Synthesis and Structural Aspects of Phosphane – Boranes Derived from Tris(diphenylphosphino)methane, $HC(PPh_2)_3$

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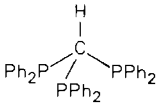
The structure of tris(diphenylphosphino)methane, $HC(PPh_2)_3$ (**1**), has been determined by X-ray diffraction. The molecules have approximate C_3 symmetry with the lone pairs at the three phosphorus atoms in an "*all-trans*" orientation. Variable-temperature NMR experiments (+35 to −90°C in CH_2Cl_2) show free intramolecular motion in solution. The partially or fully borylated adducts $HC(PPh_2)_2[PPh_2(BH_3)]$ (**2**), $HC(PPh_2)[PPh_2(BH_3)]_2$ (**3**), and $HC[PPh_2(BH_3)]_3$ (**4**) have been prepared from **1** and THF · BH_3 or $Me_2S \cdot BH_3$. For **2** and **3** the internal rotation about the phosphorus-methine carbon bonds is also essentially unhindered, but has been shown to be restricted in **4** (E_a = 31.2 kJ/mol). The chemical shifts of the methine protons in these compounds can be calculated on the basis of a BH_3 substituent constant.

Polytertiary phosphanes are an important class of compounds for a number of reasons: 1) As ligands, they are powerful chelating systems for low-valent metals[1,2]. Through steric or electronic substituent effects, their geometry and donor properties can be tailored such that e. g. access to a reactive center is limited thus favoring certain substrates over their competitors. – Through this strategy, stereo- and regioselectivity has been accomplished for a number of stoichiometric or catalytic reactions[3]. A selection of substituents can be used for inducing either solubility in specific solvents or complete insolubility by anchoring at support materials. – 2) Polytertiary phosphanes are precursors for the corresponding open-chain or (poly)cyclic phosphonium salts, phosphane – boranes, oxides, sulfides etc., which can be transformed further, e. g. into phosphonium ylides, carbodiphosphoranes, and related compounds[4,5]. α,ω-Ditertiary phosphanes like bis(diphenylphosphino)methane ("dppm") or -ethane ("dppe", "diphos") and tris(diphenylphosphino)methane ("tdppm") (1), whose crystal structure is published in this paper, are particularly prominent examples[6].

The phosphane – borane derivatives of polytertiary phosphanes containing P – B bonds have attracted little attention despite the noteworthy properties of their simple prototypes R_3P-BH_3[7]. These compounds are remarkably inert owing to a reduction in polarity of their HB and PB structural elements. A series of phosphane – boranes derived from bis(diphenylphosphino)alkanes $(C_6H_5)_2P-[CH_2]_n-P(C_6H_5)_2$ with n = 1 to 4 have already been synthesized[8,9], but only bis(borane) adducts $[CH_2]_n\ [P(C_6H_5)_2BH_3]_2$ could be isolated, with the exception of bis(diphenylphosphino)methane, which is known to form also the monoborane derivative[10].

In the present study we report on the synthesis of the mono-, bis- and trisborane adducts of the tritertiary ligand tris(diphenylphosphino)methane (1). Compounds 2 and 3 are of considerable interest owing to their vacant donor sites, which allow selective coordination to metal centers. The reducing properties of the BH_3 group and the reversibility of their bonding can lead to attractive combinations for metal deposition or cluster formation.



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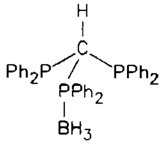

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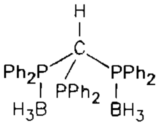

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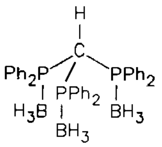

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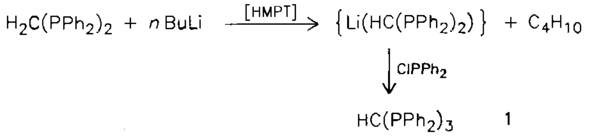
Purification, Properties, Spectroscopic Data and Crystal Structure of Tris(diphenylphosphino)methane (1)

The standard synthesis of **1** reported first by Issleib[11] uses bis(diphenylphosphino)methane (dppm) as the starting material.



$$H_2C(PPh_2)_2 + n\,BuLi \xrightarrow{[HMPT]} \{Li(HC(PPh_2)_2)\} + C_4H_{10} \xrightarrow{ClPPh_2} HC(PPh_2)_3 \quad 1$$

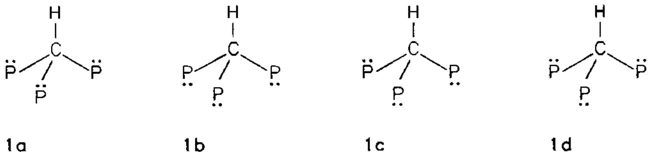
Treatment of dppm with n-butyllithium and subsequently with chlorodiphenylphosphane in benzene in the presence of hexamethylphosphoric triamide affords tris(diphenylphosphino)methane (1) in moderate yield (ca. 60%). The purity of the product is not always satisfactory[11], since separation from unreacted dppm presents a major problem, as noticeable e. g. from variations in the melting point.

Spectroscopically pure single crystal material has now been obtained by crystallization from hot ethanol on slow cooling to room temperature, as confirmed by a reproducible melting point as well as by IR, NMR, and mass spectral studies (see Experimental).

Pure **1** is only slowly oxidized in air, a great practical advantage over the peralkylated analogs $MeSi(P\textit{n}Bu_2)_3$[12] or $HC(PMe_2)_3$[13].

In solution, compound **1** has effective C_{3v} symmetry. At temperatures as low as $-90\,^{\circ}C$ neither the ^1H- and ^{13}C- nor ^{31}P-NMR spectra (of dichloromethane solutions) provide any evidence for inequivalence of the phenyl or the diphenylphosphino groups. This result is compatible with virtually free rotation of the Ph_2P groups about the P–CH bonds[14] and all P–Ph bonds. Models show, that fixed C_{3v} symmetrical conformations **1a**, **1b** are sterically impossible (Scheme 1). Free P–C bond rotation in **1** is at variance with findings for the trichalkogenides of tdppm, for which an unsymmetrical conformation (resembling formulae **1c**, **1d**) has been confirmed by NMR data for the solution state (A_2X spin systems for the ^{31}P nuclei in HC $(PXPh_2)_3$ at $-90\,^{\circ}C$ with X = O or S; see also below for the trisborane adduct) and for the crystal.

Scheme 1. Idealized conformations of $HC[P(C_6H_5)_2]_3$ (**1**) with phenyl groups omitted for clarity



1a 1b 1c 1d

The conformation of **1** in the solid state has now been determined by a single-crystal X-ray structure analysis. Compound **1** is shown to crystallize in the monoclinic space group *C*2/*c* (No. 15) with eight molecules in the unit cell (Figure 1). The structure of the individual tripod ligand **1**, which has no crystallgraphic symmetry, is presented in Figure 2.

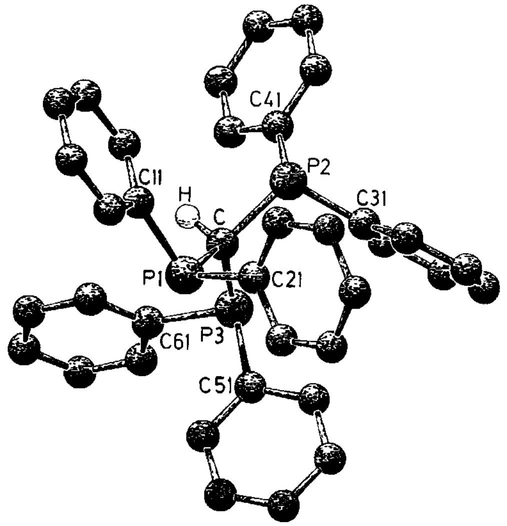


Figure 2. Molecular structure of $HC[P(C_6H_5)_2]_3$ (**1**)

Table 1. Selected interatomic distances [Å] and angles [°] in $HC[P(C_6H_5)_2]_3$ (**1**)

C-H	0.93(1)	C-P1	1.867(1)
C-P2	1.871(1)	C-P3	1.877(1)
P1-C11	1.836(1)	P1-C21	1.832(1)
P2-C31	1.835(1)	P2-C41	1.832(1)
P3-C51	1.841(1)	P3-C61	1.836(1)
H-C-P1	101.4(6)	H-C-P2	99.1(6)
H-C-P3	105.2(6)	P1-C-P2	115.15(6)
P1-C-P3	115.01(6)	P2-C-P3	117.40(6)

The P–C–P angles and the P–C distances agree with expectations based on standard data (Table 1). A comparison of the results with the molecular structure of tris(diphenylthiophosphinyl)methane (**5**) reveals differences[15]. In the free molecule **1** the lone pairs at P1, P2, and P3 are in an "*all-trans*" orientation, a good approximation to three-

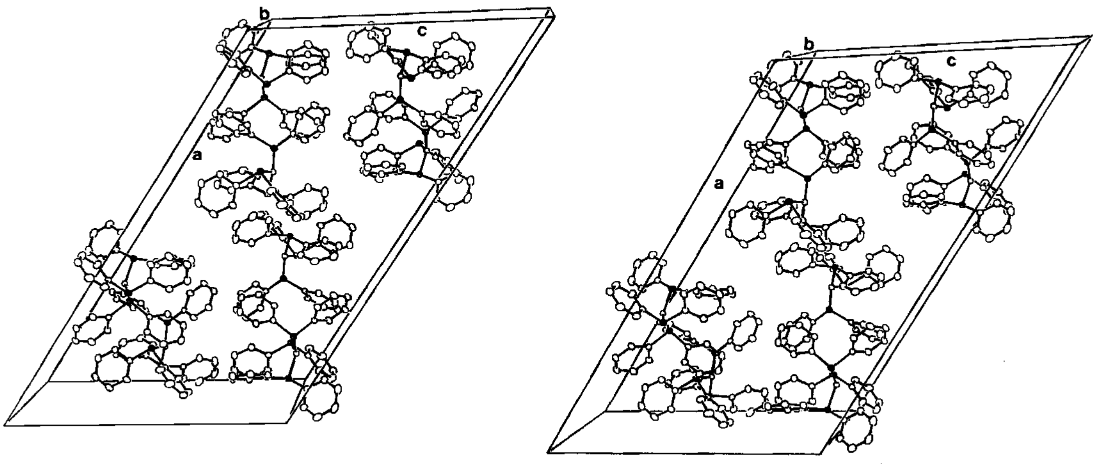


Figure 1. ORTEP stereoplot of the unit cell of $HC[P(C_6H_5)_2]_3$ (**1**)

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters for $HC[P(C_6H_5)_2]_3$ (1). Starred atoms (*) were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3) \cdot [a^2 \cdot \beta(1,1) + b^2 \cdot \beta(2,2) + c^2 \cdot \beta(3,3) + ab\cos(\gamma)\beta(1,2) + ac\cos(\beta)\beta(1,3) + bc\cos(\alpha)\beta(2,3)]$

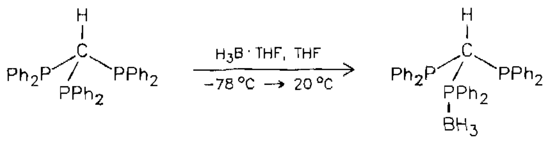
Atom	X/A	Y/B	Z/C	U(eq)
H	0.1355(5)	0.608(1)	0.0624(8)	0.007(5)*
C	0.1405(1)	0.6143(2)	0.114(1)	0.0424(5)
P1	0.07979(2)	0.67926(5)	0.08471(3)	0.0461(1)
P2	0.19541(2)	0.71450(5)	0.16526(3)	0.0441(1)
P3	0.15169(2)	0.46378(5)	0.15491(3)	0.0457(1)
C11	0.0646(1)	0.7764(2)	−0.0002(1)	0.0482(5)
C12	0.0877(1)	0.7813(2)	−0.0412(1)	0.0655(7)
C13	0.0700(1)	0.8525(2)	−0.1088(1)	0.0859(8)
C14	0.0293(1)	0.9197(3)	−0.1359(1)	0.0951(9)
C15	0.0057(1)	0.9170(3)	−0.0969(1)	0.0947(9)
C16	0.0227(1)	0.8447(2)	−0.0300(1)	0.0754(8)
C21	0.0967(1)	0.7831(2)	0.1667(1)	0.0493(6)
C22	0.1153(1)	0.8935(2)	0.1718(1)	0.0591(6)
C23	0.1264(1)	0.9667(2)	0.2358(1)	0.0756(8)
C24	0.1177(1)	0.9313(3)	0.2937(1)	0.0912(8)
C25	0.0992(1)	0.8240(3)	0.2892(1)	0.0890(8)
C26	0.0882(1)	0.7517(2)	0.2258(1)	0.0652(7)
C31	0.2345(1)	0.6716(2)	0.2745(1)	0.0457(5)
C32	0.2350(1)	0.7453(2)	0.3307(1)	0.0585(6)
C33	0.2641(1)	0.7207(2)	0.4147(2)	0.0701(8)
C34	0.2925(1)	0.6227(2)	0.4431(1)	0.0709(8)
C35	0.2928(1)	0.5483(2)	0.3885(1)	0.0611(7)
C36	0.2641(1)	0.5733(2)	0.3046(1)	0.0515(6)
C41	0.2331(1)	0.6651(2)	0.1284(1)	0.0438(5)
C42	0.2739(1)	0.7335(2)	0.1499(1)	0.0570(6)
C43	0.3018(1)	0.7140(2)	0.1183(1)	0.0672(7)
C44	0.2891(1)	0.6262(2)	0.0629(1)	0.0636(7)
C45	0.2498(1)	0.5568(2)	0.0419(1)	0.0681(7)
C46	0.2222(1)	0.5743(2)	0.0747(1)	0.0610(6)
C51	0.1197(1)	0.4558(2)	0.2077(1)	0.0479(5)
C52	0.1453(1)	0.4958(2)	0.2888(1)	0.0640(7)
C53	0.1240(1)	0.4877(2)	0.3331(1)	0.0772(8)
C54	0.0774(1)	0.4380(2)	0.2983(1)	0.0783(8)
C55	0.0526(1)	0.3966(2)	0.2191(1)	0.0822(8)
C56	0.0730(1)	0.4064(2)	0.1737(1)	0.0662(7)
C61	0.1089(1)	0.3799(2)	0.0609(1)	0.0479(6)
C62	0.0718(1)	0.4220(2)	−0.0163(1)	0.0680(7)
C63	0.0425(1)	0.3494(2)	−0.0836(1)	0.0781(8)
C64	0.0494(1)	0.2332(2)	−0.0738(1)	0.0723(8)
C65	0.0857(1)	0.1901(2)	0.0020(1)	0.0824(8)
C66	0.1156(1)	0.2615(2)	0.0691(1)	0.0696(7)

fold symmetry. By contrast, the trisulfide **5** is approaching only C_s symmetry due to a *cis*-orientation of one of the $P(S)Ph_2$ ligands. The molecular packing in crystals of compound **1** features some intermolecular phenyl stacking interactions (Figure 1), but no other close contacts are discernable. In the crystals of the trisulfide **5**, *intra*molecular phenyl stacking is more prominent.

$HC[P(S)Ph_2]_3$ **5**

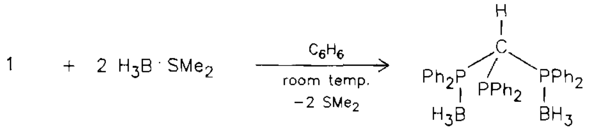
Partial Borane Adduct Formation (2, 3)

Treatment of tris(diphenylphosphino)methane (**1**) with the tetrahydrofuran adduct $H_3B{\cdot}THF$ in the molar ratio 1:2 in tetrahydrofuran in the temperature range from −78 °C to room temperature affords the *mono*-borane adduct **2** in 90% yield. Reaction of equimolar amounts of $H_3B{\cdot}THF$ with **1** under similar conditions leads to an equilibrium mixture of unreacted **1** and the monoborane adduct **2**.



1 2

Tetrahydrofuran thus appears to compete successfully with the phosphane donor centers for the BH_3 components. More efficient phosphane coordination can only be expected from a weaker auxiliary base. And in fact the synthesis of the bisborane adduct **3** can be accomplished by reaction of the dimethyl sulfide adduct $H_3B{\cdot}SMe_2$ with **1** in benzene in a molar ratio of 2:1 at room temperature in 75% yield. In agreement with these assumptions, compounds **2**–**4** loose BH_3 on heating in THF.

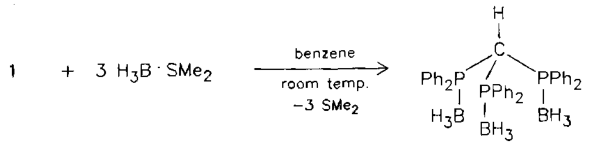


3

Compounds **2** and **3** are colorless solids, nearly insoluble in aromatic hydrocarbons and other nonpolar solvents, but readily soluble in halomethanes. Thermal decomposition is induced on melting (182 °C **2**, 192 °C **3**). The EI-mass spectra show the $M^+ - H_2$ ions. The infrared spectra exhibit the characteristic bands of the B—H symmetric and antisymmetric stretching vibrations at 2350—2450 cm^{-1}. In the ^{31}P-NMR spectra the diphenylphosphino groups of compound **2** give rise to a doublet at $\delta = -11.76$, while for compound **3** a triplet at $\delta = -6.33$ is observed. The signals of the boranatodiphenylphosphonio groups are broad resonances as a consequence of $^{31}P-^{11}B$ and $^{31}P-^{10}B$ spin/quadrupole interactions. The multiplicity of the methine proton in the ^1H-NMR spectrum of **2** is only a doublet ($\delta = 4.53$), with the $^2J(^1H,^{31}P)$ coupling unresolved. This result is in conformity with the singlet system observed for the methine proton of the trisphosphane **1** (see Experimental). (For variable-temperature NMR experiments of **2** and **3** see below.)

Synthesis and Dynamic Nuclear Magnetic Resonance of Tris(boranatodiphenylphosphonio)methane (4)

The trisborane adduct **4** is generated in 94% yield on treatment of **1** with an excess of the dimethyl sulfide—borane adduct $H_3B{\cdot}SMe_2$ under mild conditions in benzene solution. The product ist obtained as a colorless powder, which melts with decomposition at 183—185 °C. It reacts only slowly with air and moisture and is insoluble in nonpolar solvents.



4

In boiling benzene, compound **4** undergoes dissociation, and already after 1 h at 80 °C only the partially borylated compounds **2** and **3** and other decomposition products remain.

In mass-spectral studies the "parent ion"$[M+1]^+$ is only detectable after chemical ionization with isobutane. The mass spectrum also shows peaks indicating loss of H_2 and BH_3.

The ^1H- and ^{13}C-NMR signals for the methine group in **4** are shifted downfield due to the decrease in electron density caused by the BH_3 addition. The $\delta(^{31}P)$ values follow the same pattern, with **1** as the reference compound.

Table 3. ^1H-NMR data for $HC[P(C_6H_5)_2]_3(BH_3)_n$ (400 MHz, $CDCl_3$)

n	Compound		δ values Found	 Calcd.
0	$\mathit{H}C[P(C_6H_5)_2]_3$	**1**	4.16	–
1	$\mathit{H}C[P(C_6H_5)_2]_3(BH_3)$	**2**	4.53	4.58
2	$\mathit{H}C[P(C_6H_5)_2]_3(BH_3)_2$	**3**	5.05	5.00
3	$\mathit{H}C[P(C_6H_5)_2(BH_3)]_3$	**4**	5.42	5.42

The ^1H-NMR data for the methine proton of the compounds **1**–**4** are given in Table 3. In much the same manner as observed for the methylene protons in compounds $Ph_2P(X)CH_2P(Y)Ph_2$[10,16], there is an additive deshielding for the bridgehead proton corresponding to the number of boranatophosphonio groups attached to the methine carbon. For chalkogen derivates of **1**, which have been prepared earlier[11,17–19], the chemical shift of the methine proton can be calculated as

$$\delta(HC) = 4.16 + \Sigma(\text{substituent constants})$$

where the substituent constants are 0.25 (O), 0.63 (S), and 0.80 (Se)[19]. The substituent constant for a BH_3 group has now been calculated to be (5.42 ppm – 4.16 ppm)/3 = *0.42 ppm* for every BH_3 group introduced into the molecule. The data for **2** and **3** are in good agreement with this correlation (Table 3). The substituent constant for BH_3 thus appears to be larger than for oxygen (0.25), but smaller than for sulfur (0.63).

Since variable-temperature ^{31}P-NMR studies on molecules of the type $HC(PPh_2X)_3$ [X = O, S] have shown considerable barriers to rotation about the phosphorus–methine carbon bonds[15,19], while free **1** features virtually unrestricted rotation (above), it has been of particular interest to elucidate the dynamic behavior of the three new phosphane–borane adducts, especially of the symmetrical compound **4**. Figure 3 shows the $^{31}P\{^1H\}$-NMR spectra (CD_2Cl_2) of **4** for a range of temperatures. [The signal at δ = 15.09 must be attributed to bis(boranatodiphenylphosphonio)methane, those at δ = 21.31 and –6.33 to compound **3**, both present as impurities in very small amounts in the sample]. The $^{31}P\{^1H\}$-NMR spectrum of **4** is a broadened singlet (δ = 22.58) at 24°C, which begins to split into two signals at –50°C, which are finally resharpened at –91°C. Discrete couplings of an A_2X pattern are not resolved due to spin/quadrupole interactions (P/B). Compound **4** thus shows an unsymmetrical low-temperature conformation in solution with restricted P–C bond rotation. The structure presumably resembles that of the trisulfide **5** (Scheme 2, Formula **4d**).

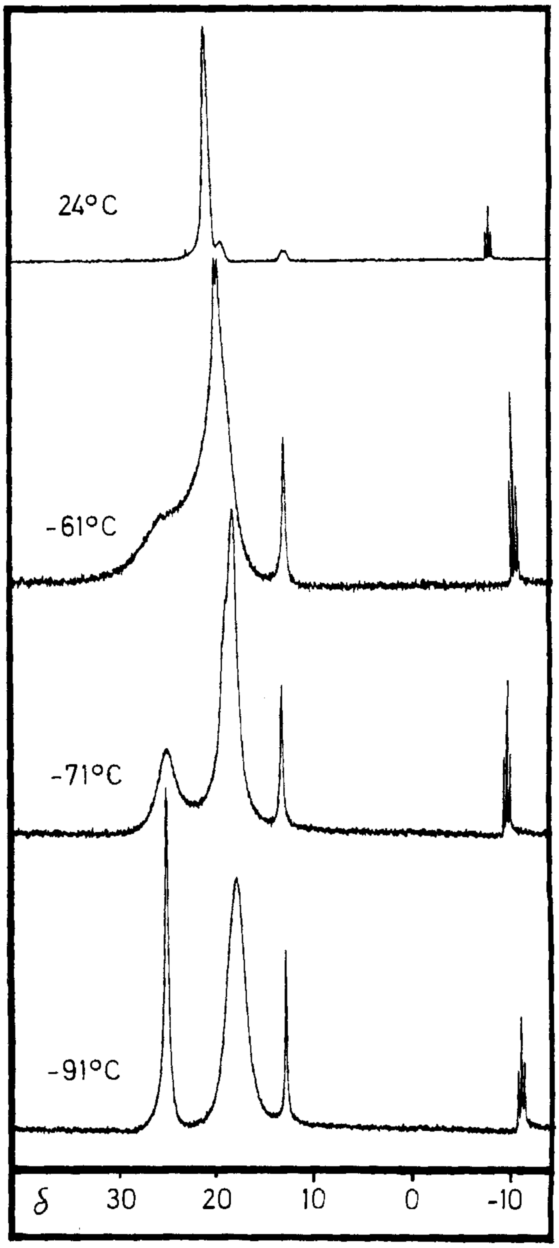


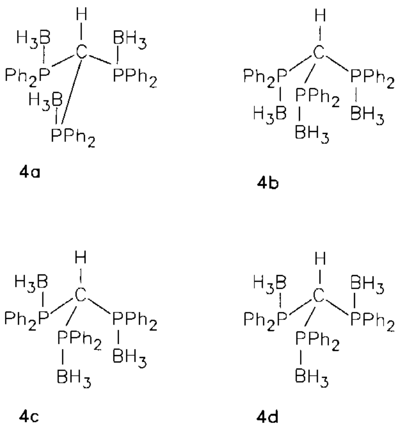
Figure 3. $^{31}P\{^1H\}$-NMR spectra (161.83 MHz, CD_2Cl_2) of $HC[P(C_6H_5)_2(BH_3)]_3$ (**4**) for a range of temperatures

With the spectral data it is possible to calculate the energy of activation for rotation about the phosphorus–methine carbon bond in **4**[20]. This value (31.2 kJ/mol) is compared

Table 4. Activation energies E_a of rotation about the phosphorus–methine carbon bond in $HC[P(C_6H_5)_2X]_3$ in CH_2Cl_2 solution

$HC[P(C_6H_5)_2X]_3$ X_3:	$(BH_3)_3$	O_3	OS_2	S_3
E_a[kJ/mol]	31.2	38.7[19]	39.6[19]	49.0[15]

Scheme 2. Idealized conformations of $HC[P(C_6H_5)_2(BH_3)]_3$ (**4**) with phenyl groups omitted for clarity



with that of other molecules of the type $HC(PPh_2X)_3$ in Table 4.

If it is assumed that the E_a values for rotation increase with the size required for the group X as the dominating parameter, the space needed for a BH_3 group would appear to be less than that of both oxygen and sulfur. As this is unlikely at least for oxygen, electrostatic contributions also seem to play a role. The spectra presented in Figure 3 also show the variable-temperature ^{31}P-NMR behavior of compound **3**. In contrast to the corresponding sulfur derivate $HC(PPh_2)[P(S)Ph_2]_2$, whose A_2X pattern at room temperature changes to an ABX pattern at temperatures below −90°C[15], it is obvious that compound **3**, present as an impurity, does not show hindered rotation in the temperature range investigated, and similar results have been obtained with compound **2**. The activation energy for the dynamic process in $HC(PPh_2)[P(S)Ph_2]_2$ has been estimated to be 29 kJ/mol[15].

This experimental fact agrees with the expectation, that the presence of a large chalcogen atom at a phosphorus atom leads to stronger repulsions and steric hindrance than the presence of a lone pair or a BH_3 group.

As might be expected, with a reduced number of BH_3 groups present in the molecules, molecular dynamics are virtually unrestricted.

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Experimental

All experiments have been carried out under dry purified nitrogen. Solvents and glassware have been dried and saturated/filled with nitrogen. [D$_1$]Chloroform and [D$_2$]dichloromethane have been used as solvents for NMR spectroscopy with tetramethylsilane, phosphoric acid, and trimethyl borate as reference compounds (Jeol JNM GX 270 and GX 400 spectrometers). – IR: FT-IR spectrometer Nicolet 5 DX. – MS: MAT 311 A (EI) and MAT 90 (CI). – Bis(diphenylphosphino)methane and all other reagents have been obtained commercially.

Tris(diphenylphosphino)methane (**1**): To a solution of bis(diphenylphosphino)methane (8.17 g, 21.3 mmol) and hexamethylphosphoric triamide (3.6 g, 20 mmol) in 100 ml of benzene 5.5 ml (1.42 g, 22 mmol) of *n*-butyllithium (4.02 M in hexane) is added dropwise at room temperature. After 1 h of vigorous stirring under reflux the orange-yellow solution of bis(diphenylphosphino)lithiomethane thus generated is treated with 4 ml (4.9 g, 22 mmol) of chlorodiphenylphosphane in 25 ml of benzene and heated under reflux for 1 h. The solvent is removed in vacuo and the residue dissolved in 150 ml of benzene and filtered through a glass frit. The clear yellow filtrate is then evaporated to dryness, and the remaining material crystallized from hot ethanol to form colorless needles in 56% yield (6.8 g), m.p. 176°C[11]. – ^{1}H NMR ($CDCl_3$): δ = 4.16 (s, 1 H, HCP_3), 7.30–7.43 and 7.57–7.65 (m, 30 H, C_6H_5). – $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 26.05 [q, ^1J(CP) = 45.8 Hz, CP_3], 128.0 (s, C-3), 128.9 (s, C-4), 134.8 [m (AXX'$_2$), *N* = 22.89 Hz, C-2], 136.6 [m (AXX'$_2$), *N* = 18.31 Hz, C-1]; ^{1}H-coupled: δ = 26.05 [dq, ^1J(CH) = 127.8 Hz, CP_3], ^1J(CH) = 161 Hz for C_6H_5. – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −9.99 (s). – MS (EI, 70 eV): *m/z*(%) = 568 (0.2) [M$^+$], 383 (100) [M$^+$ − $P(C_6H_5)_2$]. – IR (KBr): ṽ = 3058 cm^{-1}m, 1580 m, 1477 s, 1429 s, 733 vs, 690 vs.

$C_{37}H_{31}P_3$ (568.6)	Calcd.	C 78.16	H 5.50	P 16.34
	Found	C 78.06	H 5.40	P 15.70

(Boranatodiphenylphosphonio)bis(diphenylphosphino)methane (**2**): Compound **1** (900 mg, 1.6 mmol) is dissolved in 20 ml of tetrahydrofuran and treated with 3.2 ml (3.2 mmol) of a 1 M solution of THF · BH_3 in tetrahydrofuran at −78°C. The solution is slowly warmed to room temp. and concentrated in vacuo to 10 ml. The product precipitates on addition of 75 ml of *n*-pentane. After stirring for 16 h the very fine precipitate is filtered, washed with 20 ml of *n*-pentane and dried in vacuo to yield 850 mg (90%) of a colorless solid, m.p. 182°C (dec.). – ^{1}H NMR ($CDCl_3$): δ = 0.9–1.5 (br., 3 H, BH_3), 4.53 [d, $^2J(HP^V)$ = 10.9 Hz, 1 H, HCP_3], 6.9–7.8 (m, 30 H, C_6H_5). – $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 27.00 [m (AX_2YZ), *N* = 32 Hz, CP_3], 127.6–135.7 (m, C_6H_5). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −11.76 [d, $^2J(P^{III}P^V)$ = 39.2 Hz, P], 20.03 (s, br., PB). – $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ = −56.35 (s, br.). – MS (EI, 70 eV): *m/z* (%) = 580 (0.64) [M$^+$ − H_2], 568 (0.20) [M$^+$ − BH_3], 397 (0.82) [M$^+$ − PPh_2], 383 (100) [M$^+$ − BH_3 − PPh_2]. – IR (KBr): ṽ = 2404 cm^{-1}m, 2369 m [ν(BH_3)], 1096 vs [δ(BH_3)].

Bis(boranatodiphenylphosphonio)(diphenylphosphino)methane (**3**): A solution of 0.51 g (0.9 mmol) of **1** in 30 ml of benzene is treated at room temp. with a solution of SMe_2 · BH_3 (0.136 g, 1.8 mmol) in 30 ml of benzene. After 1 h the solvent is evaporated from the reaction mixture in vacuo to a volume of 5 ml and the product precipitated by addition of *n*-pentane (130 ml). The colorless solid is filtered, washed with *n*-pentane (30 ml), and dried in vacuo to yield 0.40 g (75%) of **3**, m.p. 192°C (dec.). – ^{1}H NMR ($CDCl_3$): δ = 1.2–1.9 (br., 6 H, BH_3), 5.05 [dt, $^2J(HP^V)$ = 13.4, $^2J(HP^{III})$ = 2.45 Hz, 1 H, HCP_3], 6.9–7.8 (m, 30 H, C_6H_5). – $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 28.78 [t, $^1J(CP^V)$ = 11.44 Hz, CP_3], 127.6–135.2 (m, C_6H_5). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −6.33 [t, $^2J(P^{III}P^V)$ = 49 Hz, P], 21.31 (s, br., PB). – $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ = −54.84 (s, br.). – MS (EI, 70 eV): *m/z*(%) = 594 (0.23) [M$^+$ − H_2], 503 (0.63) [M$^+$ − H_2 − BH_3 − C_6H_5], 383 (100) [M$^+$ − H_2 − 2 BH_3 − PPh_2]. – IR (KBr): ṽ = 2426 cm^{-1}m, 2394 s, 2355 m [ν(BH_3)], 1104 vs, 1072 vs [δ(BH_3)].

Tris(boranatodiphenylphosphonio)methane (**4**): Compound **1** (3.9 g, 6.85 mmol) is dissolved in 80 ml of benzene and treated with a solution of SMe_2 · BH_3 (2.59 g, 34 mmol) in 5 ml of the same solvent at room temp. for 20 h. After addition of *n*-pentane (135 ml) and stirring for another 2 h the precipitated product is filtered, washed with *n*-pentane (30 ml), and dried in vacuo to give **4** in 94% yield (3.9 g) as a colorless solid, m.p. 183–185°C (dec.). – ^{1}H

NMR ($CDCl_3$): δ = 1.1 − 1.7 (br., 9 H, BH_3), 5.42 [q, ^2J(PH) = 14.24 Hz, 1 H, HCP_3], 6.9 − 7.8 (m, 30 H, C_6H_5). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 32.2 ["d" (AX_3Y_3), *N* = 4.6 Hz, CP_3], 127.0 ["dd" ($AXX'_2YY'_2$), ^1J(CP) = 54.2 Hz, *N* = 3.05 Hz, C-1], 127.9 [m ($AXX'_2YY'_2$), *N* = 7.6 Hz, C-2], 131.1 (s, C-4), 134.5 [d, ^3J(CP) = 6.9 Hz, C-3]. − $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 24°C): δ = 22.58 (s, br.); *T* = 0, −15, −27, −40°C: δ = 22.17, 21.89, 21.66, and 21.20, resp. (s, br.); *T* = −61°C: δ_A = 24.80 (br.), δ_B = 19.46 (s); *T* = −71°C: δ_A = 25.35 (br.), δ_B = 18.62 (s); *T* = −81°C: δ_A = 25.44 (s), δ_B = 18.39 (s); *T* = −91°C: δ_A = 25.23 (s), δ_B = 18.22 (s, br.). − $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ = −54.37 (s, br.). − MS (CI): *m/z*(%) = 611 (1.3) [$(M + 1)^+$], 583 (6.8) [$(M + 1)^+ - 2\,BH_3 - H_2$], 568 (24.1) [$(M + 1)^+ - 3\,BH_3$], 397 (100) [$(M + 1)^+ - 2\,BH_3 - H_2 - P(C_6H_5)_2$]. − IR (KBr): $\tilde{\nu}$ = 2463 cm^{-1}s, 2443 m, 2353 s [ν(BH_3)], 1099 s, 1065 s [δ(BH_3)].

$C_{37}H_{40}B_3P_3$ (610.1) Calcd. C 72.84 H 6.61 P 15.23
Found C 71.68 H 6.66 P 15.07

Crystal Structure Determination of Tris(diphenylphosphino)methane, $HC[P(C_6H_5)_2]_3$ (**1**): Enraf-Nonius CAD4 diffractometer, Cu-K_α radiation, λ = 1.54184 Å, graphite monochromator, *T* = 20°C. − Crystal data: $C_{37}H_{31}P_3$, $M_{rel.}$ = 568.57, monoclinic space group *C*2/*c* (No. 15) with *a* = 32.408(1), *b* = 11.650(1), *c* = 19.652(1) Å, β = 124.73(1)°, *V* = 6098 Å^3, *Z* = 8, $d_{calcd.}$ = 1.239 g/cm^3, μ(Cu-K_α) = 19.8 cm^{-1}, *F*(000) = 2384. The intensities of 5619 reflexions were collected up to (sinΘ/λ) = 0.588 Å^{-1} (*hkl* range: +38, +13, ±22) and averaged to 4777 independent data, of which all were considered "observed". The structure was solved with direct methods (SHELXS-86[21,22]) and refined with anisotropic displacement parameters for the non-hydrogen atoms. Hydrogen atoms were refined isotropically. *R* (R_W) = 0.045 (0.035), shift/error = 0.001, *w* = $1/\sigma^2(F_o)$ for 486 refined parameters. Residual electron density: +0.23 / −0.21 eÅ^{-3}. Further details of the crystal structure determination may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information, W-7514 Eggenstein-Leopoldshafen 2, by quoting the depository number CSD-54984, the names of the authors, and the journal reference.

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