Phosphineborane Chemistry. — An Anionic Tripod Ligand Featuring Three Ylide Functions and the Structure of the Corresponding Electroneutral Double-Ylide

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In a search for a tripod ligand featuring three ylidic functions based on a phosphineborane skeleton, hydrotris(trimethylphosphonio)borate dibromide $[HB\{P(CH_3)_3\}_3]^{2+}Br_2^-$ was treated with potassium hydride in tetrahydrofuran to give the corresponding triple-ylide salt potassium hydrotris[methylido(dimethyl)phosphonio]borate, $K^+[HB\{P(CH_3)_2CH_2\}_3]^-$. In an attempt to prepare a barium salt of this tripod ligand, the electroneutral double-ylide $HB[P(CH_3)_3][P(CH_3)_2CH_2]_2$ was isolated from the reaction mixture obtained from equivalent amounts of the potassium salt and barium chloride in tetrahydrofuran with ultrasound activation. Solvent and protic impurities are the probable sources for the protonation. NMR data are presented for the double-ylide and its anionic precursor, and the crystal and molecular structure of the double-ylide has been determined by single-crystal X-ray diffraction. The unit cell of the crystals contains two independent molecules of very similar configuration. Assignments of the $P(CH_3)_3$ and $P(CH_3)_2CH_2$ units are based on bond distance and bond angle criteria.

Phosphanboran-Chemie. — Ein anionischer Tripod-Ligand mit drei Ylid-Funktionen und die Struktur des korrespondierenden elektroneutralen Doppel-Ylids

Auf der Suche nach einem Tripod-Liganden mit drei Ylid-Funktionen an einem Phosphanboran-Skelett wurde aus dem Hydrotris(trimethylphosphonio)borat-dibromid $\{HB[P(CH_3)_3]_3\}^{2+}Br_2^-$ durch Behandlung mit Kaliumhydrid in Tetrahydrofuran das korrespondierende Tripel-Ylid-Salz Kalium-hydrotris[methylido(dimethyl)phosphonio]borat, $K^+[HB\{P(CH_3)_2CH_2\}_3]^-$, hergestellt. Bei Versuchen zur Synthese eines Barium-Salzes dieses Tripod-Liganden wurde aus der Reaktionsmischung äquivalenter Mengen des Kalium-Salzes und Bariumchlorid in Tetrahydrofuran nach Behandlung mit Ultraschall das elektroneutrale Doppel-Ylid $HB[P(CH_3)_3][P(CH_3)_2CH_2]_2$ erhalten. Das Solvens und protische Verunreinigungen sind die wahrscheinlichen Proton-Quellen bei dieser Umwandlung. Für das Doppel-Ylid und seine Anion-Vorstufe werden NMR-Daten vorgelegt. Die Kristall- und Molekülstruktur des Doppel-Ylids wurde durch Einkristallröntgenbeugung bestimmt. Die Elementarzelle der Kristalle enthält zwei unabhängige Moleküle sehr ähnlicher Konfiguration. Die Zuordnung der Struktureinheiten zu den Funktionen $P(CH_3)_3$ und $P(CH_3)_2CH_2$ erfolgte nach Abstands- und Winkelkriterien.

Phosphorus ylides rank among the most powerful ligands for main group and transition metals[1]. Owing to the stabilisation of metal-to-carbon bonds through neighbouring P^+ onium charges, the chemistry of ylide complexes features some extremely robust organometallic compounds[2]. As might be expected, this is particularly true for species with difunctional, chelating ylide ligands. In such systems the ylidic functions can be attached to a variety of skeletal atoms, including also phosphine borane moieties[3]. In fact, the bifunctional ylidic ligand **B**, derived from the parent cation $[(CH_3)_3P - BH_2 - P(CH_3)_3]^+$ (**A**) through deprotonation at two of the six methyl groups by strong base[4], proved to be a particularly versatile component for ylide complexes[5].

It has been pointed out[6] that the sequence of five alternating charges in **B**, and the complete loop of six alternating charges in its complexes, may contribute significantly to the overall stability of these coordination compounds.

Attempted monodeprotonation of the cationic precursor $[(CH_3)_3P - BH_2 - P(CH_3)_3]^+$ to give the neutral ylide $(CH_3)_3P - BH_2 - P(CH_3)_2 = CH_2$ (**C**), was not successful[4-6]. The anionic species **B** produced instead is such a strong ligand, however, that even mercury(II), which is notoriously two-coordinate in organomercurials, becomes tetrahedrally tetracoordinate in a complex $Hg(B)_2$[4].

After the synthesis[7] of the first tris(phosphonio)borate dications **D** it appeared that it should be possible to convert this precursor into the corresponding tripod ligand **E** with a bridgehead boron atom and a branched system of alternating charges. This tripod **E** could be expected to be an even more powerful ligand than **A**, which could give rise to

A   B   C   D   E   F
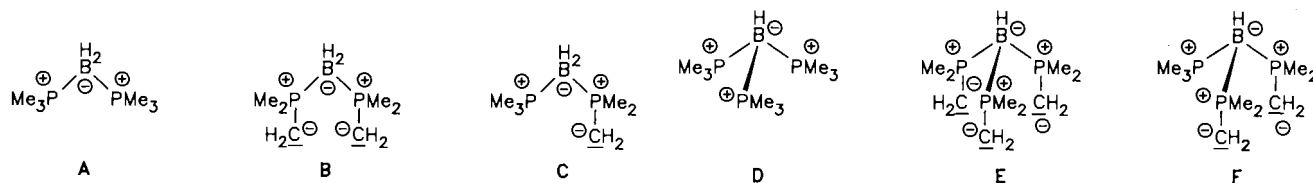
a family of both tetrahedral and octahedral organometallic compounds with facial occupation of triangular coordination sites. We report here the synthesis of the potassium salt of this anion and its conversion into the corresponding neutral ylide **F**, which (in contrast to the situation with **A** and **C**) could be isolated and structurally characterized by single crystal X-ray diffraction.

Preparation, Properties, and Spectroscopic Data of the Triple-Ylide Salt $K^+[HB\{P(CH_3)_2CH_2\}_3]^-$

Hydrotris(trimethylphosphonio)borate dibromide is readily available as a stable crystalline solid. Its structure has been established by spectroscopic and crystallographic techniques[7]. In analogy to the behaviour of the corresponding equally well characterized dihydrobis(trimethylphosphine)boron bromide[4] it was expected that treatment with strong base should lead to deprotonation of some of the methyl hydrogen to give ylidic species. It has been shown previously, that the hydrogen atoms at boron can also be exchanged by deuterium under basic conditions, but no permanent deprotonation leaving tricoordinate boron was observed[7].

When $[HB\{P(CH_3)_3\}_3]^{2+}Br_2^-$ was treated with an excess of potassium hydride in tetrahydrofuran at temperatures between -78 and $-20\,^\circ C$, no reaction was noticeable. However, after warming to room temperature the evolution of hydrogen gas became visible, and after 30 h the amount of hydrogen collected approached the limit of three equivalents. The solution turned yellow during this process, and it was obvious that the precipitate changed in appearance.

Evaporation of the solvent from the clear solution gave the pure, tetrahydrofuran-free potassium salt (Eq. 1) which is a colorless solid, pyrophoric in air, and extremely reactive towards moisture, alcohols, acetone, and halocarbon solvents. It is sparingly soluble in benzene and toluene, but dissolves readily in THF to give highly concentrated solutions.

$$[HB\{P(CH_3)_3\}_3]^{2+}Br_2^- + 3\,KH \longrightarrow$$
$$2\,KBr + 3\,H_2 + [HB\{P(CH_3)_2CH_2\}_3]^-K^+ \quad (1)$$
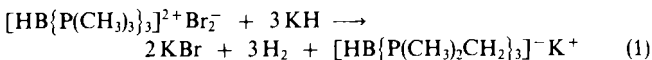
The *NMR spectra* of these solutions correspond with the proposed symmetrical formula. In the ^1H-NMR spectrum, the ylidic functions give rise to a signal shifted to high field in a very characteristic way[8]. The 3:1 ratio of the intensity of this signal and that of the signal of the remaining methyl protons (an $[A_6X]_3$ spin system) confirms that one proton has been removed from each $P(CH_3)_3$ group, as also suggested by the amount of H_2 gas evolved. In the ^{13}C-NMR spectrum, an analogous high-field shift is observed for the methylene carbon atoms as compared to the remaining methyl carbon atoms, indicating the carbanionic nature of these new functions[8]. The ^1H-decoupled ^{11}B-NMR spectrum shows a $1:3:3:1$ quadruplet as proof for three equivalent phosphorus atoms at the boron center. In the ^1H-coupled spectrum this pattern changes to a doublet of quadruplets in the form of a broadened five-line multiplet owing to very similar one-bond coupling constants $^1J(PB)$ and $^1J(BH)$. This multiplicity confirms the conservation of the hydrogen

at boron, which is otherwise difficult to detect due to quadrupole broadening of the BH signal.

Finally, the ^{31}P-NMR spectrum shows a single $1:1:1:1$ quadruplet, again indication equivalent phosphorus atoms attached to a common boron center.

According to the NMR results, the anion $[HB\{P(CH_3)_2-CH_2\}_3]^-$ thus has virtual C_{3v} symmetry in tetrahydrofuran solution.

It could be noticed in the spectra of samples stored for a longer period of time or under less thorough exclusion of moisture that carbon and in particular proton signals became broadened further with couplings less well resolved or even absent. This behaviour is typical for ylides with alkylidene and their corresponding alkyl groups present at the same phosphorus center: Inter- and intramolecular proton exchange catalyzed by protic impurities makes the protons and carbon atoms in these functions undistinguishable on the NMR time scale. First observed for $(CH_3)_3PCH_2$[8], and later for the homologous compounds $(C_2H_5)_3PCHCH_3$ or $(C_3H_7)_3PC_3H_6$ etc., this feature is now recognized as a phenomenon common for all ylidic species bearing protons at α-carbon atoms relative to phosphorus in the non-ylidic substituents[9].

Formation, NMR Data, and Crystal Structure of the Double-Ylide $(CH_3)_3PBH[P(CH_3)_2CH_2]_2$

During attempted syntheses of coordination compounds containing the triple-ylide anion $[HB\{P(CH_3)_2CH_2\}_3]^-$ as a ligand, the workup of the reaction mixtures yielded varying amounts of a yellow, crystalline, metal-free material. Like the potassium salt employed in the syntheses, this yellow product is pyrophoric in air and extremely sensitive to moisture, but unlike its precursor it is very soluble in aromatic hyrocarbons and low-melting (m. p. $96\,^\circ C$), suggesting a covalent species of low polarity.

In a typical experiment, anhydrous barium chloride was treated with two equivalents of $K^+[HB\{P(CH_3)_3CH_2\}_3]^-$ in tetrahydrofuran with ultrasound activation at room temperature for 1 week. After removal of the solvent in vacuo and extraction of the residue with toluene, yellow crystals of the product appeared on cooling of the filtrate in 27% yield. NMR data of C_6D_6 solutions and a single-crystal X-ray diffraction analysis identified the compound could as the double-ylide, suggesting *monoprotonation* of the precursor anion (Eq. 2).

$$K^+[HB\{P(CH_3)_2CH_2\}_3]^- \xrightarrow[\text{THF}]{H^+[BaCl_2]} \quad (2)$$
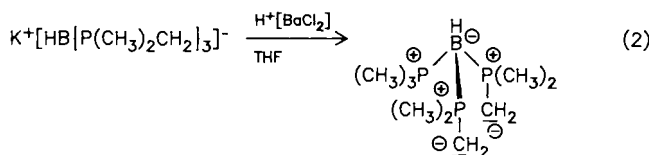
It is unknown if the metal halides play an important role in this specific monoprotonation. The incoming proton may be derived from the solvent or from traces of moisture at the glass walls or other parts of the apparatus. There is precedent for this type of serendipitous protonation of ylides of high basicity: An example in case is another potassium salt of a dialkylphosphonium-bis(alkylide) anion, which yielded the parent mono-ylide on standing in benzene or toluene solution[9-11]. Cumulated double-ylides of the general formula $R_3P=C=PR_3$ are equally sensitive and have been

shown to transform into mono-ylides and related derivatives by acquiring a proton from the environment[12].

The ^{31}P-NMR spectrum of a benzene solution of the compound shows two resonances in the intensity ratio 2:1 with the high-intensity signal at high field, as expected for two ylidic onium centers[8]. The ^{1}H-decoupled ^{11}B-NMR spectrum is a broad 1:3:3:1 quadruplet with $J(PB) = 105$ Hz. With proton coupling, the broadened dq multiplicity arises owing to the [11]B[1]H coupling with $J(BH) = 94$ Hz. Both the ^{1}H- and ^{13}C-NMR spectra are broadened due to the ^{1}H exchange processes already mentioned in the discussion of the spectra of the precursor anion (above). The proton signal of the methylide functions appears upfield relative to the signal of the methyl groups in the overall intensity ratio of 4:21. Neither the couplings nor the shift difference of the two methyl groups are well resolved.

HB[P(CH$_3$)$_2$CH$_2$]$_2$P(CH$_3$)$_3$ crystallizes in the monoclinic space group $P2_1/c$ with two independent molecules (A and B) in the asymmetric unit. The structures are shown in Figure 1. None of these molecules has any crystallographic

symmetry, though the overall geometry approaches the C_3 point group with the threefold axis coinciding with the BH bond. The boron atoms have a tetrahedral environment comprising the hydrogen atom H and three PC$_3$ units. The P−B−P angles in the BP$_3$ pyramids average to 112.5° for molecules A and B. These values are close to those found recently for the parent dication HB[P(CH$_3$)$_3$]$_3^{2+}$ (average 113.8°). The average of the six P−B distances in A and B (1.942 Å) is also close to the corresponding dimensions in the dication, and thus the PB$_3$ skeleton in the double-ylide closely resembles that of the fully protonated species[7].

It proved more difficult, however, to distinguish between methyl and methylene groups in molecules A and B, since direct localisation of hydrogens was not possible in all cases, and identification had thus to rely on P−C distances and C−P−C or B−P−C angles.

Both molecule A and molecule B exhibit one very short P−C bond [P2−C23 = 1.715(4) Å in A, P5−C53 = 1.687(4) Å in B], which clearly can be assigned to ylidic groups P=CH$_2$. There is ample experimental evidence, that P=C bonds show distances shorter than or around 1.70 Å, while P−C bond distances are typically clustered around 1.80 Å.

Molecules A and B have one further distance each around 1.74 Å [P1−C13 = 1.747(4) in A, 1.741(4) Å in B], which are likely to represent the two remaining ylide groups. All other P−C distances are close to or beyond the 1.80 Å limit

Figure 1. Molecular structure of HB[P(CH$_3$)$_3$][P(CH$_3$)$_2$CH$_2$]$_2$ (ORTEP, 50% probability ellipsoids); top: molecule A; bottom: molecule B

Table 1. Selected interatomic distances [Å] and angles [°] for the two independent molecules A and B of HB[P(CH$_3$)$_3$][P(CH$_3$)$_2$CH$_2$]$_2$

P1−B1	1.933(4)		
P1−C11	1.820(4)	P1−C12	1.813(4)
P1−C13	1.747(4)		
P2−B1	1.945(4)		
P2−C21	1.820(4)	P2−C22	1.792(4)
P2−C23	1.715(4)		
P3−B1	1.946(4)		
P3−C31	1.818(4)	P3−C32	1.756(4)
P3−C33	1.779(4)		
P4−B2	1.941(4)		
P4−C41	1.830(4)	P4−C42	1.764(4)
P4−C43	1.741(3)		
P5−B2	1.950(4)		
P5−C51	1.823(4)	P5−C52	1.836(4)
P5−C53	1.679(4)		
P6−B2	1.935(4)		
P6−C61	1.809(4)	P6−C62	1.792(4)
P6−C63	1.792(4)		
C11−P1−C12	100.9(2)	C11−P1−C13	111.3(2)
C12−P1−C13	108.2(1)	B1−P1−C11	111.6(2)
B1−P1−C12	109.8(2)	B1−P1−C13	114.1(2)
C21−P2−C22	103.2(2)	C21−P2−C23	108.9(2)
C22−P2−C23	113.9(2)	B1−P2−C21	107.3(2)
B1−P2−C22	109.5(2)	B1−P2−C23	113.5(2)
C31−P3−C32	107.9(2)	C31−P2−C33	105.7(2)
C32−P3−C33	107.6(2)	B1−P3−C31	108.5(2)
B1−P3−C32	112.8(2)	B1−P3−C33	107.6(2)
P1−B1−P2	112.9(2)	P1−B1−P3	110.9(2)
P2−B1−P3	113.8(2)		
C41−P4−C42	105.2(2)	C41−P4−C43	110.4(2)
C42−P4−C43	109.0(2)	B2−P4−C41	106.8(2)
B2−P4−C42	111.9(2)	B2−P4−C43	110.4(2)
C51−P5−C52	98.8(2)	C51−P5−C53	110.5(2)
C52−P5−C53	116.5(2)	B2−P5−C51	108.0(2)
B2−P5−C52	108.6(2)	B2−P5−C53	113.2(2)
C61−P6−C62	103.3(2)	C61−P6−C63	106.4(2)
C62−P6−C63	107.2(2)	B2−P6−C61	110.9(2)
B2−P6−C62	112.9(2)	B2−P6−C63	106.4(2)
P4−B2−P5	114.3(2)	P5−B2−P6	112.2(2)
P5−B2−P6	111.0(2)		

(Table 1). Based on the P − C distance argument, ylidic functionality is therefore tentatively assigned to carbon atoms C13, C23, C43, and C53, with the onium centers at P1, P2, P4, and P5.

These assignments are supported by some bond angle criteria: The angles C11 − P1 − C12 = 100.9(2), C21 − P2 − C22 = 103.2(2), C41 − P4 − C42 = 105.2(2), and C51 − P5 − C52 = 98.8(2)° are the smallest in the large collection of pseudo-tetrahedral angles found in molecules A and B. Since it is known that the high electron density at ylidic carbon atoms is strongly affecting the geometry of the neighbouring phosphorus atom in this sense, this finding is auxiliary evidence for the proposed allocation of the PCH₂ moieties[13,14].

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters for HB[P(CH₃)₃][P(CH₃)₂CH₂]₂

| ATOM	X/A	Y/B	Z/C	U(eq.)
P1	0.2781(1)	0.67314(3)	0.41657(9)	0.032
P2	0.0448(1)	0.63771(3)	0.53882(8)	0.030
P3	0.2340(1)	0.56320(3)	0.44212(9)	0.033
B1	0.2291(4)	0.6249(1)	0.5134(4)	0.024
C11	0.2535(5)	0.7315(1)	0.4702(4)	0.049
C12	0.4782(4)	0.6730(1)	0.4536(4)	0.039
C13	0.1846(4)	0.6675(2)	0.2517(4)	0.043
C21	0.0879(4)	0.6820(1)	0.6631(4)	0.049
C22	-0.0050(5)	0.5876(2)	0.6090(4)	0.054
C23	-0.0974(4)	0.6579(2)	0.4042(4)	0.061
C31	0.2698(4)	0.5198(1)	0.5674(4)	0.048
C32	0.3754(5)	0.5580(1)	0.3818(4)	0.057
C33	0.0615(4)	0.5464(1)	0.3187(3)	0.042
P4	0.2222(1)	0.42153(3)	0.09208(9)	0.035
P5	0.2930(1)	0.31153(3)	0.05735(8)	0.029
P6	0.4416(1)	0.39289(3)	-0.04898(9)	0.035
B2	0.2700(4)	0.3750(1)	-0.0110(4)	0.027
C41	0.0227(4)	0.4148(1)	0.0609(3)	0.051
C42	0.2406(5)	0.4791(1)	0.0438(4)	0.059
C43	0.3297(5)	0.4159(1)	0.2544(3)	0.051
C51	0.2456(4)	0.2707(1)	-0.0757(4)	0.046
C52	0.1358(5)	0.2991(1)	0.1055(4)	0.051
C53	0.4676(4)	0.3004(1)	0.1671(3)	0.048
C61	0.3918(4)	0.4382(1)	-0.1694(4)	0.048
C62	0.5082(5)	0.3463(2)	-0.1191(4)	0.065
C63	0.5983(4)	0.4144(2)	0.0828(4)	0.042
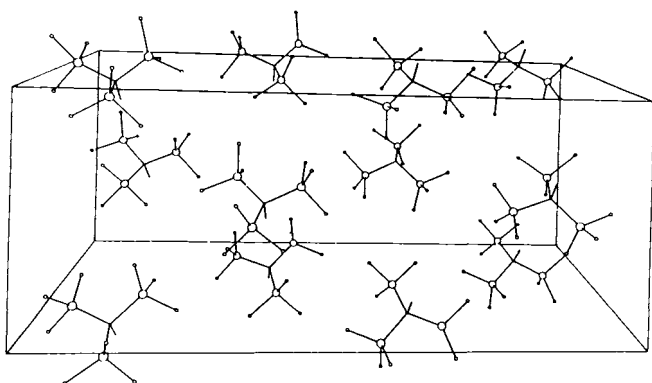
Figure 2. Packing of the HB[P(CH₃)₃][P(CH₃)₂CH₂]₂ molecules in the unit cell

Nevertheless, the question of crystal disorder has also to be addressed. It is obvious from the atomic coordinates and the displacement parameters in Table 2, that these data give no indication of severe disorder. Residual electron density found at C13 and C43 may point to alternative positioning

of methyl and methylene functions (protonation and deprotonation), but these appear to be almost neglegible. It should also be noted that the electron density at ylidic carbon atoms often gives rise to prominent peaks in final difference maps.

There is no evidence for unusual intermolecular contacts. Distances between atoms of different molecules are all beyond the van der Waals limits. The arrangement of the molecules in the unit cell is illustrated in Figure 2. Supplementary material has been deposited[15].
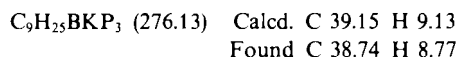
Work on the coordination chemistry of the tripod ligand [HB{P(CH₃)₂CH₂}₃]⁻ and the bidentate ylide HB[P(CH₃)₂-CH₂]₂P(CH₃)₃ is in progress.
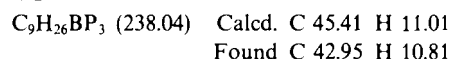
Experimental

General: All experiments were carried out under pure dry nitrogen. Glassware and solvents were purified, dried, and kept under nitrogen accordingly. [D₈]Tetrahydrofuran and [D₆]benzene were used as solvents for NMR spectroscopy with tetramethylsilane, phosphoric acid, and trimethylborate as reference compounds (Jeol GX 270 and GX 400 spectrometers).

Potassium Hydrotris[methylido(dimethyl)phosphonio]borate: Potassium hydride (5.00 g, 0.125 mol) is added to a suspension of hydrotris(trimethylphosphine)boron dibromide (6.00 g, 0.015 mol) in 80 ml of tetrahydrofuran at room temp. Slow stirring is started and continued for 30 h. Hydrogen gas is evolved, the solution turns yellow, and a very fine precipitate is formed. When the hydrogen evolution has ceased the reaction mixture is allowed to settle for 14 h or is centrifuged. The clear yellow solution is decanted from the insoluble and evaporated to dryness in vacuo. The residue is stirred with 10 ml of benzene, filtered, washed again twice with 5 ml of benzene, and dried in vacuo to yield 2.20 g (49%) of a colourless solid, m. p. 122 °C. − ¹H NMR ([D₈]THF): δ = −0.73 (br., 2H, CH₂), 1.24 (br. d, *N* = 8.8 Hz, 6H, CH₃). − ¹¹B NMR: δ = −42.9 [dq, *J*(PB) = 108, *J*(BH) = 90 Hz]; {¹H}: −42.9 [q, *J*(PB) = 108 Hz]. − ¹³C{¹H} NMR: δ = 1.7 ("d", *N* = 32 Hz, CH₂), 24.9 (br. d, *N* = 45 Hz, CH₃). − ³¹P{¹H} NMR: δ = −17.0 [q, *J*(PB) = 108 Hz].

C₉H₂₅BKP₃ (276.13) Calcd. C 39.15 H 9.13
Found C 38.74 H 8.77

Hydrobis[methylido(dimethyl)phosphonio](trimethylphosphonio)borate: A solution of the potassium salt (above) in 70 ml of THF, prepared from 4.80 g (0.012 mol) of the dibromide, is stirred with 1.25 g (0.006 mol) of anhydrous barium dichloride for 7 d at ambient temp. under ultrasound irradiation. The solvent is removed in vacuo and the residue extracted with 25 ml of toluene. The filtered extract is concentrated and cooled to give 0.99 g (27%) of crystalline product, m. p. 96 °C. − ¹H NMR ([D₆]benzene): δ = 0.0 (br., 4H, CH₂), 1.30 (br., 21H, CH₃). − ¹¹B NMR: δ = −45.6 [dq, *J*(PB) = 105, *J*(BH) = 94 Hz]; {¹H}: −45.6 [q, *J*(PB) = 105 Hz]. − ¹³C{¹H} NMR: δ = 3.0 (br., CH₂), 12.5 (br., P(CH₃)₂], 23.5 [br., P(CH₃)₃]. − ³¹P{¹H} NMR: δ = −22.1 (br., PCH₂), −6.7 [br., P(CH₃)₃].

C₉H₂₆BP₃ (238.04) Calcd. C 45.41 H 11.01
Found C 42.95 H 10.81

Crystal Structure Determination of the Double-Ylide HB[P-(CH₃)₃][P(CH₃)₂CH₂]₂: Syntex P2₁ diffractometer, Mo-Kₐ radi-

ation, $\lambda = 0.71069$ Å, graphite monochromator, $T = -45$°C. — Crystal data: $C_9H_{26}BP_3$, $M = 238.04$, space group $P2_1/c$ with $a = 9.660(1)$, $b = 28.541(3)$, $c = 11.374(1)$ Å, $\beta = 112.70(1)°$, $V = 2892.97$ Å^3, $Z = 8$, $d_{calcd.} = 1.093$ gcm^{-3}, $\mu(Mo\text{-}K_\alpha) = 3.7$ cm^{-1}, $F(000) = 1040$. The intensities of 4932 reflexions were collected up to $(\sin \Theta/\lambda) = 0.572$ Å^{-1} (hkl range: $+11$, $+32$, ± 13) and averaged to 4535 independent data, 3465 of which with $F_o \geq 4.0\sigma(F_o)$ were considered "observed". The structure was solved with direct methods (SHELXS-86[16]) and refined with anisotropic displacement parameters for the non-hydrogen atoms. Hydrogen atoms were assigned constant values $U_{iso} = 0.05$ Å^2. $R(R_w) = 0.045$ (0.045), $w = 1/\sigma^2(F_o)$ for 235 refined parameters. Residual electron density: 0.38/ -0.33 eÅ^{-3}.

CAS Registry Numbers

$\mathbf{E} \cdot \mathbf{K}^\oplus$: 121314-03-2 / $\mathbf{F}$: 121314-04-3 / $[HB\{P(CH_3)_3\}_3]^{2+}Br_2^-$: 119846-58-1

[1] H. Schmidbaur, *Acc. Chem. Res.* **8** (1975) 62.
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