$[(C_5Me_5)_2Co(CO)_3(\mu\text{-}CO)(\mu_3\text{-}CMe)]$, 1.932 (6) Å.[49] The Co–C(1) distance is slightly longer than the Co–$[\mu\text{-}C(SMe)_2]$ distance in **4**, 1.916 (2) Å.[38]

The Co–C(1)–Fe(1) and Fe(1)–C(1)–Fe(2) angles of 81.8° and 84.5°, respectively, are in the range observed for closed μ_3-carbyne complexes.[30,40b] The plane defined by Co–C(1)–Fe(1) makes a dihedral angle of 128.9° with the Co–C(1)–S plane. The Co–C(1)–S triangle has a C–S distance of 1.740 (6) Å, substantially shorter than the C(2)–S distance 1.837 (7) Å and shorter than that observed in **4**, 1.789 (2) Å.[38] It is much less than the C–S single bonds in ethylene sulfide, 1.819 (1) Å, and tetrahydrothiophene, 1.839 (1) Å.[50] It is slightly shorter than C(sp^2)–S bonds (1.75–1.78 Å)[51,52] but longer than the C–S distance in thiophene, 1.718 (5) Å.[53] Thus it would appear that the C–S bond in **2a** has some double-bond character. Molecular orbital calculations[38] on **4** suggest that the Co–C–S triangle is stabilized by σ bonding from p orbitals on carbon and sulfur and back-donation from cobalt d orbitals into the π* orbital located mainly on these two atoms. The bonding in the Co–C(1)–S triangle of **2a** is probably very similar. The stability of this triangle in both **2a** and **4** may account for their reactions with phosphines, which lead to the replacement of a CO group on the Co rather than displacement of the coordinated sulfur (eq 2 and ref 38).

As can be seen in Figures 1 and 2 the basic geometries of **2a** and **3a** are very similar. The greater electron density provided by PPh_3 substitution causes shortening of the Co–CO bonds (Co–C(3) = 1.67 (3) Å; Co–C(6) = 1.80 (2) Å in **3a** vs. 1.780 (8) and 1.897 (7) Å, respectively, in **2a**). In addition, the Co–C(1) distance is ~0.06 Å shorter in **3a** possibly as a result of greater d–π* back-bonding into the C–SMe fragment. As a consequence, the Fe(2)–C(1) distance is ~0.04 Å longer. The greater steric requirements of PPh_3 as compared with CO are probably responsible for the Fe(1)–Co–P angle (125.1°) being larger than the Fe(1)–Co–C(7) angle (115.9°) in **2a**.

Acknowledgment. This material is based upon work supported by the National Science Foundation under Grant CHE-8100419 (R.J.A.). X-ray diffraction studies were supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Materials Sciences Division, under Contract No. W-7405-ENG-82.

Registry No. **1a**, 76189-80-5; **1b**, 76157-30-7; **2a**, 96211-43-7; **2b**, 96211-44-8; **3a**, 96211-45-9; **3b**, 96211-46-0; **3** (PR_3 = dppe), 96211-52-8; **3c**, 96211-47-1; **3d**, 96211-48-2; **3e**, 96211-49-3; **3f**, 96211-50-6; 3f (PR_3 = dppm), 96211-51-7; dppe, 1663-45-2; $Na[Co(CO)_4]$, 14878-28-5; $Co_2(CO)_8$, 10210-68-1; $Cp_2Fe_2(CO)_3CS$, 67113-80-8; $[Cp_2Fe_2(CO)(\eta'\text{-dppm})(\mu\text{-}CO)(\mu\text{-}CSMe)]BF_4$, 96227-22-4; PPh_3, 603-35-0; PEt_3, 554-70-1; PCy_3, 2622-14-2; $PHPh_2$, 829-85-6; $PMePh_2$, 1486-28-8; $Ph_2PCH_2PPh_2$, 2071-20-7.

Supplementary Material Available: Tables of anisotropic thermal parameters for non-hydrogen atoms and calculated and observed structure factors (11 pages). Ordering information is given on any current masthead page.

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New Difunctional Phosphine–Borane Species as Ligands for Organometallic Compounds

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Convenient high yield syntheses have been developed for the molecules $(CH_3)_3PBH_2P(CH_3)_2{=}X$, where X = O (**1**) and X = S (**4**). $(CH_3)_3PBH_2Br$ can be treated with $K[P(CH_3)_2O]$ or $K[(CH_3)_2PS]$ to give **1** or **4**, respectively. Routes via the intermediates $[(CH_3)_3PBH_2P(CH_3)_2Cl]Cl$, **2**, $[(CH_3)_3PBH_2P(CH_3)_2OCH_3]Cl$, **3**, or $[(CH_3)_3PBH_2P(CH_3)_2NHCH_3]Cl$, **5**, are possible but offer no advantages. However, the conversion of **1** into **4** using P_2S_5 is an acceptable alternative preparation for **4** (45% yield). An imine $(CH_3)_3PBH_2P(CH_3)_2{=}NCH_3$, **6**, was generated from **5** with $n\text{-}C_4H_9Li$ but could not be separated from LiCl. **1** and **4** are easily metalated at one of the $P(CH_3)_3$ methyl groups to yield products for which the formula $Li[CH_2(CH_3)_2PBH_2P(CH_3)_2{=}X]$, where X = O (**7**) and X = S (**9**) is proposed. These reagents afford spirobicyclic complexes with $BeCl_2$ (**8** from **1** via **7**) and $ZnCl_2$ or $CdCl_2$ (**10** and **11**, respectively, from **4** via **9**). All materials were characterized by elemental analyses and spectral data.

Introduction

The stability of metal-to-carbon σ-bonds in organometallic compounds is a function of the nature of the substituents attached to the metal center and the organic ligands. Among the large variety of possible combinations, organic ligands bearing a positively charged onium center proved to be one of the most efficient systems to yield unusual bond characteristics. These unusual properties result from electronic, steric, and mechanistic effects associated with the electronegativity and the bulkiness of the ligand and its stability toward classical reductive elimination. The most thoroughly studied systems are the organometallic derivatives of the ylides of phosphorus and sulfur, as summarized in a number of review articles in the recent literature.[1–3] It has been pointed out previously[4]

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(1) Schmidbaur, H. *Angew. Chem.* **1983**, *95*, 980; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 907; *Acc. Chem. Res.* **1975**, *8*, 62.

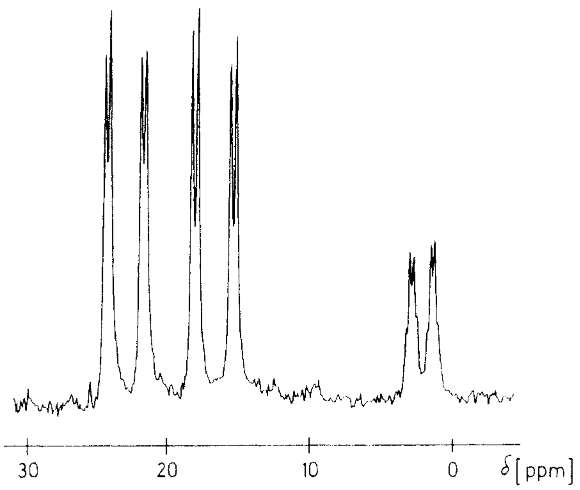
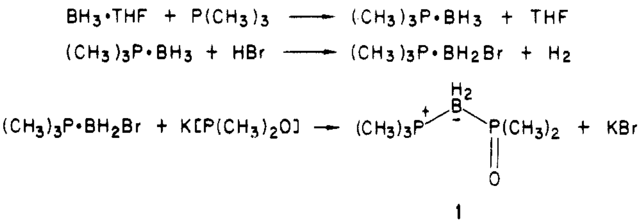
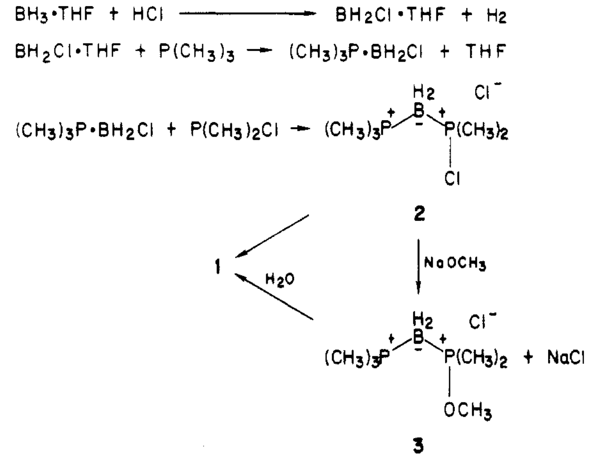


Figure 1. $^{13}C\{^1H\}$ NMR spectrum of the zinc complex **10** in C_6D_6 at 30 °C. The high-field resonance at δ 2.0 represents the diastereotopic methylene hydrogen atoms.

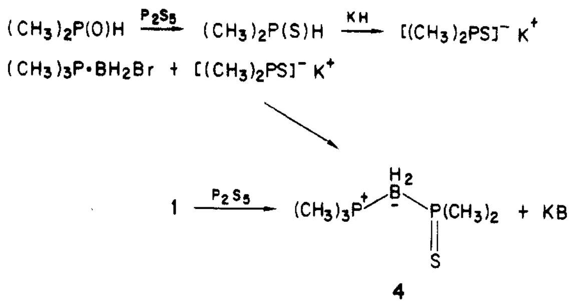
Scheme I



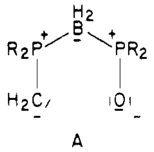
Scheme II



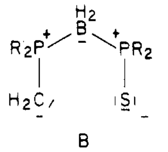
Scheme III



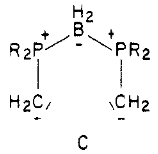
that a few related types of ligands, based, e.g., on phosphine imine or phosphine–borane skeletons, also exhibit quite remarkable properties, but the growth of their organometallic chemistry was much slower than the evolution of ylide coordination chemistry.[4-10] Information on the scope of this area is still rudimentary and is limited to only a small number of papers.[4-13] The present report covers an extension of earlier work, some of which was the subject of a preliminary communication,[13] and draws attention to new chelate systems with a combination of phosphonium methylide and phosphine oxide or sulfide donor centers, respectively, connected through a borohydride bridge (A and B). These ligands are expected to coordinate effectively to "hard" or "soft" metal acceptors, not unlike the symmetrical isoelectronic double ylides C.[5-10] Finally, C is related to the corresponding methine- or nitrido-bridged species $HC[PR_2CH_2]_2^-$ and $N[PR_2CH_2]_2^-$, which were described in a series of reports a few years ago.[14-16]



A



B



C

Results

Synthesis of the Ligand Precursors $(CH_3)_3PBH_2P(CH_3)_2X$ (X = O and S). Parent molecules for anionic ligands of type A and B, preferably the species in which the methylide carbon is protonated, must be considered. Compounds of this constitution have not yet been reported. A synthetic pathway has now been found for the fully methylated homologue **1** from simple starting materials ($BH_3{\cdot}THF$, $P(CH_3)_3$, and $K^+(CH_3)_2PO^-$) according to Scheme I. In two other attempts, the chlorine functional phosphine–borane **2** and the methoxy derivate **3** were synthesized, both of which on hydrolysis should also give the oxide **1** (Scheme II). Though both **2** and **3** could be isolated in a pure state, their hydrolysis gave only disappointingly low yields of the desired final product (**1**).

For the synthesis of the sulfur compound **4**, a route analogous to Scheme I proved to be feasible. Dimethylphosphinous acid was converted into the sulfur compound with P_2S_5 in methylene chloride at −20 °C and then treated with KH to afford potassium dimethylthiohypophosphite. This product on reaction with $(CH_3)_3PBH_2Br$ gave **4** in an overall yield of ca. 40%. Alternatively, compound **1** could be treated with P_2S_5 under similar conditions as $(CH_3)_2P(O)H$ (above) to generate the sulfur analogue, again in

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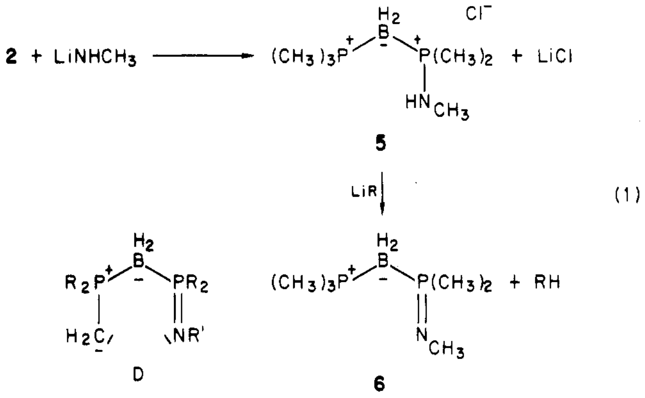
ca. 40% yield (Scheme III).

In order to have a broader choice of reactants available, an amino derivative, 5 was also synthesized according to eq 1. Though it turned out to be of no advantage for the preparation of 1 or 4 (e.g., through hydrolysis), it is of interest as a precursor for a chelating ligand, D, with a nitrogen donor site (6).



Properties and Spectral Data of the Phosphine–Boranes 1–6. The phosphine oxide 1 and sulfide 4 are colorless crystalline solids, which can be easily sublimed in vacuo. They are completely stable to oxygen and water (1 is hygroscopic) and freely soluble in polar organic solvents and aromatic hydrocarbons. Even solutions in water show no signs of decomposition. 4 is also sparingly soluble in pentane. Thus, it appears that the phosphine–borane skeleton of both compounds is remarkably inert, a feature noted before only for the symmetrical bis(phosphino)boronium salts. The chlorophosphine–borane 2 can be crystallized from CH_2Cl_2 or $CHCl_3$ as colorless, moisture-sensitive needles, which slowly decompose on heating or on prolonged storage at room temperature.

The methoxy derivate 3 is thermally more stable, but the crystals (from $CHCl_3$) are hygroscopic.

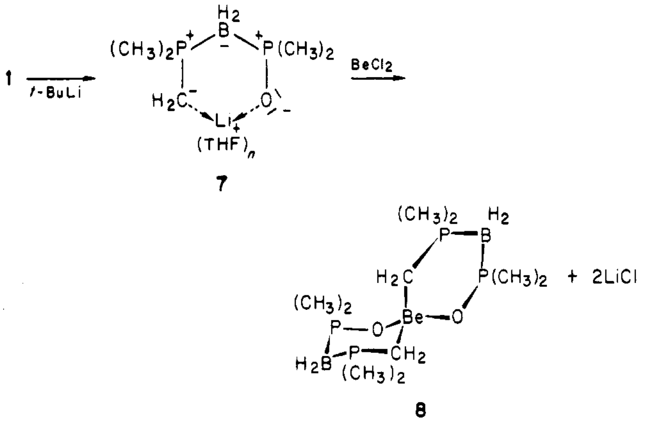
The ^{31}P NMR spectra of compounds 1–6 are characterized by two distinct 1:1:1:1 quartet resonances with ^{31}P–^{11}B couplings of ca. 120 Hz. Accordingly, the $^{13}C\{^1H\}$ and ^1H resonances appear as two doublets of doublets with the expected overall intensity ratios of 3:2 for the $(CH_3)_3P$ and $(CH_3)_2P$ groups, respectively. In the ^{11}B spectrum of 1, a doublet of doublets of triplets is also additional evidence for the proposed structure. Only very broad signals were observed for the hydrogen atoms attached to boron. For 3 and 5, the presence of the methoxy or amino group leads to additional resonances (Table I).

In the IR spectra, $\nu(BH_2)$ vibrations are easily identified in the region around 2400 cm^{-1}. 1 has a diagnostic $\nu(P{=}O)$ absorption at 1120 cm^{-1}, and for 2 $\nu(PCl)$ appears at 501 cm^{-1}. Stretching frequencies for the P–O–C group in 3 are tentatively assigned at 1035 and 965 cm^{-1}.

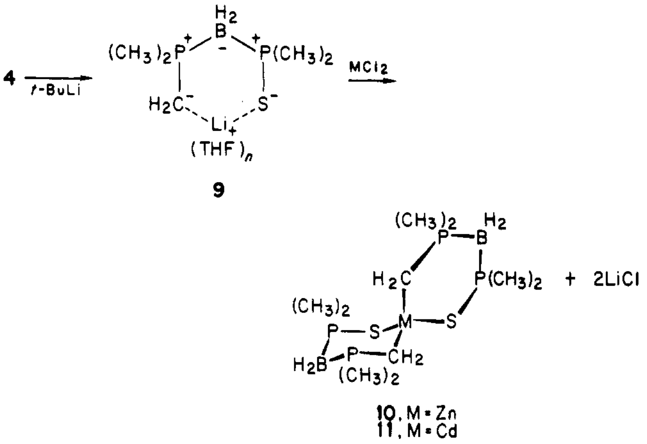
EI mass spectra of compounds 1 and 4 show the parent ions M^+ with high intensity and in the expected isotopic ratio. The main fragment ions are listed in Table I.

Generation of the Chelate Anions and Complexation. Treatment of 1 or 4 with *tert*-butyllithium in THF at low temperature leads to selective metalation of one of the methyl groups at the $(CH_3)_3P$ moiety. The lithiated products form yellow solutions in THF, and further reactions can be carried out in situ.

For the complexation of the oxide ligand 7 with its "hard" donor center, beryllium(II) was chosen as a typical "hard" acceptor. The expected compound 8 could be isolated through vacuum sublimation, but for unknown reasons the yields were rather disappointing at a little more than 10%.



The sulfide ligand of 9 reacts with the "soft" acceptor centers zinc(II) and cadmium(II) to give the spiro chelate complexes 10 and 11, respectively. Yields of the colorless, sublimable, air-stable zinc complex were in excess of 60%. The cadmium analogue was far less thermally stable, and extensive decomposition occurred during sublimation and workup. A major problem in the purification was the separation from unreacted 4, which shows similar solubility properties. Careful fractional sublimation turned out to be most effective.



Complexes 8, 10, and 11 were characterized by elemental analyses and NMR, IR, and mass spectral data. The results are summarized in Table I and in the Experimental Section. The NMR spectra are similar to those of the precursor molecules 1 and 4, with some significant differences in the ^{31}P chemical shifts and in the relative intensities of the methyl resonances. The CH_2 groups generated in the metalation process give rise to high-field ^1H and ^{13}C resonances of complex multiplicity due to extensive P–P couplings and diastereotopic hydrogen atoms as expected for a tetrahedral structure. Though the CH_3 groups at each type of phosphorus atom are also chemically nonequivalent, their chemical shift differences are obviously too small to be detectable in the ^{13}C or ^1H spectra except for compound 8.

The IR spectrum of compound 8 shows the $\nu(P{=}O)$ absorption at 1065 cm^{-1}. This reduction of 55 cm^{-1} as compared to the value for 1 is clearly a consequence of $Be{\leftarrow}O{=}P$ coordination. The $\nu(BH_2)$ bands are largely unchanged in 8 (2395 and 2350 cm^{-1}) as well as in 10 and 11. Molecular ions are observed in the EI mass spectra in low intensity for all three compounds.

Discussion

It has been shown previously that phosphine–boranes, $R_3P{\cdot}BH_3$, $(R_3P)_2BH_2^+$, or $(R_2PBH_2)_n$, have remarkable physical and chemical properties due to an unusually low

Table I. NMR Data of Compounds 1–6, 8, 10, and 11 and Mass Spectra of 1, 4, 8, 10, and 11[a]

		NMR, δ (*J*, Hz)			
		^{31}P	^{1}H	^{13}C	MS (70 eV, EI, 70–100 °C), *m/e* (rel int)
1[b]	PMe_3	−5.5 q (78)	1.57 d (12.0)	11.4 dd (42, 5)	166 (9), 165 (4), 151 (4), 105 (67), 89 (18), 77 (27), 76 (100), 61 (55)
	PMe_2	50.2 q (124)	1.45 d (11.0)	21.1 br d (45)	
2	PMe_3	−9.1 q (89)	1.47 d (12.5)	11.3 dd (46, 6)	
	PMe_2	90.1 q (98)	2.10 d (10.0)	19.2 dd (34, 3)	
3[c]	PMe_3	−8.0 q (79)	1.20 d (12.5)	10.9 dd (45,4)	
	PMe_2	104.2 q (101)	1.50 d (10.5)	13.1 dd (44, 4)	
	OMe		3.32 d (12.0)	53.7 d (10)	
4	PMe_3	−7.3 q (85)	0.52 d (11.2)	11.2 dd (43, 4)	182 (50), 181 (13), 121 (45), 89 (31), 76 (100), 61 (41)
	PMe_2	10.9 q (103)	1.02 d (11.2)	25.3 br d (36)	
5	PMe_3	−8.2 q (107)	1.83 d (12)	11.0 dd (44,4)	
	PMe_2	43.5 q (100)	1.80 d (11)	12.4 dd (48, 5)	
	NMe		2.68 dd (14, 5.5)		
	NH		5.42 br		
6[d]	PMe_3		0.90 d (11)		
	PMe_2		1.20 d (10)		
	NMe		2.90 d (20)		
8	PMe_2	−5.1 dq (95, 15)	1.27 d (11.0)	15.6 dd (42, 3)[f]	339 (100), 338 (70), 324 (47), 252 (26), 190 (25), 174 (>100), 105 (83), 76 (>100)
	PMe_2O	63.6 dq (107)	1.10 m	20.8 d (44)	
	CH_2		−0.13 d (16.0)	6.7 br[g]	
10	PMe_2	−2.0 q (100)	0.71 d (11.2)	16.7 dd (41, 6)	426 (0.8), 425 (0.3), 365 (1.5), 351 (0.7), 289 (1.7), 277 (0.25), 245 (6), 182 (63), 76 (100)
	PMe_2S	18.3 q (90)	1.07 d (11.0)	23.0 dd (38.5)	
	CH_2		−0.22 d (15.2)	2.0 dd (22, 4)[g]	
11	PMe_2	−0.7 q (99)	0.68 d (11.0)	17.4 dd (41, 6)[h]	476 (0.04), 415 (0.13), 295 (0.44), 294 (0.15), 207 (0.57), 182 (90.3), 76 (100)
	PMe_2S	19.2 q (94)	1.04 d (10.6)	23.9 dd (39.5)	
	CH_2		−0.26 d (13.8)[e]	1.3 dd (24, 2)	

[a] Compounds **1**, **4**, **6**, **8**, **10**, and **11** were dissolved in C_6D_6 and compounds **2**, **3**, and **5** in $CDCl_3$. [b] ^{11}B = −31.2 ppm, ddt, $J(^{11}B^{1}H)$ = 99 Hz. [c] ^{11}B = −33.7 ppm, dd, $\{^{1}H\}$. [d] Containing LiCl. [e] $^{2}J(^{111,113}Cd^{1}H)$ = 53.2 Hz, not resolved. [f] Diastereotopic methyl groups. [g] Diastereotopic hydrogen atoms. [h] $^{1}H(^{111,113}Cd^{13}C)$ = 23.0 Hz, not resolved.

hydridic character of the B–H bonds and a robust phosphorus–boron backbone.[4] It has now been demonstrated that related molecules with P═O and P═S functions also exhibit similar features. Both **1** and **4** are inert, water-soluble species of high thermal stability. Upon metalation, metal-to-carbon-to-phosphorus linkages are formed in which the stabilizing influence of the phosphonium center is significant also for the metal-to-carbon bond, as reported earlier for systems of the general formula C. The presence of "hard" or "soft" auxiliary donor functions in A or B broadens the scope of this coordination chemistry considerably, and it is to be anticipated that complexes can be prepared for many metals of the periodic table. Presently, the number of examples is very limited, but their properties have confirmed the basic concept, and extensions are certainly possible.

Experimental Section

The experimental procedures and instrumentation have been decribed in two previous papers.[10,17] Tetrahydrofuran–borane[18] and trimethylphosphane–borane[18] were obtained via standard preparations. For trimethylphosphine–bromoborane and -chloroborane, a new synthesis was employed.[13,19] Dimethylphosphine oxide was supplied from Hoechst AG, Knapsack, and converted into its potassium salt as described in the literature.[20] Trimethylphosphine and chlorodimethylphosphine were also gifts from Hoechst AG, but samples were also prepared following literature procedures.[21,22] All other reagents were commercial products.

[(Trimethylphosphine)dihydroboryl]dimethylphosphine Oxide, 1 [≡ (Trimethylphosphonio)(dimethyloxophosphato-*P*)dihydroborate(1−)]. A suspension of potassium dimethyloxophosphate was prepared from 4.78 g of dimethylphosphine oxide (61.2 mmol) and 2.46 g of KH (61.3 mmol) in 100 mL of THF at 0 °C. To this suspension was added a solution of 10.3 g of trimethylphosphine–bromoborane (61.2 mmol) in 30 mL of THF slowly at 0 °C with stirring. Stirring of the mixture was continued for 16 h at 20 °C. The KBr precipitate was filtered and the solvent removed from the filtrate in vacuo. The residue was crystallized from diethyl ether/pentane at −30 °C: yield 8.3 g (82%); mp 79 °C. Anal. Calcd for $C_5H_{17}BOP_2$ (165.95): C, 36.19; H, 10.33. Found: C, 35.98; H, 9.93.

[(Trimethylphosphine)dihydroboryl]chlorodimethylphosphonium Chloride, 2 [≡ (Trimethylphosphonio)(chlorodimethylphosphonio)dihydroborate(1−) Chloride]. An 8.20-g sample of trimethylphosphine–chloroborane and 6.36 g of chlorodimethylphosphine (65.9-mmol each) were mixed at 0 °C and the mixture slowly heated to 70 °C. After 2 h, the mixture had solidified. Volatiles were removed under vacuum, and the remaining product was washed with 50 mL of ether and dissolved in 100 mL of CH_2Cl_2. After filtration from undissolved material, the clear solution was concentrated and ether was added until crystallization ensued. Cooling to −30 °C gave a yield of 11.21 g (77%) of clear, colorless needles, mp 84 °C. Anal. Calcd for $C_5H_{17}BCl_2P_2$ (220.86): C, 27.19; H, 7.76. Found: C, 27.77; H, 7.92.

[(Trimethylphosphine)dihydroboryl]dimethylmethoxyphosphonium Chloride, 3 [≡ (Trimethylphosphonio)(dimethylmethoxyphosphonio)dihydroborate(1−) Chloride]. A suspension of 1.97 g of compound **2** (8.9 mmol) in 20 mL of THF was treated with 0.48 g of $NaOCH_3$ (8.9 mmol) in 10 mL of THF for 16 h at 0–20 °C. The solvent was removed from the reaction mixture in vacuo and replaced by 20 mL of CH_2Cl_2. After filtration and concentration in vacuo, crystallization was induced by addition of ether. Cooling to −30 °C gave 1.74 g (90%) of product, mp 130 °C (with decomposition). Anal. Calcd for $C_6H_{20}BClOP_2$ (216.44): C, 33.30; H, 9.31. Found: C, 33.08; H, 9.28.

[(Trimethylphosphine)dihydroboryl]dimethylphosphine Sulfide, 4 [≡ (Trimethylphosphonio)(dimethylthioxophosphato-*P*)dihydroborate(1−)]. (a) A suspension of potassium dimethylthioxophosphate was prepared from 0.94 g of dimethylphosphine sulfide (10 mmol) and 0.40 g of KH (10 mmol) in 20 mL of toluene at 0 °C. A solution of 1.69 g of trimethylphosphine–bromoborane (10 mmol) in 10 mL of toluene was added

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at 0 °C and the reaction mixture stirred for 16 h at 20 °C. After filtration the solvent was removed from the filtrate in vacuo. The residue was crystallized from ether/pentane at −30 °C; yield 1.44 g (79%).

(b) A 0.46-g sample of P_2S_5 was added in small portions to a solution of 1.66 g of compound 1 (10 mmol) in 2 mL of CH_2Cl_2 at −20 °C with stirring. After 2 h of further stirring at +20 °C, the solvent was removed and the residue sublimed in vacuo (60 °C, 10^{-3} torr): yield 0.82 g (45%); mp 87 °C. Anal. Calcd for $C_5H_{17}BP_2S$ (182.01): C, 33.00; H, 9.41; P, 34.03; S, 17.62. Found: C, 33.00; H, 9.10; P, 33.69; S, 18.34.

[(Trimethylphosphine)dihydroboryl]dimethyl(methylamino)phosphonium Chloride, 5 [≡ (Trimethylphosphonio)(dimethyl(methylamino)phosphonio)dihydroborate(1−) Chloride]. Following the procedure described for compound 3 (above) using $LiNHCH_3$ instead of $NaOCH_3$, a sample of salt 5 was obtained. Yields were not determined; mp 117 °C (with decomposition). Anal. Calcd for $C_6H_{21}BClNP_2$ (215.45): C, 33.45; H, 9.82. Found: C, 33.43; H, 9.77.

[(Trimethylphosphine)dihydroboryl]dimethylphosphine Methylimine, 6 [≡ (Trimethylphosphonio)(dimethyl(methylimino)phosphoranyl)dihydroborate(1−)]. Treatment of compound 5 with an excess of $LiNHCH_3$ in ether gave a low yield of the imine 6, which was only identified by its ^1H NMR spectrum (Table I). It could not be separated from the lithium chloride present in the sample.

Beryllium Bis[[(dimethyloxophosphato)dihydroboryl]dimethylphosphonium methylide], 8 [≡ Bis[[(μ-dihydroborato)(1−)](dimethyloxophosphato)(dimethylphosphonium methylido)]beryllium]. A 0.96-g sample of compound 1 (5.8 mmol) was treated with 3.51 mL of a 1.65 M solution of *tert*-butyllithium (in hexane) at −78 °C in 10 mL of THF. After the reaction mixture was kept for 1 h at room temperature, 0.23 g of $BeCl_2$ (2.9 mmol) was added to the clear yellow solution (containing 7). THF was replaced by toluene after 16 h, LiCl was filtered off, and the filtrate was evaporated to dryness. The residue could be purified by vacuum sublimation (60–100 °C at 10^{-4} torr): yield 0.11 g (11%); mp 59 °C. Anal. Calcd for $C_{10}H_{32}B_2BeO_2P_4$ (338.89): C, 35.44; H, 9.52. Found: C, 35.39; H, 9.24. The freshly sublimed material is colorless, not very sensitive to air and moisture, soluble in polar organic solvents, and sparingly soluble in pentane. Samples stored at 20 °C for 4 weeks were no longer soluble, however, and could not be sublimed.

Zinc and Cadmium Bis[[(dimethylthiooxophosphato)dihydroboryl]dimethylphosphonium methylides], 10 and 11 [≡ Bis[[μ-dihydroborato(1−)](dimethylthiooxophosphato)(dimethylphosphonium methylido)]zinc and -cadmium]. A 1.00-g sample of compound 4 (5.5 mmol) was dissoled in 10 mL of THF and treated with 3.18 mL of a 1.73 M hexane solution of *tert*-butyllithium at −78 °C. A clear yellow solution of **9** was obtained after 1 h at room temperature. A 0.37-g sample of anhydrous $ZnCl_2$ or 0.50 g of $CdCl_2$ (2.75 mmol) were added to this solution, and the reaction mixture was stirred for 16 h at 20 °C. Workup was carried out as described for **8**, sublimation temperature 100 °C (**10**) and 125 °C (**11**) at 10^{-4} torr. Unreacted **4** was separated from **10** first at 60 °C (10^{-3} torr). **4** formed during sublimation of **11** by decomposition was removed from the sublimate by heating to 60 °C at 10^{-4} torr: yield 0.71 g (60%) and mp 89 °C for **10**; 0.40 g (31%) and mp 123 °C for **11**. Anal. Calcd for $C_{10}H_{32}B_2P_4S_2Zn$ (427.38): C, 28.10; H, 7.55; Zn, 15.30. Found: C, 28.70; H, 7.54; Zn, 14.70. Anal. Calcd for $C_{10}H_{32}B_2P_4S_2Cd$ (474.41): C, 25.32; H, 6.80. Found: C, 26.82; H, 6.84.

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