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Phosphine-Boranes Based on the 7-Phosphanorbornene Framework: a Regioselective Approach to the Monoboranes of the Dimers of Phospholes

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Abstract—The reaction of dimers of phosphole oxides (**3a**–**e**) with an excess of dimethylsulfide borane follows an unexpected route to give phosphine-boranes **5a**–**e** based on the 7-phosphanorbornene framework in a regioselective manner and in good yields. In small quantities, the diboranes (**10a**–**e**), that can be synthesized in acceptable yields by the reaction of the corresponding diphosphines **12a**–**e** with borane, were also formed.

The P-heterocyclic derivatives of phosphine-boranes are versatile intermediates in organic syntheses. The phosphole-boranes were useful in the preparation of functional phospholes,[1] as well as in the synthesis of a new type of phosphole dimer.[2] A few dihydrophosphole-boranes were utilised in hydrozirconation[3] and in ring enlargement.[4] The use of a tetrahydrophosphole-borane as precursor for a trialkyl-type chiral phosphine ligand was also reported.[5] Only one example of an endocyclic phosphine-borane that is part of a five-membered ring is known.[6] The possibilities for the utilisation of 1,2-dihydrophosphinine-boranes[4] and 1,2-dihydro-1,2-azaphosphinine-boranes[7] in ring enlargement were examined. Several five-, six- and seven-membered heterocyclic phosphine-boranes were also described.[4,8]

It is known that the formation of unsaturated phosphine-boranes from the corresponding phosphines and dimethylsulfide borane (BMS) might be accompanied by reductive side reactions.[1,4] We found that the double bonds with electron-withdrawing substituent at one end were easily reduced by the borane; moreover, in case of the presence of two double bonds in the molecule, saturation of the electron-poor double bond took place in a selective manner. Thus, the reaction of 1,2-dihydrophosphinine oxides (**1**) with one equivalent of the BMS reagent followed by hydrolysis afforded the corresponding 1,2,3,6-tetrahydrophosphinines (**2**) in good yields[9] (Scheme 1).

We thought that the above procedure might be suitable for the selective reduction of the double bond of the 2-phospholene moiety of dimers **3** (Scheme 2). We wished to obtain new precursors of the dimers of phospholes that are valuable ligands in coordination chemistry.[10]

It was observed, however, that the reaction of dimers **3a**–**e** with BMS resulted in a change in the functionality of the bridging P-moiety, rather than selective reduction of the 2,3-double-bond. Thus, the bridging P=O group was transformed to a P→BH_3 function, while the other P=O unit remained intact (Scheme 2). The use of one equivalent of the BMS reagent led to a conversion of less than 50%, but by increasing its quantity up to three equivalents, the phosphine-boranes (**5a**–**e**) were obtained in good yields (68–81%) after column chromatography.

Structure of the products (**5a**–**e**) was confirmed by ^{31}P, ^{11}B, ^{1}H and ^{13}C NMR, as well as mass spectroscopic data.[5] ^{31}P NMR spectra of the products (**5**) revealed a doublet of 36–40 Hz at δ_P=53–58 and a multiplet due to the coupling with the ^{11}B atom at a downfield shift, as δ_P=127–136. The ^{13}C NMR chemical shifts and couplings were in the expected region. Signals of the C(3), C(3a) and C(7a) skeletal carbon atoms were split by both phosphorus atoms. The ^{1}J(P(8),C) couplings are significantly smaller than the ^{1}J(P(1),C) couplings (32–36 vs. 74–100 Hz on the skeletal carbon atoms). The EI mass spectra of the phosphine-boranes (**5**) showed the molecular ions in only low intensity (≤3%), the major fragmentations involved the loss of BH_3 and that of P–Ar. Elemental composition of the products (**5**) was confirmed by HR-FAB mass spectroscopy. The

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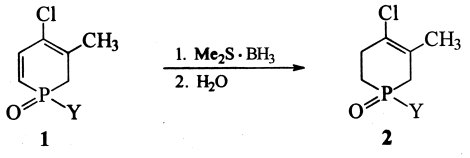


Scheme 1.

phosphine-boranes (**5**) could be stored well with the careful exclusion of the moisture and air.

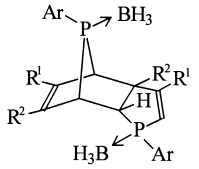
This is the first case where tertiary phosphine oxides are converted to the corresponding phosphine-boranes by a single reagent. Moreover, the transformation is chemoselective: neither the other P-centre, nor the double bonds are involved. It is an additional advantage that the boranes are formed under mild conditions and the yields are good. Only one analogous reaction, the conversion of $(Me_2P(S))_2$ to cyclic $(Me_2PBH_3)_3$ by sodium borohydride at 250°C was reported.[11]

In the mechanism proposed, the first step is the nucleophilic attack of the phosphoryl oxygen of the P(8) atom on the boron atom of the borane to give species **6**. Then a hydride anion shift may lead to an intermediate with a pentacoordinated phosphorus atom (**7**). Species **7** with a trigonal bipyramidal geometry is stabilised by the stepwise loss of the elements of BH_2OH to yield phosphine **9**. The phosphine (**9**) so obtained reacts fast with excess of borane to form the borane complex **5** (Scheme 3).

The deoxygenation of tertiary phosphine oxides by borane has not been described. The reducing ability of tetraalkyldiboranes was, however, studied on different P=O compounds.[12] The deoxygenation by lithium aluminium hydride is a more expedient method that was useful before the spread of silanes, such as trichlorosilane or phenylsilane.[13] Our procedure is a good alternative to Imamoto's method converting tertiary phosphine oxides into the corresponding boranes by reaction with $LiAlH_4$ in the presence of $CeCl_3$ and $NaBH_4$ in one flask.[14]

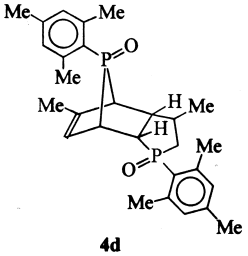
As regards the sight-selectivity of the above procedure, it is known that the two P-centers in the dimers of phosphole oxides may display different reactivity. This is demonstrated by the reaction of the dimer of 1-diethylamino-3-methylphosphole oxide with one equivalent of trichlorosilane in the presence of pyridine to result in the transformation of the bridging $Et_2N–P=O$ function to a P–Cl unit.[15] The ring strain of the 7-phosphanorbornene framework may be responsible for the special reactivity of the bridging phosphorus moiety involved in polytopical rearrangements. C(4)–P(8)–C(7) angles of 83.0°[16] and 80.2°[17] were reported for the dimers of phosphole oxides with methyl or tri-*tert*-butylphenyl substituent on the phosphorus atom.

GC–MS and ^{31}P NMR analyses of the crude reaction mixtures from the interaction of dimers **3a–e** and BMS revealed that some (ca. 2%) of the corresponding diboranes (**10a–e**) was also formed. Structures **10** were also confirmed by HR-FAB.

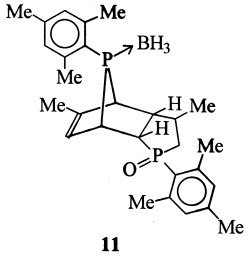


10 R^1, R^2 and Ar as Scheme 2

The crude mixture from the reaction of dimer **3d** and BMS was analysed further by GC–MS, FAB and HR-FAB. Interestingly, traces of the originally desired product **4d**,[18] as well as a small amount of compound **11**[19] could be detected. It can be seen that, although only to a small extent, the selective reduction of the electron-poor 2,3-double-bond of dimer **3d** occurred.



4d



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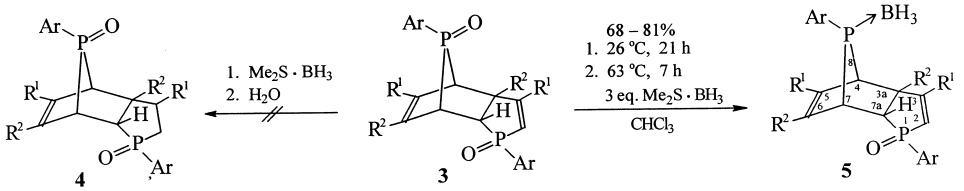
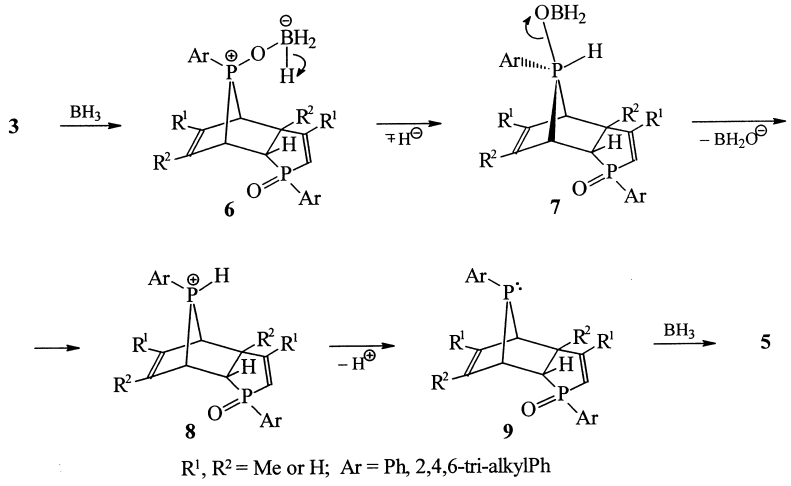
It was not possible to get the diboranes (**10**) in a larger proportion by using more of the BMS reagent with prolonged reaction times. Another approach involving the stereospecific deoxygenation of the dimers (**3a–e**) of phosphole oxides by two equivalents of trichlorosilane[16] followed by reaction with borane was, however, useful in the preparation of the diboranes (**10a–e**) (Scheme 4). Products **10** were obtained in 41–57% yield after column

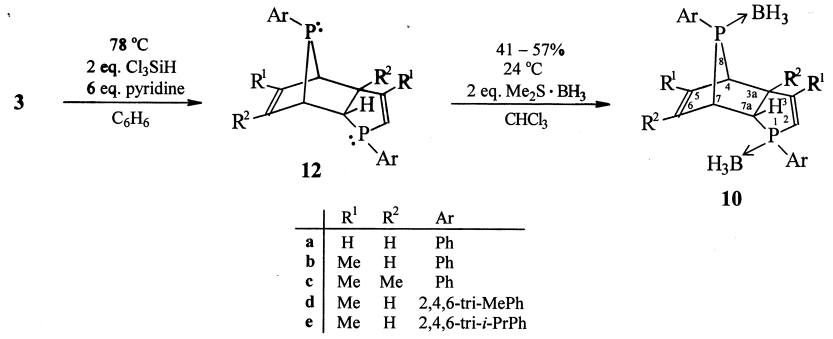


	R^1	R^2	Ar
a	H	H	Ph
b	Me	H	Ph
c	Me	Me	Ph
d	Me	H	2,4,6-tri-MePh
e	Me	H	2,4,6-tri-*i*-PrPh

Scheme 2.



Scheme 3.

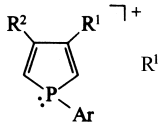


	R¹	R²	Ar
a	H	H	Ph
b	Me	H	Ph
c	Me	Me	Ph
d	Me	H	2,4,6-tri-MePh
e	Me	H	2,4,6-tri-*i*-PrPh

Scheme 4.

chromatography. The diboranes (**10**) were of 95% purity with mainly dioxide **3** as the impurity.

The diboranes (**10a**–**e**) were characterised by ^{31}P, ^{11}B and ^{13}C NMR, as well as EI-mass spectroscopical, FAB and HR-FAB data. Due to the coupling with the ^{11}B atoms, there were two multiplets in the ^{31}P NMR spectra of the diboranes (**10a**–**e**). The molecular ions did not appear in the EI-mass spectra of the products (**10**), only the M–BH_3 and the M–2BH_3 fragments could be found. All molecular weights were, however, confirmed by spectra obtained by the FAB technique. In the EI-mass spectra of diboranes **10a**–**c**,**e**, the corresponding phosphole fragment (**13a**–**c**,**e**) was the base peak.



R¹, R² and Ar as Scheme 4

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Both P(V) and P(III) phosphole dimers are known to undergo de-dimerisation. The EI-mass spectra of mixed phosphole oxide dimers revealed the presence of 1–37% of the monomers.[20] Thermal fragmentation of the phosphole dimers afforded the monomers in 2–20%.[21]

The diboranes (**10**) may be regarded as precursors of diphosphines **12** that are useful ligands in transient metal complexes.[22] Protection of the otherwise air-sensitive phosphines as boranes makes possible their storage.[23] Attempted decomplexation of the diboranes (**10**) under standard conditions[23] using two equivalents of diethylamine in toluene at 40°C led to complicated mixtures containing some of the diphosphine (**12**) and by-products deriving probably from the loss of the bridging P-moiety. Possibilities for the decomplexation of the monoboranes (**5**) and diboranes (**10**) will be soon explored by us.

In summary, a selective method was found for the transformation of a series of bis(phosphine oxides) (**3**) to the corresponding monoboranes (**5**). Not only one of the P-centers, but the double bonds also remained intact. The general applicability of the BMS reagent in the P=O to P→BH_3 conversion and the utilisation of the above method in the synthesis of unsaturated phosphine-boranes is further investigated. The diborane derivatives (**10**) of phosphole dimers prepared from the dioxides (**3**) in two steps are potential precursors of diphosphines (**12**).

Experimental

The ^{31}P, ^{13}C and ^{1}H NMR spectra were taken on a Bruker DRX-500 spectrometer operating at 202.4, 125.7 and 500 MHz, respectively. Chemical shifts are downfield relative to 85% H_3PO_4 or TMS. The couplings are given

in Hz. EI-mass spectra were obtained on a MS-902 spectrometer at 70 eV. FAB measurements were conducted on a reverse geometry VG ZAB-2SEQ instrument using a 30 kV Cs^+ ion gun and 8 kV accelerating voltage.

Phosphole oxide dimers **3a**–**c** and **3e** were synthesised as described earlier.[16,24] Dimer **3d** was prepared in a similar way. Yield: 81%; ^{31}P NMR ($CDCl_3$) δ 58.8 (d, P_1) 81.0 (d, P_8), ^3J(P,P)=38.2; ^{1}H NMR ($CDCl_3$) δ 1.59 (s, 3H, C_3–Me[a]), 2.0 (s, 3H, C_5–Me[a]), 2.22 (s, 3H, ArMe), 2.24 (s, 3H, ArMe), 2.49 (s, 3H, ArMe), 2.57 (s, 6H, ArMe), 2.59 (s, 3H, ArMe), 6.13 (d, J=10.8, 1H, C_6–H), 6.16 [d, $^2J(P_1–H)$=24.6, 1H, C_2–H]; ^{13}C NMR ($CDCl_3$)[25] δ 19.6 [d, $^3J(P_1–C)$=17.1, C_3–Me], 19.8 [d, $^3J(P_8–C)$=2.3, C_5–Me], 21.0 (s, $C_{4'}$–Me[b]), 21.1 (s, $C_{4''}$–Me[b]), 23.2 [d, ^3J(P–C)=6.0, $C_{2'}$–Me[c]], 23.4 [d, ^3J(P–C)=4.7, $C_{2''}$–Me[c]], 23.9 [d, ^3J(P–C)=3.7, $C_{6'}$–Me[c] and $C_{6''}$–Me[c]], 42.2 [dd, $^1J(P_1–C)$=74.7, $^2J(P_8–C)$=13.2, C_{7a}], 47.6 [d, $^1J(P_8–C)$=59.5, C_7], 51.7 [d, $^1J(P_8–C)$=64.5, C_4], 52.1 [dd, $^2J(P_1–C)=^2J(P_8–C)$=12.8, C_{3a}], 123.2 [dd, $^3J(P_1–C)$=9.0, $^2J(P_8–C)$=4.7, C_6], 124.5 [d, $^1J(P_8–C)$=92.5, $C^d_{1''}$], 128.1 [d, $^1J(P_1–C)$=95.5, C^d_2], 129.9 [d, $^3J(P_8–C)$=11.1, $C^e_{3''}$], 130.0 [d, $^3J(P_8–C)$=11.3, $C^e_{5''}$], 130.6 [d, $^3J(P_1–C)$=11.3, $C^e_{3'}$ and $C^e_{5'}$], 130.4 [d, $^1J(P_1–C)$=102.0, $C^d_{1'}$], 136.5 [d, $^2J(P_8–C)$=12.1, C_5], 140.5 ($C^f_{2'}$), 140.6 (s, $C^f_{2''}$ and $C^f_{4'}$), 140.9 ($C^f_{4''}$), 141.0 (s, $C^f_{6'}$), 141.2 (s, $C^f_{6''}$), 157.6 [dd, ^2J(P1–C)=23.7, ^3J(P8–C)=9.1, C3] [a,b]may be reversed, [c–f]tentative assignment; MS, *m/z* (relative intensity) 464 (M^+, 100), 449 (M–Me, 18), 298 (M–ArPO, 92).

General procedure for the preparation of monophosphine-boranes 5a–e

To 0.7 mmol of dimer **3a**–**e** in 10 ml of absolute chloroform was added 1.05 ml of 2 M dimethylsulfide borane in THF solution (2.1 mmol) and the mixture stirred at room temperature for 20 h and then at the boiling point for 7 h. After the addition of 1 ml of water, the mixture was stirred for 10 min and then filtered. The organic phase of the filtrate was separated and dried ($MgSO_4$). The crude product obtained after evaporating the volatile components was purified by column chromatography (2% methanol in chloroform, silica gel) to give products **5a**–**e** as semicrystalline solids.

3,10-Diphenyl-3,10-diphosphatricyclo[5.2.1.0^{2,6}]deca-4,8-diene 3-oxide 10-borane (5a).[26] Yield: 78%; ^{31}P NMR ($CDCl_3$) δ 56.1 [d, ^3J(P,P)=36.1, P_1], 128.8 (m, P_8); ^{11}B NMR ($CDCl_3$) δ −35.1; ^{1}H NMR ($CDCl_3$) δ 5.98 [d, ^3J(H,H)=4.9, 1H, C_5–H], 6.28 [bd, ^2J(P,H)=24.4, 1H, C_2–H], 6.63 [d, ^3J(H,H)∼5, 1H, C_6–H], 6.85 [dd, ^3J(P,H)=42.8, ^3J(H,H)=8.1, 1H, C_3–H]; ^{13}C NMR ($CDCl_3$)[25] δ 39.8 [dd, $^1J(P_1–C)$=77.4, $^2J(P_8–C)$=15.6, C_{7a}], 42.3 [d, $^1J(P_8–C)$=31.6, C_7], 44.4 [d, $^1J(P_8–C)$=34.4, C_4], 50.4 [dd, $^2J(P_1–C)$=13.3, $^2J(P_8–C)$=17.7, C_{3a}], 126.3 [d, $^1J(P_8–C)$=45.9, $C_{1''}$], 128.7 [d, $J(P_8–C)$=9.2, $C^a_{3''}$], 128.9 [d, $J(P_1–C)$=12.2, $C^b_{3'}$], 129.2 (s, C_6), 129.7 [d, $^1J(P_1–C)$=91.3, C_2], 130.7 [d, $J(P_1–C)$=10.0, $C^b_{2'}$], 131.3 (s, $C_{4''}$), 132.3 [d, $J(P_1–C)$=2.2, $C_{4'}$], 133.0 [d, $^1J(P_1–C)$=100.7, $C_{1'}$], 132.8 [$J(P_8–C)$=8.3, $C^a_{2''}$], 134.12 (s, C_5), 150.5 [dd, $^2J(P_1–C)$=20.8, $^3J(P_8–C)$=10.3, C_3] [a,b]may be reversed; MS, *m/z* (relative intensity) 336 ($M-BH_3$, 10), 228 (336−PhP, 57), 227 (228−H, 100); FAB, M+H=351; HR-FAB, $(M+H)_{measured}$=351.1184, $C_{20}H_{22}BOP_2$ requires 351.1239 for the ^{11}B isotope.

3,10-Diphenyl-5,8-dimethyl-3,10-diphosphatricyclo-[5.2.1.0^{2,6}]deca-4,8-diene 3-oxide 10-borane (5b).[26] Yield: 74%; ^{31}P NMR ($CDCl_3$) δ 55.4 [d, ^3J(P,P)=37.2, P_1], 127.8 (m, P_8); ^{11}B NMR ($CDCl_3$) δ −35.0; ^{1}H NMR ($CDCl_3$) δ 1.68 (s, 3H, C_3–Me[a]), 2.11 (s, 3H, C_5–Me[a]), 5.76 [d, ^2J(P,H)=23.6, 1H, C_2–H], 6.24 (s, 1H, C_6–H); ^{13}C NMR ($CDCl_3$)[25] δ 18.9 (s, C_5–Me), 19.7 [d, $^3J(P_1–C)$=17.0, C_3–Me], 41.4 [dd, $^1J(P_1–C)$=74.6, $^2J(P_8–C)$=15.7, C_{7a}], 41.8 [d, $^1J(P_8–C)$=31.5, C_7], 48.6 [d, $^1J(P_8–C)$=35.5, C_4], 53.0 [dd, $^2J(P_1–C)$=11.5, $^2J(P_8–C)$=17.9, C_{3a}], 124.4 [d, $^1J(P_1–C)$=99.6, C_2], 126.8 [d, $^1J(P_8–C)$=46.7, $C_{1''}$], 127.3 (s, C_6), 128.6 [d, $J(P_8–C)$=9.5, $C^b_{3''}$], 128.8 [d, $J(P_1–C)$=12.0, $C^c_{3'}$], 130.7 [d, $J(P_1–C)$=9.9, $C^c_{2'}$], 131.1 (s, $C^d_{4'}$), 132.0 (s, $C^{4''d}$), 132.2 [d, $J(P_8–C)$=8.3, $C^b_{2''}$], 133.4 [d, $^1J(P_1–C)$=101.0, $C_{1'}$], 138.8 (s, C_5), 161.2 [dd, $^2J(P_1–C)$=21.7, ^3J(P8–C)=8.6, C3] [a–d]may be reversed; MS, *m/z* (relative intensity) 378 (M^+, 2), 364 ($M-BH_3$, 23), 256 (364−PhP, 87), 255 (256−H, 100); FAB, M+H=379; HR-FAB, $(M+H)_{measured}$=379.1502, $C_{22}H_{26}BOP_2$ requires 379.1552 for the ^{11}B isotope.

3,10-Diphenyl-5,6,8,9-tetramethyl-3,10-diphosphatricyclo[5.2.1.0^{2,6}]deca-4,8-diene 3-oxide 10-borane (5c).[26] Yield: 72%; ^{31}P NMR ($CDCl_3$) δ 52.6 [d, ^3J(P,P)=39.9, P_1], 135.7 (m, P_8); ^{11}B NMR ($CDCl_3$) δ −30.9; ^{1}H NMR ($CDCl_3$) δ 1.43 (s, 3H, C_{3a}–Me[a]), 1.74 (s, 3H, C_3–Me[a]) 1.77 (s, 3H, C_6–Me[a]), 1.94 (s, 3H, C_5–Me[a]), 5.79 [d, ^2J(P,H)=23.0, 1H, C_2–H]; ^{13}C NMR ($CDCl_3$)[25] δ 15.7 (s, C_6–Me[b]), 16.0 (s, C_5–Me[b]), 17.2 [d, $^3J(P_1–C)$=18.9, C_3–Me], 24.2 (s, C_{3a}–Me), 47.5 [dd, $^1J(P_1–C)$=75.3, $^2J(P_8–C)$=17.2, C_{7a}), 47.6 [d, $^1J(P_8–C)$=29.9, C_7], 56.1 [d, $^1J(P_8–C)$=32.7, C_4], 59.3 [dd, $^2J(P_1–C)$=12.0, $^2J(P_8–C)$=17.3, C_{3a}), 122.1 [d, $^1J(P_1–C)$=99.5, C_2), 128.4 [d, $J(P_8–C)$=9.2, $C^c_{3''}$], 128.7 [d, $J(P_1–C)$=12.0, $C^d_{3'}$], 129.8 [d, $^1J(P_8–C)$=52.7, $C_{1''}$], 130.2 (s, $C_{4''}$), 130.5 [d, $J(P_1–C)$=10.6, $C^d_{2'}$], 130.6 [d, $J(P_8–C)$=8.3, $C^c_{2''}$], 131.8 [d, $^4J(P_1–C)$=2.0, $C_{4'}$], 134.0 [d, $^1J(P_1–C)$=99.9, $C_{1'}$], 135.2 (s, C_5), 135.8 [d, J(P–C)=3.4, C_6], 166.9 [dd, $^2J(P_1–C)$=22.0, $^3J(P_8–C)$=6.9, C3][1] tentative assignment, [b–d]may be reversed; MS, *m/z* (relative intensity) 392 ($M-BH_3$, 15), 284 (392−PhP, 43), 269 (284−Me, 100); FAB, M+H=407; HR-FAB, $(M+H)_{measured}$=407.1809, $C_{24}H_{30}BOP_2$ requires 407.1865 for the ^{11}B isotope.

3,10-Di(2′,4′,6′-trimethylphenyl-)5,8-dimethyl-3,10-diphosphatricyclo[5.2.1.0^{2,6}]deca-4,8-diene 3-oxide 10-borane (5d).[26] Yield: 81%; ^{31}P NMR ($CDCl_3$) δ 58.1 [d, ^3J(P,P)=37.3, P_1], 132.8 (m, P_8); ^{11}B NMR ($CDCl_3$) δ −34.7; ^{1}H NMR ($CDCl_3$) δ 1.64 (s, 3H, C_3'Me[a]), 2.04 (s, 3H, C_5'Me[a]), 2.26 (s, 3H, ArMe), 2.29 (s, 3H, ArMe), 2.44 (s, 3H, ArMe), 2.49 (s, 3H, ArMe), 2.56 (s, 6H, ArMe), 6.19 (s, 1H, C_6(H), 6.22 [d, ^2J(P,H)=24.3, 1H, C_2–H]; ^{13}C NMR ($CDCl_3$)[25] δ 19.0 (s, C_5–Me), 19.8 [d, $^3J(P_1–C)$=17.1, C_3–Me], 21.1 (s, $C_{4'}$–Me, $C_{4''}$–Me), 23.6 [d, $^3J(P_1–C)$=5.2, $C_{2'}$–Me[b]], 23.7 [d, $^3J(P_1–C)$=4.7, $C_{6'}$–Me[b]], 24.0 [d, $^3J(P_8–C)$=3.7, $C_{2''}$–Me, $C_{6''}$–Me], 41.9 [dd, $^1J(P_1–C)$=74.4, $^2J(P_8–C)$=17.0, C_{7a}], 46.5 [d, $^1J(P_8–C)$=32.4, C_7], 51.1 [d, $^1J(P_8–C)$=35.0, C_4], 52.2 [dd, $^2J(P_1–C)$=12.0, $^2J(P_8–C)$=18.4, C_{3a}], 123.0 [d, $^1J(P_8–C)$=45.6, $C_{1''}$], 126.7 (s, C_6), 128.0 [d, $^1J(P_1–C)$=96.9, C_2], 130.1

[d, $^3J(P_8–C)$=7.5, $C^c_{3''}$], 130.2 [d, $^3J(P_8–C)$=7.7, $C^c_{5''}$], 130.9 [d, $^3J(P_1–C)$=11.2, $C_{3'}$, $C_{5'}$], 139.8 (s, $C^d_{4'}$), 140.6 (s, $C^d_{4''}$), 140.7 (s, $C^d_{2''}$), 140.8 (s, $C^d_{6''}$), 140.9 [d, $^2J(P_1–C)$=8.2, $C^d_{2'}$], 141.1 [d, $^2J(P_1–C)$=7.5, $C^d_{6'}$], 141.5 [d, $^2J(P_8–C)$=2.0, C_5], 158.1 [dd, $^2J(P_1–C)$=23.0, $^3J(P_8–C)$=9.7, C_3] [a–c]may be reversed, [d]tentative assignment; MS, *m/z* (relative intensity) 462 (M^+, 3), 448 (M−BH_3, 36), 329 (448−Ar, 23), 298 (448−ArP, 64), 297 (298−H, 54), 119 (Ar, 100); FAB, M+H=463; HR-FAB, $(M+H)_{measured}$=463.2434, $C_{28}H_{38}BOP_2$ requires 463.2491 for the ^{11}B isotope.

3,10-Di(2′,4′,6′-tri-*i*-propylphenyl-)5,8-dimethyl-3,10-diphosphatricyclo[5.2.1.0^{2,6}]deca-4,8-diene 3-oxide 10-borane (5e).[26] Yield: 68%; ^{31}P NMR ($CDCl_3$) δ 57.3 [d, $^3J(P,P)$=36.8, P_1], 127.3 (m, P_8); ^{11}B NMR ($CDCl_3$) δ −33.1; ^1H NMR ($CDCl_3$) δ 1.61 (s, 3H, C_3–Me^a), 2.0 (s, 3H, C_5–Me^a), 6.12 (s, 1H, C_6–H), 6.21 [d, ^2J(P,H)=24.1, 1H, C_2–H][b]; ^{13}C NMR ($CDCl_3$)[25] δ 18.7 (s, C_5–Me), 19.4 [d, $^3J(P_1–C)$=17.1, C_3–Me], (23.6 (s, *ortho*-CH(*C*H_3)$_2$), 24.2 (s, $C_{4'}$–CH(*C*H_3)$^c_2$), 25.3 (s, $C_{4''}$–CH(*C*H_3)$^c_2$), 32.0 [d, $^3J(P_8–C)$=4.7, $C_{2''}$–*C*HMe^d_2, $C_{6''}$–*C*HMe^d_2), 32.3 [d, $^3J(P_1–C)$=5.7, $C_{2'}$–*C*HMe^d_2, $C_{6'}$–*C*HMe^d_2), 34.0 (s, $C_{4'}$–*C*HMe^e_2), 34.2 (s, $C_{4''}$–*C*HMe^e_2), 43.1 [dd, $^1J(P_1–C)$=74.8, $^2J(P_8–C)$=17.1, C_{7a}], 47.4 [d, $^1J(P_8–C)$=31.7, C_7], 52.2 [dd, $^2J(P_1–C)$=11.7, $^2J(P_8–C)$=18.7, C_{3a}], 52.8 [d, $^1J(P_8–C)$=35.1, C_4], 120.7 [d, $^1J(P_8–C)$=44.3, $C_{1''}$], 122.1 [d, $^3J(P_1–C)$=7.6, $C^f_{3'}$], 122.2 [d, $^3J(P_1–C)$=7.7, $C^f_{5'}$], 122.5 [d, $^3J(P_8–C)$=11.2, $C_{3''}$, $C_{5''}$], 126.9 (s, C_6), 127.4 [d, $^1J(P_1–C)$=96.6, C_2], 130.4 [d, $^1J(P_1–C)$=103.2, $C_{1'}$], 138.7 (s, C_5), 151.3 (s, $C^g_{4'}$, $C^g_{4''}$), 151.4 (s, $C^g_{6'}$), 152.0 (s, $C^g_{2''}$, $C^g_{6''}$), 152.2 [d, $^2J(P_1–C)$=7.5, $C^g_{2'}$], 158.2 [dd, $^2J(P_1–C)$=23.5, $^3J(P_8–C)$=9.3, C_3] [a,c,e,f]may be reversed, [b]signals of the *i*-Pr groups are overlapped in the range of δ_H 1.10–1.35, [d,g]tentative assignment; MS, *m/z* (relative intensity) 630 (M^+, 2), 616 (M−BH_3, 31), 413 (616−Ar, 100), 382 (616−ArP, 42), 381 (382−H, 53), 203 (Ar, 85); FAB, M+H=631; HR-FAB, $(M+H)_{measured}$=631.4294, $C_{40}H_{62}BOP_2$ requires 631.4369 for the ^{11}B isotope.

General procedure for the preparation of bis(phosphine-boranes) 10a–e

To 2.63 mmol of dimer **3a**–**e** in 25 ml of degassed benzene was added 1.28 ml (15.8 mmol) of pyridine and 0.58 ml (5.26 mmol) of trichlorosilane and the mixture was stirred at the boiling point for 4 h. Contents of the flask were filtered and the filtrate evaporated, finally under high vacuum, to leave an oily residue of **10a**–**e** in quantitative yield. The diphosphine (**10a**–**e**) so obtained was dissolved in 30 ml of degassed dichloromethane and treated with 3.0 ml of 2 M dimethylsulfide borane in THF solution (6.0 mmol) at room temperature. After a 2 h reaction time, 1 ml of water was added and the mixture stirred for 10 min. The precipitated material was removed by filtration and the organic phase dried ($MgSO_4$). The crude product obtained after evaporating the volatile components was purified by column chromatography (2% methanol in chloroform, silica gel) to give diboranes **10a**–**e** as semicrystalline solids in a purity of ca. 95% according to ^{31}P NMR.

3,10-Diphenyl-3,10-diphosphatricyclo[5.2.1.0^{2,6}]deca-4,8-diene 3,10-diborane (10a).[26] Yield: 57%; ^{31}P NMR ($CDCl_3$) δ 47.5 (m, P_1), 129.2 (m, P_8); ^{11}B NMR ($CDCl_3$) δ −36.6 and −35.7; ^{13}C NMR ($CDCl_3$)[25] δ 40.5 [dd, $^1J(P_1–C)$=40.1, $^2J(P_8–C)$=17.8, C_{7a}], 42.4 [dd, $^2J(P_1–C)$=5.5, $^1J(P_8–C)$=30.9, C_7], 42.9 [d, $^1J(P_8–C)$=33.8, C_4], 54.1 [d, $^2J(P_8–C)$=16.9, C_{3a}], 125.9 [d, $^1J(P_1–C)$=48.4, $C^a_{1'}$], 126.0 [d, $^1J(P_8–C)$=46.0, $C^a_{1''}$], 128.2 [d, J(P–C)=9.5, $C^b_{3''}$], 128.6 [d, J(P–C)=9.9, $C^b_{37'}$], 130.4 [d, $J(P_1–C)$=49.6, C_2], 130.4 (s, C^c_6), 130.8 (s, $C^c_{4'}$), 131.3 (s, $C^c_{4''}$), 131.5 [d, J(P–C)=9.2, $C^b_{2'}$], 132.3 [d, J(P–C)=8.1, $C^b_{2''}$], 133.3 (s, C_5), 149.2 [dd, $^2J(P_1–C)$=6.1, $^3J(P_8–C)$=9.5, C_3]; [a]may be reversed, [b,c]tentative assignment; MS, *m/z* (relative intensity) 334 (M−BH_3, 36), 320 (334−BH_3, 43), 211 (M−PhPBH_3–BH_3–H, 34), 160 ($C_{10}H_9P$, 100); FAB, M+H=349; HR-FAB, $(M+H)_{measured}$=349.1569, $C_{20}H_{25}B_2P_2$ requires 349.1618 for the ^{11}B isotope.

3,10-Diphenyl-5,8-dimethyl-3,10-diphosphatricyclo-[5.2.1.0^{2,6}]deca-4,8-diene 3,10-diborane (10b).[26] Yield: 41%; ^{31}P NMR ($CDCl_3$) δ 45.9 (m, P_1), 129.2 (m, P_8); ^{11}B NMR ($CDCl_3$) δ −35.8 (broad signal); ^{13}C NMR ($CDCl_3$)[25] δ 19.0 (C_5–Me), 19.3 [d, $^3J(P_1–C)$=12.2, C_3–Me], 42.2 [dd, $^1J(P_1–C)$=40.2, $^2J(P_8–C)$=17.7, C_{7a}], 42.5 [dd, $^2J(P_1–C)$= 5.8, $^1J(P_8–C)$=30.6, C_7], 47.7 [d, $^1J(P_8–C)$=34.9, C_4], 56.9 [d, $^2J(P_8–C)$=19.3, C_{3a}], 120.6 [d, $^1J(P_1–C)$=54.2, C_2], 127.5 (s, C_6), 128.6 [d, J(P–C)=9.1, $C^a_{3''}$], 128.8 [d, J(P–C)=9.7, $C^a_{3'}$], 131.1 (s, $C^b_{4''}$), 131.3 (s, $C^b_{4'}$), 131.8 [d, J(P–C)=9.5, $C^a_{2'}$], 132.1 [d, J(P–C)=8.4, $C^a_{2''}$], 139.8 (s, C_5), 159.4 [dd, $^2J(P_1–C)$=7.3, $^3J(P_8–C)$=9.6, C_3], signals of the $C_{1'}$ and $C_{1''}$ atoms are overlapped in the range of 131.6–132.2; [a,b]tentative assignment; MS, *m/z* (relative intensity) 362 (M−BH_3, 11), 348 (362−BH_3, 32), 239 (M−PhPBH_3–BH_3–H, 68), 174 ($C_{11}H_{11}P$, 100); FAB, M+H=377; HR-FAB $(M+H)_{measured}$=377.1837, $C_{22}H_{29}B_2P_2$ requires 377.1931 for the ^{11}B isotope.

3,10-Diphenyl-5,6,8,9-tetramethyl-3,10-diphosphatri-cyclo[5.2.1.0^{2,6}]deca-4,8-diene 3,10-diborane (10c).[26] Yield: 54%; ^{31}P NMR ($CDCl_3$) δ 40.4 (m, P_1), 144.6 (m, P_8); ^{11}B NMR ($CDCl_3$) δ −35.5 and −30.8; ^{13}C NMR ($CDCl_3$)[25] δ 16.3 (C_6–Me^a), 17.4 (C_5–Me^a), 17.5 (C_3–Me^a), 24.8 (C_{3a}–Me), 47.8 [dd, $^1J(P_1–C)$=37.2, $^2J(P_8–C)$=20.0, C_{7a}], 48.7 [dd, $^2J(P_1–C)$=5.5, $^1J(P_8–C)$=29.4, C_7], 56.4 [d, $^1J(P_8–C)$=31.3, C_4], 63.5 [d, $^2J(P_8–C)$=17.0, C_{3a}], 116.7 [d, $^1J(P_1–C)$=54.7, C_2], 128.6 [d, J(P–C)=9.2, $C^b_{3''}$], 128.9 [d, J(P–C)=9.7, $C^b_{3'}$], 130.0 [d, $^1J(P_8–C)$=53.4, $C^c_{1''}$], 130.4 (s, $C^d_{4''}$), 130.8 [d, J(P–C)=8.0, $C^b_{2''}$], 131.0 (s, $C^d_{4'}$), 131.2 [d, J(P–C)=9.2, $C^b_{2'}$], 133.6 [d, $^1J(P_1–C)$=49.6, $C^c_{1'}$], 135.6 [d, $^2J(P_8–C)$=3.0, C_6], 136.9 (s, C_5), 166.1 [dd, $^2J(P_1–C)$=$^3J(P_8–C)$=7.0, C_3]; [a,b]tentative assignment, [c,d]may be reversed; MS, *m/z* (relative intensity) 390 (M−BH_3, 10), 376 (390−BH_3, 42), 267 (M−PhPBH_3–BH_3–H, 13), 188 ($C_{12}H_{13}P$, 100); FAB, M+H=405; HR-FAB, $(M+H)_{measured}$=405.2179, $C_{24}H_{33}B_2P_2$ requires 405.2244 for the ^{11}B isotope.

3,10-Di(2′,4′,6′-trimethylphenyl-)5,8-dimethyl-3,10-di-phosphatricyclo[5.2.1.0^{2,6}]deca-4,8-diene 3,10-diborane (10d).[26] Yield: 45%; ^{31}P NMR ($CDCl_3$) δ 52.4 (m, P_1), 133.3 (m, P_8); ^{11}B NMR ($CDCl_3$) δ −33.9 (broad signal); ^{13}C NMR ($CDCl_3$)[25] δ 18.9 (s, C_5–Me), 19.2 [d, $^3J(P_1–C)$=12.3, C_3–Me], 20.9 (s, $C_{4'}$–Me^a), 21.0 (s, $C_{4''}$–Me^a), 23.9 [d, ^3J(P–C)=4.9, $C_{2'}$–Me^b, $C_{6'}$–Me^b], 24.0 [d, ^3J(P–C)=4.5, $C_{2''}$–Me^b, $C_{6''}$–Me^b], 41.8 [dd, $^1J(P_1–C)$=38.5, $^2J(P_8–C)$=19.3, C_{7a}], 46.3 [dd, $^1J(P_8–C)$=31.7,

$^2J(P_1–C)$=6.0, C_7], 50.5 [d, $^1J(P_8–C)$=34.0, C_4], 55.6 [dd, $^2J(P_1–C)$=2.0, $^2J(P_8–C)$=17.2, C_{3a}], 117.2 [d, $^1J(P_1–C)$=55.9, C_2], 122.7 (s, C_6), 123.3 [d, ^1J(P–C)=52.8, $C^c_{1''}$], 129.2 [d, ^1J(P–C)=48.0, $C^c_{1'}$], 130.5 [d, ^3J(P–C)=8.2, $C^d_{3''}$, $C^d_{5''}$], 130.7 [d, ^3J(P–C)=8.0, $C^d_{3'}$, $C^d_{5'}$], 139.9 (s, $C^e_{4'}$, $C^e_{4''}$), 140.1 [d, $^2J(P_8–C)$=2.2, C_5], 140.6 (s, $C^e_{2'}$), 140.7 (s, $C^e_{6'}$, $C^e_{6''}$), 141.0 (s, $C^e_{2''}$), 156.4 [dd, $^2J(P_1–C)=^3J(P_8–C)$=9.9, C_3]; [a,c]may be reversed, [b,d,e]tentative assignment; MS, *m*/*z* (relative intensity) 446 (M−BH_3, 2), 432 (446−BH_3, 6), 281 (M−ArPBH_3–BH_3–H, 100), 216 ($C_{14}H_{17}P$, 32); FAB, M+H=461; HR-FAB $(M+H)_{measured}$=461.2786, $C_{28}H_{41}B_2P_2$ requires 461.2870 for the ^{11}B isotope.

3,10-Di(2′,4′,6′-tri-*i*-propylphenyl-)5,8-dimethyl-3,10-diphosphatricyclo[5.2.1.0^{2,6}]deca-4,8-diene 3,10-diborane (10e).[26] Yield: 42%; ^{31}P NMR ($CDCl_3$) δ 49.9 (m, P_1), 128.1 (m, P_8); ^{11}B NMR ($CDCl_3$) δ −33.1 and −30.9; ^{1}H NMR ($CDCl_3$) δ 1.63 (s, 3H, C_3–Me[a]), 1.99 (s, 3H, C_5–Me[a]), 6.0 [d, ^2J(P,H)=31.3, 1H, C_2–H], 6.14 (s, 1H, C_6–H)[b]; ^{13}C NMR ($CDCl_3$)[25] δ 19.1 (s, C_5–Me), 19.5 [d, $^3J(P_1–C)$=12.1, C_3–Me], (24.0 (s, *ortho*-CH–CH_3)$_2$), 25.6 (s, $C_{4'}$–CH(CH_3)$^c_2$), 26.4 (s, $C_{4''}$–CH(CH_3)$^c_2$), 32.8 [d, $^3J(P_8–C)$=6.3, $C_{2''}$–CHMe$^d_2$, $C_{6''}$–CHMe$^d_2$), 33.0 [d, $^3J(P_1–C)$=6.7, $C_{2'}$–CHMe$^d_2$, $C_{6'}$–CHMe$^d_2$), 34.5 (s, $C_{4'}$–CHMe$_2$ and $C_{4''}$–CHMe$_2$), 44.3 [dd, $^1J(P_1–C)$=39.3, $^2J(P_8–C)$=19.1, C_{7a}], 47.7 [dd, $^1J(P_8–C)$=37.3, $^2J(P_1–C)$=5.0, C_7], 53.0 [d, $^1J(P_8–C)$=34.6, C_4], 56.1 [dd, $^2J(P_1–C)$=2.5, $^2J(P_8–C)$=19.4, C_{3a}], 121.1 [d, ^1J(P–C)=45.7, $C^e_{1''}$], 122.5 [d, ^3J(P–C)=7.4, $C^f_{3'}$], 122.9 [d, ^3J(P–C)=7.4, $C^f_{5'}$], 123.2 [d, ^3J(P–C)=7.4, $C^f_{3''}$ and $C^f_{5''}$], 124.6 [d, $^1J(P_1–C)$=54.5, C_2], 128.1 [d, $^2J(P_8–C)$=4.0, C_6), 129.2 (d, ^1J(P–C)=49.1, $C^e_{1'}$], 139.7 (s, C_5), 151.3 (s, $C^g_{4'}$, $C^g_{4''}$ and $C^g_{6'}$), 151.9 (s, $C^g_{6''}$), 152.5 [d, $^2J(P_8–C)$=7.6, $C^g_{2''}$], 152.7 [d, $^2J(P_1–C)$=8.8, $C^g_{2'}$], 156.2 [dd, $^2J(P_1–C)=^3J(P_8–C)$=8.8, C_3]; [a,c,e]may be reversed, [b]signals of the *i*-Pr groups are overlapped in the range of δ_H 1.16–1.40, [d,f,g]tentative assignment; MS, *m*/*z* (relative intensity) 614 (M−BH_3, 40), 600 (614−BH_3, 100), 365 (M−ArPBH_3–BH_3–H, 68), 300 ($C_{20}H_{29}P$, 98); FAB, M+H=629; HR-FAB $(M+H)_{measured}$=629.4672, $C_{40}H_{65}B_2P_2$ requires 629.4748 for the ^{11}B isotope.

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18. For **4d**: FAB, 467 (M+H); HR-FAB, $(M+H)_{measured}$= 467.2169, $C_{28}H_{37}O_2P_2$ requires 467.2269.
19. For **11**: FAB, 465 (M+H); HR-FAB, $(M+H)_{measured}$= 465.2581, $C_{28}H_{40}BOP_2$ requires 465.2647.
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25. The carbon atoms of P_2–Ar are marked by $C_{n'}$, while those of P_8–Ar by $C_{n''}$.
26. According to the IUPAC nomenclature, the following numbering was used for naming products **5** and **10**: