N.N. Godovikov, A.N. Degtyarev, V.I. Bregadze, M.I. Kabachnik, Izv. Akad. Nauk SSSR Ser. Khim. 11 (1975) 2568. (c) W.E. Hill, L.M. Silva-Triviño, Inorg. Chem. 18(2) (1979) 361. (d) F. Teixidor, C. Viñas, M.M. Abad, R. Núñez, R. Kivekäs, R. Sillanpää, J. Organomet. Chem. 503 (1995)193.

[4] (a) R.N. Grimes, Carboranes, Academic Press, New York, 1970. (b) R.N. Grimes, Metal Interactions with Boron Clusters, Plenum, New York, 1982. (c) G.A. Olah, G.K.S. Prakash, R.E. Williams, L.E. Field, K. Wade, Hypercarbon Chemistry, Wiley, New York, 1987.

[5] (a) S. Hermánek, J. Plesek, V. Gregor, B. Stibr, J. Chem. Soc. Chem. Commun. (1977) 561. (b) S. Hermánek, Chem. Rev. 92 (1992) 325. (c) S. Hermánek, J. Machécek, J. Fusek, V. Blechta, The Borane, Carborane, Carbocation Continuum, Wiley, New York, 1999, p. 367.

[6] F. Teixidor, C. Viñas, R.W. Rudolph, Inorg. Chem. 25 (1986) 3339.

[7] M.A. Fox, J.A.H. Macbride, R.J. Peace, K Wade, J. Chem. Soc. Dalton Trans. (1998) 401.

[8] (a) J. Jaballas, T. Onak, J. Organomet. Chem. 550 (1998) 101. (b) M. Hofman, M.A. Fox, R. Greatrex, R.E. Williams, P.V. Schleyer, J. Organomet. Chem. 550 (1998) 331. (c) M.B. Ezhova, H.M. Zhang, J.A. Maguire, N.S. Hosmane, J. Organomet. Chem. 550 (1998) 409. (d) J. Plesek, B. Stibr, D. Hnyk, T. Jelinek, S. Hermánek, J.D. Kennedy, M. Hofman, P.V. Schleyer, Inorg. Chem. 37 (1998) 3902. (e) J. Holub, B. Stibr, D. Hnyk, J. Fusek, I. Cisarova, F. Teixidor, C. Viñas, Z. Plzak, P.V. Schleyer, J. Am. Chem. Soc. 119 (1997) 7750. (f) X.M. Yang, H.J. Jiao, P.V. Schleyer, Inorg. Chem. 36 (1997) 4897.

[9] L.D. Quin, J.G. Verkade, Phosphorus-31 NMR. Spectral Properties in Compound Characterization and Structural Analysis, VCH, Denton, TX, 1994.

[10] J.H. Nelson, Coord. Chem. Rev. 139 (1995) 245.

[11] H. Beall, Boron Hydride Chemistry, Academic Press, New York, 1975 (Chapter 9).

[12] (a) A.V. Kazantsev, M.N. Zhubekova, Zh. Obshch. Khim. 41(9) (1971) 2027. (b) V.P. Balema, S. Blaurock, E. Hey-Hawkins, Z. Naturforsch. 53b (1998) 1273.

[13] (a) R.A. Wiesboeck, M.F. Hawthorne, J. Am. Chem. Soc. 86 (1964) 1642. (b) P.M. Garret, F.N. Tebbe, M.F. Hawthorne, J. Am. Chem. Soc. 86 (1964) 5016. (c) M.F. Hawthorne, D.C. Young, P.M. Garret, D.A. Owen, S.G. Schwerin, F.N. Tebbe, P.M. Wegner, J. Am. Chem Soc. 90 (1968) 862.

[14] L.I. Zakharkin, V.N. Kalinin, Tetrahedron Lett. (1965) 407.

[15] (a) C. Viñas, R. Núñez, F. Teixidor, R. Kivekäs, R. Sillanpää, Organometallics 15 (1996) 3850. (b) C. Viñas, M.A. Flores, R. Núñez, F. Teixidor, R. Kivekäs, R. Sillanpää, Organometallics 17 (1998) 2278.

[16] D.G. Gorenstein, Phosphorus-31 NMR. Principles and Applications, Academic Press, Orlando, FL, 1984, p. 23.

[17] (a) J.H. Letcher, J.R. Van Wazer, Top. Phosphorus Chem. 5 (1967) 75. (b) J.R. Van Wazer, J.H. Letcher, Top. Phosphorus Chem. 5 (1967) 192.

[18] (a) S.O. Grim, W. McFarlane, Nature 208 (1995) 995. (b) J.G. Verkade, L.D. Quin, Methods in Stereochemical Analysis, vol. 8, VCH, Deerfield Beach, FL, 1987, p. 89.

[19] L. Maier, Helv. Chim. Acta 49 (1966) 1718.

[20] E. Fluck, J. Lorenz, Z. Naturforsch. 22b (1967) 1095.

[21] V.I. Bregadze, Chem. Rev. 92 (1992) 209.

[22] R. Kivekäs, F. Teixidor, C. Viñas, R. Nuñez, Acta Crystallogr. Sect. C51 (1995) 1868.

[23] M.A. McWhannell, G.M. Rosair, A.J. Welch, F. Teixidor, C. Viñas, Acta Crystallogr. Sect. C52 (1996) 3135.

[24] R. Kivekäs, R. Sillanpää, F. Teixidor, C. Viñas, R. Nuñez, Acta Crystallogr. Sect. C52 (1994) 2027.

[25] (a) C.A. Tolman, Chem. Rev. 77 (1977) 313. (b) C.A. McAuliffe, Comprehensive Coordination Chemistry, vol. 2, Pergamon, Oxford, 1987, p. 989. (c) R.G. Goel, T. Allman, Can. J. Chem. 60 (1982) 716. (d) M. Wada, S. Higashizaki, A. Tsuboi, J. Chem. Res. (S) (1985) 38.

[26] (a) M.M. Fein, J.E. Paustian, J. Bobinski, B.M. Lichstein, N. Mayes, N.N. Schwartz, M.S. Cohen, Inorg. Chem. 2 (1963) 1111. (b) Z.G. Lewis, A.J. Welch, Acta Crystallogr. Sect. C49 (1993) 705.

[27] R. Kivekäs, R. Sillanpää, F. Teixidor, C. Viñas, R. Núñez, Acta Crystallogr. Sect. C51 (1995) 1864.

[28] R. Sillanpää, R. Kivekäs, F. Teixidor, C. Viñas, R. Núñez, Acta Crystallogr. Sect. C52 (1996) 2223.

[29] L.I. Zakharkin, M.N. Zhubekova, A.V. Kazantsev, Zh. Obshch. Khim. 5 (1972) 42.

[30] TEXSAN, Molecular Structure Corporation, Version 5.0 MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA, 1989.

[31] G.M. Sheldrick, SHELX-97, University of Göttingen, Germany, 1997.