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Synthesis and Coordination of a Cleft-Stabilized Triphosphazane Hydride: $C_6H_4N_2[P(S)(NEt_2)_2]_2PH$

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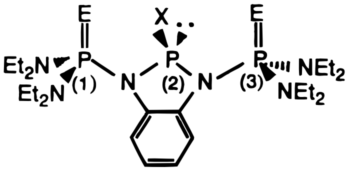
Reaction of the molecular cleft-containing triphosphazane $C_6H_4N_2[P(S)(NEt_2)_2]_2PCl$ (**2**) with $LiBH_4$ yields the borane-coordinated triphosphazane hydride $C_6H_4N_2[P(S)(NEt_2)_2]_2P(BH_3)H$ (**3**). The complex is strongly associated; free hydride $C_6H_4N_2[P(S)(NEt_2)_2]_2PH$ (**4**) can be obtained by treatment of **3** with tertiary amines. Complex **3** reacts with (norbornadiene)$Mo(CO)_4$ to form triphosphazane complexes $\{C_6H_4N_2[P(S)(NEt_2)_2]_2PH\}Mo(CO)_3$ (**5**), $\{C_6H_4N_2[P(S)(NEt_2)_2]_2P(BH_2)\}Mo(CO)_4$ (**6**), and $\{C_6H_4N_2[P(S)(NEt_2)_2]_2P(BH_2)\}Mo(CO)_5$ (**7**). Under more vigorous conditions **2** and $Mo(CO)_6$ yield **5** and $\{C_6H_4N_2[P(S)(NEt_2)_2]_2PH\}Mo(CO)_4$ (**8**). Compounds **3**−**8** were characterized by spectral data. X-ray analyses were performed on **6** and **7**: **6**, monoclinic, $P2_1/c$, $a = 10.6350(10)$ Å, $b = 18.979(3)$ Å, $c = 18.204(3)$ Å, $\beta = 91.750(10)°$, $V = 3672.6(9)$ Å^3, $Z = 4$, $R = 0.044$, $R_w = 0.038$; **7**, triclinic, $P\bar{1}$, $a = 11.080(2)$ Å, $b = 11.253(3)$ Å, $c = 17.739(4)$ Å, $\alpha = 94.86(2)°$, $\beta = 104.57(2)°$, $\gamma = 101.85(2)°$, $V = 2073.2(8)$ Å^3, $Z = 2$, $R = 0.040$, $R_w = 0.047$. Structures are compared, and the influence of the molecular cleft on reaction outcome and the involvement of the peripheral sulfur atoms in coordination are discussed.

Introduction

Skeletally stabilized triphosphazanes (**1**)[1−4] react with a variety of reagents regioselectively at P(2) in the molecular "cleft" created between the bulky $-P(E)(NEt_2)_2$ groups. Reactivity studies show the cleft to be large enough to accommodate alkoxy and alkylamino groups (X) in size up to *i*-PrO− and Et_2N-, respectively;[1a,5] modeling studies establish the average cleft width to be 6.0 ∓ 0.5 Å in disulfide **1** (E = S, X = NEt_2). This cleft can protect the P−X functionality within it, allowing for stabilization of bonds that might not be isolable in a less protected environment. In addition, since there are proximately located sulfur donor atoms; they too could help stabilize groups bonded at P(2) within the cleft. One bond of interest is the P−H bond, a bond which in aminophosphines is known to be highly reactive and which can be useful in subsequent derivatization reactions.[6−11] In this paper, we report the synthesis of a P(2)−H-containing triphosphazane hydride and its borane adduct and studies of these new compounds with molybdenum carbonyl complexes.



1 (E = O, S, Se)

Experimental Section

Apparatus and Materials. Phosphorus-31 (121.4 MHz) and ^{11}B (96.2 MHz) NMR spectra were obtained on Varian Gemini and VXR300S spectrometers, respectively. ^1H NMR spectra were obtained on Varian Gemini 300 and VXR300S (300 MHz) NMR spectrometers. ^{31}P, ^1H, and ^{11}B chemical shifts downfield from 85% H_3PO_4 (external), Me_4Si (internal), and $BF_3 \cdot OEt_2$ (external) are reported as positive ($+\delta$). IR spectra (4000−400 cm^{-1}) were obtained using an IBM IR/32 Type 9132 spectrometer. Mass spectra were obtained at 70 eV with a VG Analytical 7070 EQ-HF spectrometer. Mass spectral data refer to the major peak of the respective envelope. Chemical ionization (CI^+ and CI^-) was achieved using isobutane as the ionizing gas. Exact mass analyses were referenced to perfluorokerosene. X-ray diffraction data were collected on a Nicolet P3/F automated diffractometer equipped with a graphite monochromator and low-temperature attachment. All manipulations were carried out using standard vacuum line, glovebag, or Schlenk techniques under dry N_2.[12] Flash chromatography was carried out as described by Still et al.[13] A 650 or 450 mL column was packed (15 cm) with silica gel 60 (230−400 mesh). Compounds were eluted with the necessary solvent mixture under N_2 pressure at 5 cm/min. Elemental analyses were performed by Huffman Laboratories Inc., Golden, CO, and Desert Analytics, Tucson, AZ.

Toluene (over Na/benzophenone or CaH_2) and CH_2Cl_2 were distilled before use. Silica gel (EM Science), KBr (Baker, oven dried), $Mo(CO)_6$ (Strem Chemicals), $LiBH_4$ (laboratory supply), $BH_3 \cdot THF$ (Aldrich), petroleum ether, ethyl acetate, and deuterated solvents were used

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as received. $C_6H_4N_2[P(S)(NEt_2)_2]_2PCl$ (**2**)[1] and nor•$Mo(CO)_4$ (nor = norbornadiene)[14] were prepared as described previously.

$C_6H_4N_2[P(S)(NEt_2)_2]_2P(BH_3)H$ (3) and $C_6H_4N_2[P(S)(NEt_2)_2]_2PH$ (4). Compound **2** (0.32 g, 0.55 mmol) and $LiBH_4$ (0.035 g, 1.6 mmol) were allowed to react in toluene (50 mL), during which a precipitate formed. After 18 h, the solution was filtered to remove LiCl and unreacted $LiBH_4$. Evaporation of solvent yielded pure **3**. $^{31}P\{^1H\}$ NMR (toluene-d_8): δ 99.0 [br s, 1P; $P(BH_3)H$], 65.2 (d, 2P, $^2J_{PNP}$ = 13.4 Hz; P═S), from ^{1}H-coupled spectrum, $^1J_{PH}$ = 450 Hz. $^{11}B\{^1H\}$ NMR (toluene-d_8): δ −33.5 [br s; $P(BH_3)H$]. ^{1}H NMR toluene-d_8): δ 9.23 (d, 1H, $^1J_{HP}$ = 450 Hz; PH), 7.25 (mult, 2H; C_6H_4 meta), 6.75 (mult, 2H; C_6H_4 ortho), 3.14 (m, 16H; NCH_2CH_3), 1.01 (t, 12H, $^3J_{HH}$ = 7.1 Hz; CH_2CH_3), 0.86 (t, 12H, $^3J_{HH}$ = 7.1 Hz; NCH_2CH_3). Molecular mass: calcd for $C_{22}H_{48}N_6BP_3S_2$, 564.2688 amu; found (EI$^-$, exact mass) M$^+$, 564.2220 amu.

Compound **3** also formed immediately upon reaction of BH_3•THF (0.20 mL, 0.20 mmol) with a THF solution of **2** (0.030 g, 0.05 mmol). Besides resonances for **3**, the reaction mixture showed ^{11}B NMR resonances at δ 0.4, −13.7, and −34.6 due to unreacted BH_3•THF, BH_2Cl•THF (or BH_2Cl•$NHEt_2$), and BH_3•$NHEt_2$,[15] respectively, from which **3** could not be separated.

Reactions of **2** with NaH, $LiAlH_4$, or L-Selectride [$LiB(sec\text{-}Bu)_3H$] in THF yielded complex mixtures which contained minor amounts of **4**. Isolation of **4** from these reaction mixtures was not accomplished.

Compound **4** was obtained by allowing **3** in toluene to react with excess amine (NH_3, Et_3N, *n*-Bu_3N, or pyridine). Attempts to free **4** of the amine•BH_3 complex by recrystallization or column chromatography failed; hence spectral characterization of **4** was limited to **4**/amine−borane mixtures. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 74.1 (t, 1P, $^2J_{PNP}$ = 54.5 Hz; PH), 65.6 (d, 2P; P═S); from ^{1}H-coupled spectrum, $^1J_{PH}$ = 148 Hz. Molecular mass: calcd for $C_{22}H_{45}N_6P_3S_2$, 550.2360 amu; found (EI$^+$, exact mass) M$^+$, 550.2348 amu. Thermolysis of 3 at 70 °C results in slow conversion to **4**; however, the rapid reaction of **4** with traces of H_2O in the system at 70 °C made this synthesis infeasible.

Reactions of 3. (A) With norMo(CO)$_4$. $\{C_6H_4N_2[P(S)(NEt_2)_2]_2PH\}Mo(CO)_3$ (5), $\{C_6H_4N_2[P(S)(NEt_2)_2]_2P(BH_2)\}Mo(CO)_4$ (6), and $\{C_6H_4N_2[P(S)(NEt_2)_2]_2P(BH_2)\}Mo(CO)_5$ (7). **3** (1.2 g, 2.2 mmol) was combined with norMo(CO)$_4$ (1.2 g, 4.0 mmol) in toluene (50 mL). Gas evolution occurred at room temperature. After 12 h, the ^{31}P NMR spectrum showed mainly resonances due to **5** and **6** (**5**:**6** = 1:2.2). Crystals of **6** formed upon standing. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 200.5 [br mult, 1P; $C_6H_4N_2P(BH_2)Mo$], 69.3 [d of d, 1P, $^2J_{PP}$ = 40.8 Hz, $^4J_{PP}$ = 5.9 Hz; P(S)Mo], 67.2 [d of d, 1P, $^2J_{PP}$ = 78.2 Hz; $P(S)BH_2$]. $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ −13.8 [br mult; $P(BH_2)Mo$]. ^{1}H NMR (CD_2Cl_2): δ 6.8−7.0 (m, 4H; C_6H_4), 3.20 (m, 16H; NCH_2CH_3), 1.64 [br s, 2H; $P(BH_2)Mo$], 1.00−1.24 (br mult, 24 H; NCH_2CH_3). IR (KBr, cm^{-1}): 2462 (m, ν_{BH}), 2421 (m, ν_{BH}), 1974 (m, ν_{CO}), 1901 (vs, ν_{CO}), 1881 (vs, ν_{CO}), 1848 (vs, ν_{CO}). NMR spectra of **6** were temperature independent between −80 and +70 °C.

After repeated crystallizations of **6** from toluene, removal of solvent in vacuo, and extraction of the crystalline solid with CH_2Cl_2, **5** was obtained. Crystals of **5** were not adequate for X-ray analysis. $^{31}P\{^1H\}$ NMR (toluene-d_8): δ 133.4 [t, 1P, $^2J_{PP}$ = 123.4 Hz; P(H)-$Mo(CO)_3$], 79.5 [d, 2P; $P(S)Mo(CO)_3$]; from ^{1}H coupled spectrum, $^1J_{PH}$ = 350 Hz. Molecular mass: calcd for $C_{25}H_{45}N_6P_3S_2O_3Mo$, 732.1262 amu; found (EI$^+$, exact mass) 732.1311 amu, MS (EI$^+$) M$^+$ *m*/*e* 732 (100%).

A solution of **6** in CH_2Cl_2 (ca. 0.4 M) was allowed to stand at room temperature. During 7 days, a black intractable precipitate formed. **7** was the sole product in solution as determined by ^{31}P NMR spectral analysis. Evaporation of solvent yielded **7**, which after chromatography (50/50 toluene/CH_2Cl_2 eluent) was obtained pure. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 205.8 [br mult, 1P; $P(BH_2)Mo$], 63.2 (d, 2P, $^2J_{PP}$ = 16.0 Hz; PS). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ −12.8 [br mult; $P(BH_2)Mo$]. ^{1}H NMR (CD_2Cl_2): δ 6.7−7.0 (m, 4H; C_6H_4), 3.12 (m, 16H; NCH_2CH_3), 1.6 [br s, 2H; $P(BH_2)Mo$], 1.22 (t, 12H, $^3J_{HH}$ = 7.1 Hz; NCH_2CH_3), 1.04 (t, 12H, $^3J_{HH}$ = 7.1 Hz; NCH_2CH_3). The ^{31}P NMR spectrum was temperature dependent: 24 °C (AX_2 pattern, $^2J_{PP}$ = 17.9 Hz); T_c = −50 °C; −90 °C (broadened ABX), δ 200.5 (1P, J = 24.4; P_X), 64.5 (1P; P_A), 55.5 (1P, P_B). IR (KBr, cm^{-1}): 2466 (m, ν_{BH}), 2418 (w, ν_{BH}).

Table 1. Crystal Data and Details of the Structure Determination for **6** and **7**

	6	**7**
formula	$C_{26}H_{46}BN_6O_4P_3S_2Mo$	$C_{27}H_{46}BN_6O_5P_3S_2Mo\cdot{}^1/_2C_6H_6$
fw	770.5	837.5
space group	$P2_1/c$	$P\bar{1}$
crystal system	monoclinic	triclinic
a, Å	10.6350(10)	11.080(2)
b, Å	18.979(3)	11.253(3)
c, Å	18.204(3)	17.739(4)
α, deg	90.0	94.86(2)
β, deg	91.750(10)	104.57(2)
γ, deg	90.0	101.85(2)
V, Å^3	3672.6(9)	2073.2(8)
Z	4	2
d_{obs}, g/cm^3	1.393	1.342
μ, cm^{-1}	0.623	0.559
λ, Å (Mo Kα)	0.7103	0.7103
T, K	295−297	298
programs	SHELXTL PLUS	SHELXTL PLUS
R, R_w	0.044, 0.038	0.040, 0.047
goodness of fit	1.16	1.32

(B) With Mo(CO)$_6$. $\{C_6H_4N_2[P(S)(NEt_2)_2]_2PH\}Mo(CO)_4$ (8) and 5. A solution of **3** in toluene was heated with a 5-fold excess of $Mo(CO)_6$ at 70 °C for 40 h. The ^{31}P NMR spectrum of the resulting solution showed resonances due to **8** and **5** (**8**:**5** = 1.5:1). Continued heating of the solution further converted **8** to **5**. **8** and **5** could not be completely separated by crystallization or column chromatography; hence **8** was characterized by spectral analysis of **8**/**5** mixtures. $^{31}P\{^1H\}$ NMR (toluene-d_8): δ 98.5 [d of d, 1P, $^2J_{PP}$ = 35.8, $^2J_{PP}$ = 87.8; $P(H)Mo(CO)_4$], 68.5 [d, 1P; $P(S)Mo(CO)_4$], 63.8 (d, 1P; PS); from ^{1}H-coupled spectrum, $^1J_{PH}$ = 320 Hz.

X-ray Analysis. (A) 6. Yellow cubic (0.2 × 0.2 × 0.1 mm) crystals formed in the toluene reaction solution. Experimental conditions for data collection and values for cell parameters are listed in Table 1. Cell dimensions were determined by a least-squares fit of the setting angles for 25 reflections, 2θ = 23.9−35.0°. Crystal integrity was monitored by measuring three check reflections after every 97 reflections. Only random variations were observed over the course of the data collection. The structure was solved by direct methods.[16] The molecule was refined anisotropically, except for the non-borane hydrogen atoms, which were included in idealized positions. The borane hydrogen atoms were located in the difference map in the expected positions. Final positional parameters for **6** are given in Table 2.

(B) 7. Slow evaporation of a **7**/benzene solution produced clear colorless (0.5 × 0.3 × 0.2 mm) crystals. **7** crystallized with a half molecule of benzene. Experimental conditions for data collection and values for cell parameters are listed in Table 1. Cell dimensions were determined by a least-squares fit of the setting angles for 25 reflections, 2θ = 27.3−33.6°. Crystal integrity was monitored by measuring three check reflections after every 97 reflections. Only random variations were observed over the course of the data collection. The structure was solved by direct methods.[16] The molecule was refined anisotropically, except for the non-borane hydrogen atoms, which were included in idealized positions. The borane hydrogen atoms were located in the difference map in the expected positions. Final positional parameters are given in Table 3.

Results and Discussion

Reactions of the triphosphazane chloride **2** with $LiBH_4$ or BH_3•THF readily yield the borane-coordinated triphosphazane hydride **3** (Scheme 1), although the latter reaction is less

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Table 2. Atomic Coordinates[a] ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **6**

atom	x/a	y/b	z/c	U_{eq}[b]
Mo(1)	3510(1)	463(1)	2439(1)	38(1)
S(1)	4764(1)	1157(1)	1453(1)	50(1)
S(2)	1411(1)	2138(1)	3564(1)	52(1)
P(1)	3535(1)	1691(1)	816(1)	35(1)
P(2)	2246(1)	1528(1)	2205(1)	33(1)
P(3)	−101(1)	1796(1)	2952(1)	37(1)
B(1)	2512(4)	2396(2)	2746(3)	48(1)
N(1)	2165(3)	1691(2)	1243(1)	38(1)
N(2)	577(3)	1505(2)	2204(2)	36(1)
N(3)	4049(3)	2495(2)	684(2)	44(1)
N(4)	3219(3)	1358(2)	−9(2)	44(1)
N(5)	−1125(3)	2424(2)	2815(2)	50(1)
N(6)	−861(3)	1148(2)	3317(2)	50(1)
C(1)	917(3)	1698(2)	953(2)	37(1)
C(2)	28(3)	1549(2)	1487(2)	38(1)
C(3)	−1229(4)	1454(2)	1298(2)	49(1)
C(4)	−1623(4)	1567(3)	570(3)	63(1)
C(5)	−794(5)	1754(3)	58(2)	62(1)
C(6)	502(4)	1827(3)	235(2)	52(1)
C(11)	4571(4)	955(3)	3227(2)	54(1)
C(12)	2309(5)	−63(2)	1753(3)	55(1)
C(13)	4687(4)	−362(2)	2472(2)	54(1)
C(14)	2627(4)	86(3)	3271(3)	59(1)
O(1)	5144(5)	1192(3)	3706(3)	98(2)
O(2)	1586(6)	−371(3)	1403(3)	93(2)
O(3)	5365(4)	−831(2)	2488(3)	84(1)
O(4)	2112(5)	−113(3)	3781(3)	96(2)
C(31)	5111(6)	2813(3)	1065(4)	83(2)
C(32)	6051(7)	3119(7)	542(9)	138(5)
C(33)	3265(5)	2986(3)	246(3)	65(1)
C(34)	2680(13)	3555(5)	687(8)	125(4)
C(41)	2604(4)	662(2)	−49(2)	52(1)
C(42)	1979(8)	525(4)	−779(4)	87(2)
C(43)	4139(6)	1478(3)	−583(2)	61(1)
C(44)	5218(5)	943(3)	−584(3)	69(2)
C(51)	−666(5)	3145(3)	2669(4)	71(2)
C(52)	−663(10)	3342(4)	1868(6)	109(3)
C(53)	−2472(4)	2312(3)	2694(3)	59(1)
C(54)	−3273(5)	2759(4)	3190(5)	86(2)
C(61)	−1415(5)	1266(4)	4036(3)	72(2)
C(62)	−732(11)	943(8)	4678(4)	123(4)
C(63)	−750(5)	414(3)	3075(3)	65(1)
C(64)	−2055(9)	98(4)	2907(5)	97(3)

[a] Atoms have occupancies of 1.0. [b] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Atomic Coordinates[a] ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **7**

atom	x/a	y/b	z/c	U_{eq}[b]
Mo(1)	3809(1)	6853(1)	1628(1)	46(1)
S(1)	6970(1)	9818(1)	2820(1)	48(1)
S(2)	2928(1)	8193(1)	3831(1)	50(1)
P(1)	6006(1)	11015(1)	2456(1)	34(1)
P(2)	3974(1)	8841(1)	2475(1)	35(1)
P(3)	1738(1)	8994(1)	3094(1)	40(1)
B(1)	4541(3)	9043(3)	3627(2)	45(1)
N(1)	4465(2)	10213(2)	2100(1)	34(1)
N(2)	2438(2)	9174(2)	2378(1)	37(1)
N(3)	6309(2)	11708(2)	1711(1)	38(1)
N(4)	6169(2)	12148(2)	3144(1)	45(1)
N(5)	288(2)	8137(2)	2705(2)	47(1)
N(6)	1539(2)	10237(2)	3542(2)	47(1)
C(1)	3369(3)	10592(2)	1666(2)	35(1)
C(2)	2228(3)	9991(3)	1808(3)	36(1)
C(3)	1062(3)	10192(3)	1419(2)	48(1)
C(4)	1028(3)	11034(3)	894(2)	53(1)
C(5)	2150(3)	11648(3)	760(2)	51(1)
C(6)	3329(3)	11430(3)	1139(2)	43(1)
C(31)	7301(3)	12862(3)	1860(2)	58(1)
C(32)	6954(5)	13708(4)	1270(3)	92(2)
C(33)	6159(3)	10926(3)	972(2)	51(1)
C(34)	7375(4)	10610(4)	868(3)	75(2)
C(41)	5420(4)	13106(3)	2970(2)	65(2)
C(42)	4244(4)	12908(4)	3252(3)	92(2)
C(43)	6886(4)	12225(3)	3964(2)	63(1)
C(44)	8148(4)	13131(5)	4184(3)	101(2)
C(51)	−61(3)	7275(3)	1977(2)	55(1)
C(52)	−1387(4)	7230(4)	1458(3)	87(2)
C(53)	−534(3)	7850(4)	3242(2)	70(2)
C(54)	−583(4)	6617(4)	3502(3)	96(2)
C(61)	2414(3)	10869(3)	4312(2)	57(1)
C(62)	1815(4)	10706(5)	4977(2)	85(2)
C(63)	428(3)	10777(4)	3244(2)	64(2)
C(64)	792(4)	12065(4)	3063(3)	89(2)
C(81)	2628(4)	5868(3)	2192(3)	65(2)
C(82)	2286(4)	7161(3)	813(2)	63(2)
C(83)	5054(3)	7585(3)	1026(2)	51(1)
C(84)	3679(4)	5290(3)	951(3)	74(2)
C(85)	5352(3)	6599(3)	2453(2)	57(1)
O(81)	1980(3)	5234(3)	2463(2)	99(2)
O(82)	1416(3)	7295(3)	350(2)	96(2)
O(83)	5749(3)	7866(3)	658(2)	73(1)
O(84)	3621(4)	4417(3)	558(2)	123(2)
O(85)	6220(3)	6450(3)	2894(2)	88(1)
C(91)	2844(8)	5238(7)	4677(4)	123(4)
C(92)	4867(10)	5808(5)	4498(3)	120(4)
C(93)	6058(8)	5610(6)	4797(4)	124(4)

[a] Atoms have occupancies of 1.0. [b] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

desirable because **3** is formed along with chloroborane·THF adducts (BH_2Cl·THF and $BHCl_2$·THF), from which it is difficult to separate. The $LiBH_4$ reduction of **2** is closely analogous to that used by Nöth for the synthesis of $(Me_2N)_2PH{\cdot}BH_3$.[17] Spectral data allow the characterization of 3. The ^{31}P NMR spectrum exhibits an AX_2 pattern[18] containing a P−H resonance with a 450 Hz $^1J_{PH}$ coupling characteristic of a λ^4 coordinated phosphorus center [P(2)].[19] The ^{11}B NMR resonance is a broad, poorly resolved multiplet whose chemical shift is typical of aminophosphine-coordinated BH_3 groups.[1,18,19] Broadening of the ^{31}P and ^{11}B resonances occurs apparently due to the nearby quadrupolar ^{14}N nuclei; consequently ^{31}P couplings to the borane ^{11}B and ^1H nuclei are not resolved.

The BH_3 group in **3** is strongly coordinated and it, unlike the previously studied triphosphazane $C_6H_4N_2[P(S)(NEt_2)_2]_2P(BH_3)NEt_2$,[5] is not significantly dissociated at 25 °C. Hence, the BH_3 cannot be removed as B_2H_6 in vacuo at 25 °C and only slowly at 70 °C. However, upon reaction of **3** with a tertiary amine, the BH_3 group is displaced as the amine·BH_3 complex, thus forming the free hydride **4**. Since compound **4** and the amine·BH_3 complexes were not separable by crystallization or chromatographic techniques, **4** was characterized in this mixture. Again, the distinct ^{31}P NMR AX_2 spectral pattern and the 148 Hz $^1J_{PH}$ coupling shown by the unique phosphorus make clear the presence of the three-coordinate P(2)−H unit.[19] Attempts to prepare **4** free of BH_3 by reducing **2** with NaH, $LiAlH_4$, or L-Selectride, using reactions analogous to those successful in syntheses of $(R_2N)_2PH$ (R = Me, *i*-Pr, Me_3Si),[7,8,10,11] led only to intractable complex mixtures. Triphosphazane **4** is quite reactive toward moisture and/or atmospheric oxygen, similar to other reported $(R_2N)_2PH$ compounds.[7,8,10,11]

Triphosphazane **3** reacts with nor·$Mo(CO)_4$ or $Mo(CO)_6$ to form coordinated triphosphazanes (Scheme 2). Under mild conditions, 12 h at 25 °C, **3** reacts with nor·$Mo(CO)_4$ to form the **4**·$Mo(CO)_3$ complex **5** and the borane complex **6**. The NMR spectrum of complex **6** exhibits an ABX spectrum,[18] indicative

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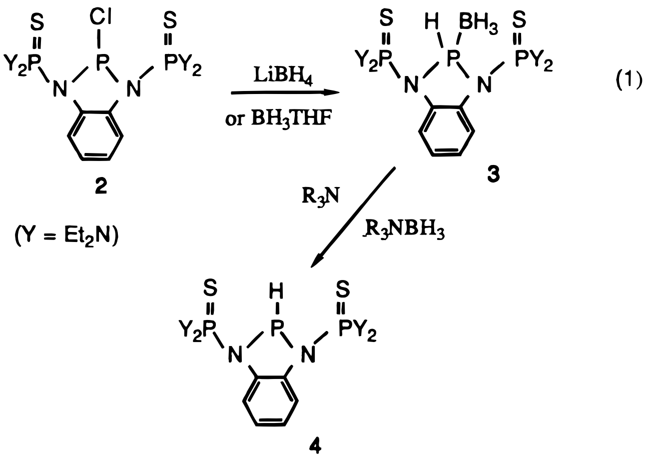
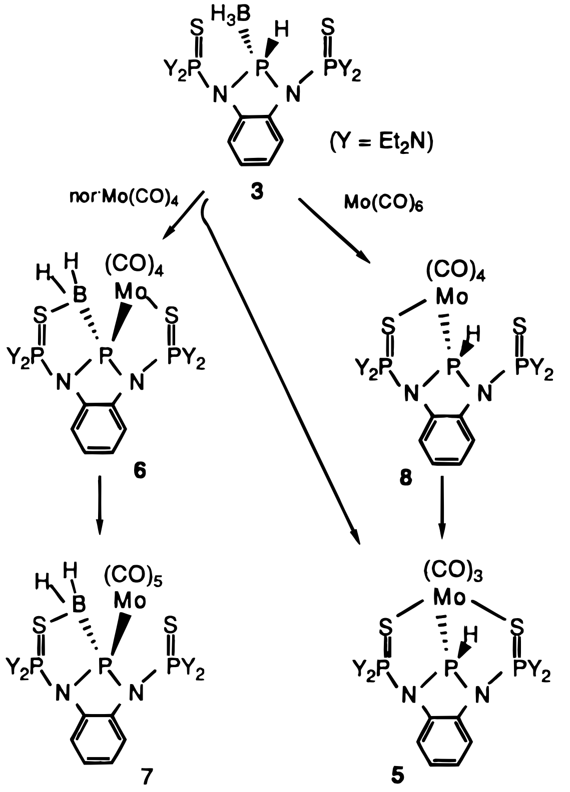
Scheme 1



Scheme 2



of a triphosphazane containing three different phosphorus sites; that the Mo moiety is coordinated at P(2) in both cases is clear, δ occurring at 200.5 and 133.4 for **5** and **6**, respectively, far removed from δ 99.0 displayed by reactant **3**. Furthermore, complex **6** shows no P−H bond in either the IR or the ^{31}P NMR spectrum. The IR spectrum displays absorptions characteristic of a $Mo(CO)_4$ group.[20,21] Upon standing, **6** crystallized from the reaction solution, leaving **5**, which could be obtained only from the supernatant as an amorphous solid.

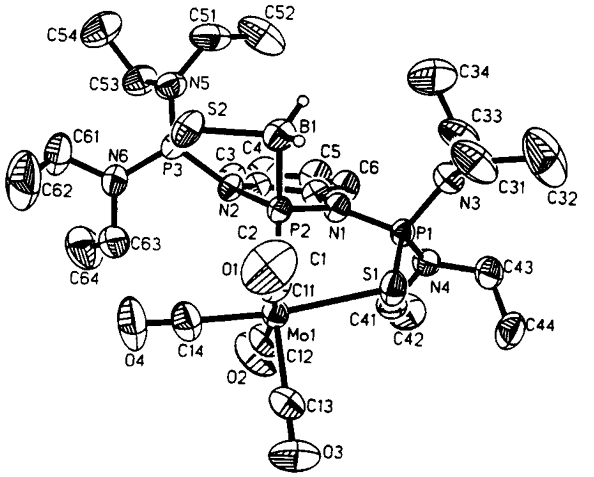


Figure 1. Structure and numbering scheme for **6**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms, except those on BH_2 groups, are omitted for clarity.

Table 4. Selected Structural Parameters for **6**

(a) Distances (Å)			
Mo(1)−S(1)	2.622(1)	Mo(1)−P(2)	2.457(1)
Mo(1)−C(11)	2.026(4)	Mo(1)−C(12)	2.022(5)
Mo(1)−C(13)	2.004(4)	Mo(1)−C(14)	1.944(5)
S(1)−P(1)	1.996(1)	S(2)−P(3)	2.034(1)
S(2)−B(1)	1.983(5)	P(1)−N(1)	1.673(3)
P(1)−N(3)	1.640(3)	P(1)−N(4)	1.654(3)
P(2)−B(1)	1.937(5)	P(2)−N(1)	1.779(3)
P(2)−N(2)	1.775(3)	P(3)−N(2)	1.654(3)
P(3)−N(5)	1.630(4)	P(3)−N(6)	1.624(4)
N(1)−C(1)	1.414(4)	N(2)−C(2)	1.416(4)
C(11)−O(1)	1.141(7)	C(12)−O(2)	1.145(7)
C(13)−O(3)	1.146(6)	C(14)−O(4)	1.156(7)
(b) Angles (deg)			
S(1)−Mo(1)−P(2)	75.8(1)	S(1)−Mo(1)−C(11)	88.2(1)
P(2)−Mo(1)−C(11)	91.9(1)	S(1)−Mo(1)−C(12)	98.7(1)
P(2)−Mo(1)−C(12)	88.1(1)	C(11)−Mo(1)−C(12)	172.9(2)
S(1)−Mo(1)−C(13)	94.8(1)	P(2)−Mo(1)−C(13)	170.3(1)
C(11)−Mo(1)−C(13)	90.3(2)	C(12)−Mo(1)−C(13)	90.9(2)
S(1)−Mo(1)−C(14)	170.5(2)	P(2)−Mo(1)−C(14)	99.4(1)
C(11)−Mo(1)−C(14)	83.6(2)	C(12)−Mo(1)−C(14)	89.3(2)
C(13)−Mo(1)−C(14)	90.3(2)	Mo(1)−S(1)−P(1)	108.4(1)
P(3)−S(2)−B(1)	98.2(1)	S(1)−P(1)−N(1)	107.1(1)
S(1)−P(1)−N(3)	110.0(1)	N(1)−P(1)−N(3)	111.5(2)
S(1)−P(1)−N(4)	116.5(1)	N(1)−P(1)−N(4)	105.4(2)
N(3)−P(1)−N(4)	106.3(2)	Mo(1)−P(2)−B(1)	122.8(1)
Mo(1)−P(2)−N(1)	108.9(1)	B(1)−P(2)−N(1)	110.7(2)
Mo(1)−P(2)−N(2)	121.5(1)	B(1)−P(2)−N(2)	98.7(2)
N(1)−P(2)−N(2)	89.1(1)	S(2)−P(3)−N(2)	101.5(1)
S(2)−P(3)−N(5)	111.3(1)	N(2)−P(3)−N(5)	115.1(2)
S(2)−P(3)−N(6)	114.4(1)	N(2)−P(3)−N(6)	108.6(2)
N(5)−P(3)−N(6)	106.1(2)	S(2)−B(1)−P(2)	95.2(2)
P(1)−N(1)−P(2)	116.2(2)	P(1)−N(1)−C(1)	130.4(2)
P(2)−N(1)−C(1)	112.7(2)	P(2)−N(2)−P(3)	116.8(2)
P(2)−N(2)−C(2)	112.6(2)	P(3)−N(2)−C(2)	124.1(2)
N(1)−C(1)−C(2)	112.5(3)	N(2)−C(2)−C(1)	112.5(3)
Mo(1)−C(11)−O(1)	174.8(5)	Mo(1)−C(12)−O(2)	175.6(4)
Mo(1)−C(13)−O(3)	179.6(4)	Mo(1)−C(14)−O(4)	177.2(5)

The structure of **6** is established by single crystal X-ray analysis. The structure and numbering scheme are shown in Figure 1. Bond distances and angles are listed in Table 4. The compound is a triphosphazane in which the central phosphorus P(2) is bonded to both BH_2 and $Mo(CO)_4$ groups. Although H atoms were not located, the bonding situation and ^{1}H NMR spectral integrals indicate that the coordinated borane unit is a BH_2 group. There seems to be no B−H···Mo agostic interaction, since the Mo···B distance of ca. 4 Å is much larger than distances of 2.4−2.6 Å seen typically in molecules that contain B−H−Mo bridge bonds [e.g. $Mo(CO)_5(BH_4)^-$].[22,23] Bonding in the triphosphazane P_3N_2 skeleton is closely similar to others

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[20] (a) King, R. B.; Fu, W.-K. *Inorg. Chem.* **1986**, *25*, 2384. (b) King, R. B.; Fu, W.-K.; Holt, E. M. *Inorg. Chem.* **1986**, *25*, 2394.

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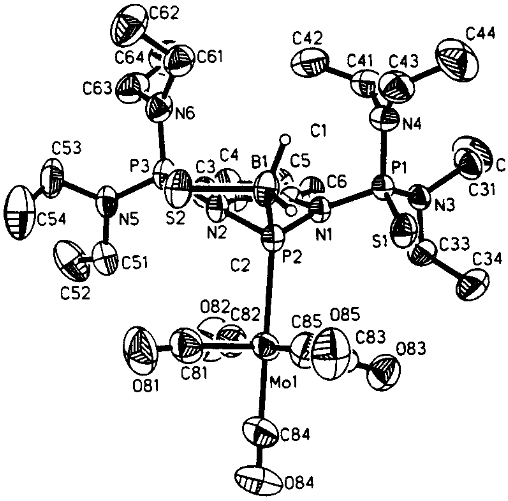

Figure 2. Structure and numbering scheme for **7**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms, except those on BH$_2$ groups, are omitted for clarity.

reported,[1] except that, because of the coordination of S atoms to BH$_2$ and Mo groups, the skeleton is twisted into an s-shaped arrangement. The differences in observed P═S distances suggests that bonding of the P═S groups is stronger to the Mo(CO)$_4$ than to the BH$_2$ unit; hence the S(2)−P(3) and S(1)−P(1) distances are 2.034 and 1.996 Å, respectively. Bonding distances in the Mo(CO)$_4$ unit are normal, and only angles to atoms in the S(1)−Mo−P(2) plane are unusual. The S(1)−Mo−P(2) angle of 75.8° is small and compensated for by larger P(2)−Mo−C(14) and S(1)−Mo−C(13) angles of 99.4 and 94.8°, respectively. The Mo−P(2) distance of 2.46 Å is typical for a phosphazane−molybdenum(0) complex. The P(2)−B distance of 1.937 Å is in the range of normal P−B single bonds observed in compounds such as (tetramethylpiperidino)(Cl)B−PHMes,[24,25] consistent with the P−B bond being free of multiple-bond character. Thus the complex can be regarded as a triphosphazane (**1**) in which X is a BH$_2$ group, leaving P(2) as a 2 e donor toward Mo. Both the BH$_2$ and Mo(CO)$_4$ achieve coordinative saturation by finally coordinating to S(2) and S(1), respectively, of the P(S)(NEt$_2$)$_2$ groups. Bond angles around P(2) are distorted from tetrahedral; the Mo−P(2)−B angle of 122.8° is larger and the N(1)−P(2)−N(2) angle of 89.1° is smaller, typical of previously studied triphosphazanes.[1,5]

Although **6** was sufficiently stable to isolate and characterize, it does undergo slow conversion in toluene solution to another new complex **7**. Upon standing of **6** at 25 °C for 7 days, its spectral features disappear as a black intractable precipitate and **7** appear. Compound **7** forms in low yield and likely is the result of a complex disproportionation process. The ^{31}P NMR spectrum of **7** is of AX$_2$ type. As with **6**, the P(2) resonance is shifted far downfield to δ 205.8. The IR spectrum shows B−H absorptions and neither the IR nor the ^{31}P NMR spectrum indicates the presence of a P−H bond, confirming that the complex is not a triphosphazane hydride.

Single-crystal X-ray analysis of **7** confirms its structure as a triphosphazane complex with structural and bonding features much like **6** (Figure 2, Table 5) in that the central phosphorus P(2) is bonded to both BH$_2$ and molybdenum carbonyl moieties. The major difference is that only the BH$_2$ group is coordinated to one of the exo P(S)(NEt$_2$)$_2$ groups. The S(1)−B distance is 1.983 Å, allowing the central P$_3$N$_2$ skeleton to adopt the typically observed situation where the terminal [P(1),P(3)] and endo [P(2)] phosphorus atoms are above and below, respectively, the mean C$_6$N$_2$ skeletal plane. In addition, the P═S distance of the coordinated P(3)═S is longer (2.020 Å) than that of the uncoordinated unit, P(1)═S (1.940 Å), a distance typical of P═S bonds in other aminophosphine sulfides.[1,5,]12[6,27] As in **6**, the bond angles around P(2) are somewhat distorted from tetrahedral in that the N−P−N angle is smaller (89.1°) and the Mo−P(2)−B angle is larger (122.2°).

Table 5. Selected Structural Parameters for **7**

(a) Distances (Å)

Mo(1)−P(2)	2.534(1)	Mo(1)−C(81)	2.048(4)
Mo(1)−C(82)	2.038(4)	Mo(1)−C(83)	2.036(4)
Mo(1)−C(84)	2.002(4)	Mo(1)−C(85)	2.040(4)
S(1)−P(1)	1.940(1)	S(2)−P(3)	2.020(1)
S(2)−B(1)	1.980(4)	P(1)−N(1)	1.690(2)
P(1)−N(3)	1.660(3)	P(1)−N(4)	1.640(3)
P(2)−B(1)	1.959(4)	P(2)−N(1)	1.771(2)
P(2)−N(2)	1.787(3)	P(3)−N(2)	1.652(3)
P(3)−N(5)	1.637(2)	P(3)−N(6)	1.632(3)
N(1)−C(1)	1.430(4)	N(2)−C(2)	1.431(4)
C(81)−O(81)	1.131(6)	C(82)−O(82)	1.144(5)
C(83)−O(83)	1.143(5)	C(84)−O(84)	1.135(6)
C(85)−O(85)	1.130(5)	C(91)−C(92)	1.309(13)
C(91)−C(93A)	1.391(10)	C(92)−C(93)	1.364(14)
C(93)−C(91A)	1.391(10)		

(b) Angles (deg)

P(2)−Mo(1)−C(81)	91.9(1)	P(2)−Mo(1)−C(82)	90.1(1)
C(81)−Mo(1)−C(82)	91.8(2)	P(2)−Mo(1)−C(83)	96.1(1)
C(81)−Mo(1)−C(83)	171.2(2)	C(82)−Mo(1)−C(83)	91.8(2)
P(2)−Mo(1)−C(84)	179.5(1)	C(81)−Mo(1)−C(84)	88.5(2)
C(82)−Mo(1)−C(84)	89.6(2)	C(83)−Mo(1)−C(84)	83.5(2)
P(2)−Mo(1)−C(85)	88.4(1)	C(81)−Mo(1)−C(85)	89.0(2)
C(82)−Mo(1)−C(85)	178.3(1)	C(83)−Mo(1)−C(85)	87.6(2)
C(84)−Mo(1)−C(85)	91.9(2)	P(3)−S(2)−B(1)	97.1(1)
S(1)−P(1)−N(1)	105.4(1)	S(1)−P(1)−N(3)	118.1(1)
N(1)−P(1)−N(3)	104.0(1)	S(1)−P(1)−N(4)	113.4(1)
N(1)−P(1)−N(4)	111.6(1)	N(3)−P(1)−N(4)	104.0(1)
Mo(1)−P(2)−B(1)	122.2(1)	Mo(1)−P(2)−N(1)	116.5(1)
B(1)−P(2)−N(1)	112.4(1)	Mo(1)−P(2)−N(2)	111.7(1)
B(1)−P(2)−N(2)	97.6(1)	N(1)−P(2)−N(2)	89.1(1)
S(2)−P(3)−N(2)	101.9(1)	S(2)−P(3)−N(5)	114.6(1)
N(2)−P(3)−N(5)	107.5(1)	S(2)−P(3)−N(6)	111.6(1)
N(2)−P(3)−N(6)	116.4(1)	N(5)−P(3)−N(6)	105.1(1)
S(2)−B(1)−P(2)	99.3(1)	P(1)−N(1)−P(2)	118.5(1)
P(1)−N(1)−C(1)	129.6(2)	P(2)−N(1)−C(1)	110.2(2)
P(2)−N(2)−P(3)	120.1(1)	P(2)−N(2)−C(2)	109.5(2)
P(3)−N(2)−C(2)	126.1(2)	P(1)−N(3)−C(31)	120.4(2)
N(2)−C(2)−C(1)	112.3(2)	N(1)−C(1)−C(2)	112.8(2)
Mo(1)−C(81)−O(81)	173.8(4)	Mo(1)−C(83)−O(83)	172.5(3)
Mo(1)−C(82)−O(82)	177.9(3)	Mo(1)−C(84)−O(84)	178.5(4)
Mo(1)−C(85)−O(85)	178.2(4)		

In contrast to that observed for the structurally related complex **6**, the ^{31}P NMR spectrum of **7** is temperature dependent. Down to −20 °C the spectrum is AX$_2$ in type. However, below −20 °C broadening begins and coalescence occurs (T_c = −50 °C).[28] The ABX spectrum at −90 °C shows only one $^2J_{PNP}$ coupling constant, presumably from coupling between P(2) and the BH$_2$-coordinated "frozen" P(S)(NEt)$_2$ group. It is assumed that the frozen structure is similar to that seen in the solid state (Figure 2). The NMR spectral features indicate that at room temperature the system is fluxional, allowing free rotation of the P(S)(NEt$_2$)$_2$ groups around the *endo* P−N bonds and on average both P(S)(NEt$_2$)$_2$ units coordinate to the central BH$_2$ group. At low temperature this process is slowed and the predominant structure is one in which the system

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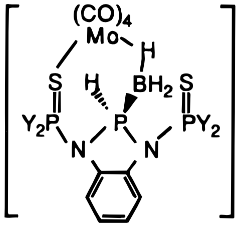
is frozen in the unsymmetrical form. A similar rotation of $P(S)(NEt_2)_2$ groups in **6** which would allow both to coordinate to the BH_2 group does not easily occur, perhaps because such rotation would require breaking of both a Mo−S and a B−S bond.

Under more vigorous reaction conditions, **3** reacts with $Mo(CO)_6$ at 70 °C during 70 h to form complex **8**, followed by **5**, both new complexes which involve $Mo(CO)_4$ and $Mo(CO)_3$ coordination of the triphosphazane hydride **4**. Since these were not separable by crystallization or chromatography, **8** was characterized tentatively from an **8**/**5** mixture. Samples of **5** adequate for characterization were obtained from nor·$Mo(CO)_4$/**3** reactions described above. The ^{31}P NMR spectra show that neither contain borane units and that both contain a P−H bond at the central phosphorus atom. The ABX and AX_2 patterns displayed by **8** and **5** indicate unsymmetrical and symmetrical coordinations, respectively, of the molybdenum moieties to the triphosphazane molecules. The chemical shifts of the P(2) phosphorus at δ 98.5 (**8**) and 133.4 (**5**) appear reasonable for aminophosphine-coordinated molybdenum complexes.[20] Furthermore, both spectra show large $^1J_{PH}$ couplings, 350 and 320 Hz for **5** and **8**, respectively, very different from the $^1J_{PH}$ seen in **4** and characteristic of Mo−coordinated λ^4 P−H bond containing sites.[20,21]

The **3**/nor·$Mo(CO)_4$ reactions lead primarily to BH_2-coordinated products whereas the more vigorous **3**/$Mo(CO)_6$ reactions form triphosphazane hydride complexes, a situation suggesting differences in reaction mechanism. In the $Mo(CO)_6$ reactions, there might be sufficient dissociation of the BH_3 from **3** at 70 °C to allow its reaction with the thermally formed $Mo(CO)_5$ and $Mo(CO)_4$ moieties. Although there was no evidence for formation of a **3**·$Mo(CO)_5$ complex, it could be formed as a reactive intermediate in the system prior to **6**. After formation of **8**, with thermal disociative loss of CO from the $Mo(CO)_4$ unit, **5** can form in which the second P═S unit coordinates to the sixth site on molybdenum.

In contrast, the nor·$Mo(CO)_4$ reaction occurs under milder conditions, with retention of the B−P bond and with elimination of H_2 in a reaction which appears to be activated by the presence of the molybdenum carbonyl species. This reaction is unusual because it involves metal moiety activation of perhaps both B−H and P−H bonds in the same complex. It is known that H_2 can be eliminated from the P(H)−B(H) units of phosphine−boranes; however, these reactions typically occur at temperatures in excess of 100 °C.[17,29] How activation in the **3**/nor·$Mo(CO)_4$ reaction occurs is unclear, although it could occur through intermediate coordination of the $Mo(CO)_4$ group to one $P(S)(NEt_2)_2$ group and a B−H bond of the BH_3 unit to form complex **9**. Similar coordination in a molybdophosphenium−borane complex, involving a Mo−H_μ−B−P bonding arrangement, was reported earlier.[23] Complex **9**, upon H_2 loss, phosphorus coordination to the Mo center, and coordination of the other $P(S)(NEt_2)_2$ group to the BH_2 moiety, could yield the finally observed **6**. Studies of the activation process and the extrapolation of it to other systems are in progress currently.



9 (Y = Et_2N)

Acknowledgment. We gratefully acknowledge support for this work by National Science Foundation Grants CHE 8312856 and CHE 8714951 and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Supporting Information Available: Tables of crystal data and refinement details, anisotropic thermal parameters, hydrogen atom positions, complete bond distances and angles, and least-squares planes (22 pages). Ordering information is given on any current masthead page.

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