Table III. Crystal Data for $Mo_2Cl_6(PEt_3)_4$

formula	$C_{24}H_{60}Cl_6Mo_2P_4$
fw	877.23
space group	*Pnma*
a, Å	20.368 (2)
b, Å	19.308 (2)
c, Å	10.6404 (7)
V, Å^3	4185 (1)
Z	4
d_{calc}, g/cm^3	1.39
μ(Cu Kα), cm^{-1}	101.83
radiation (monochromated in incident beam)	Cu Kα (λ = 1.54178 Å)
temp, °C	20
transm factors: max, min	1.000, 0.641
R^a	0.052
$R_w{}^b$	0.072

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

dinitrogen prior to use. Instruments used were as follows: FTIR, Nicolet 5DXC; magnetic susceptibility balance, Johnson Matthey; UV/vis, Schimadzu UV-240, X-ray diffractometer, Enraf-Nonius CAD-4. The elemental analysis was by Midwest Microlab, Indianapolis, IN. $MoCl_3(THF)_3$ was prepared according to the literature.[24] PEt_3 was purchased from Strem Chemicals and used as received.

Preparation of $Mo_2Cl_6(PEt_3)_4$. $MoCl_3(THF)_3$ (0.62 g, 1.47 mmol) was reacted with PEt_3 (0.45 mL, 3.05 mmol) in 10 mL of THF. After being stirred for 2 h, the clear yellow solution was evaporated under reduced pressure to a residue. After addition of toluene (10 mL), the resulting yellow-orange solution was refluxed for 10 min. The color of the solution turned dark pine green. Golden brown crystals of the pure product crystallized upon cooling to room temperature. Yield: 0.31 g (48%). An additional crop (0.06 g) was obtained by cooling the mother solution to −20 °C. Anal. Calcd for $C_{24}H_{60}Cl_6Mo_2P_4$: C, 32.9; H, 6.9; Cl, 24.2; P, 14.1. Found: C, 33.2; H, 6.9; Cl, 23.2; P, 13.5. $\chi_g = 11.69 \times 10^{-6}$ cgsu; $\mu_{eff} = 5.05\ \mu_B$ (molar diamagnetic correction -480×10^{-6} cgsu).

IR (Nujol mull; cm^{-1}): 1420 m, 1280 w, 1265 m, 1045 s, 765 s, 750 sh, 735 m, 720 s. UV/vis [toluene; nm (ϵ/cm^{-1} mol^{-1} L)]: 302 (9200), 345 (6000), 370 (5500), 606 (340).

X-ray Crystallography. A single crystal was glued to the inside of a thin-walled glass capillary, which was then sealed under dinitrogen and mounted on the diffractometer. The cell determination, data collection and reduction, and semiempirical absorption correction[25] were routine. Systematic absences from the data indicated the space group as either *Pnma* or *Pn*2$_1$*a* (nonstandard setting of *Pna*2$_1$). The centrosymmetric choice was suggested by intensity statistics and was adopted for the refinement. The successful refinement shows that this was the correct choice. The structure was solved by direct methods and refined by alternate full-matrix least-squares cycles and difference Fourier maps. The two equatorial phosphine ligands [those binding through atoms P(2) and P(3)] had all the ethyl groups disordered among two symmetry-related positions. All the carbon atoms of these groups were refined at half-occupancy and were left isotropic. Hydrogen atoms were not included in the refinement. Selected crystal data are in Table III, positional and equivalent isotropic thermal parameters are listed in Table I, and selected bond distances and angles are assembled in Table II.

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Supplementary Material Available: For $Mo_2Cl_6(PEt_3)_4$, full tables of crystal data, anisotropic displacement parameters, and bond distances and angles (4 pages); tables of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

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Syntheses of *closo*-1-Methylphosphadodecaborane(12), $B_{11}H_{11}PCH_3$, and *nido*-7-Methylphosphaundecaborane(13), $B_{10}H_{12}PCH_3$, from the $[B_{11}H_{13}]^{2-}$ Anion and Their Molecular Structures

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The anion $[B_{11}H_{14}]^-$ can function as both a Brønsted base and a Brønsted acid. Protonation[1] of $[B_{11}B_{14}]^-$ at low temperature yields *nido*-undecaborane(15), $B_{11}H_{15}$, while deprotonation[2] yields the tridecahydroundecaborate(2−) dianion, $[B_{11}H_{13}]^{2-}$. Recently reported syntheses[3] of alkali-metal salts of $[B_{11}H_{14}]^-$ from the reaction of pentaborane(9), B_5H_9, with MH (M = Na, K) provide a good source for obtaining $[B_{11}H_{13}]^{2-}$ in a relatively simple way and have prompted renewed studies of the chemistry of this dianion. From the reaction of $[B_{11}H_{13}]^{2-}$ with $P(CH_3)Cl_2$ in tetrahydrofuran we have obtained *closo*-1-methyl-phosphadodecaborane(12), $B_{11}H_{11}PCH_3$. However, from the reaction in diethyl ether, *nido*-7-methylphosphaundecaborane(12), $B_{10}H_{12}PCH_3$, was obtained, a phosphaborane prepared previously by a different route.[4] While molecular structures of these types of phosphaboranes have been proposed based upon ^{11}B NMR spectra, no actual structure determinations have been reported. In the present report, syntheses of $B_{11}H_{11}PCH_3$ and $B_{10}H_{12}PCH_3$ and their molecular structures as determined by single-crystal X-ray analyses are described.

Experimental Section

Materials were handled by using standard vacuum-line and inert-atmosphere techniques. B_5H_9 (Callery Chemical Co.) was purified by passing it through a U-trap maintained at −78 °C and collected in a second U-trap cooled to −111 °C. NaH (Aldrich) was obtained as a mineral oil dispersion. The oil was washed away with dry pentane, and the hydride was stored in a controlled-atmosphere glovebox until use. Glyme (1,2-dimethoxyethane), tetrahydrofuran (THF), and toluene were distilled from sodium benzophenone ketyl before use. Hexane was distilled from CaH_2 before use. ^{11}B and 2D ^{11}B–^{11}B NMR ($\delta(Et_2O\cdot BF_3)$ = 0.00 ppm), ^{1}H (δ(TMS) = 0.00 ppm), and ^{31}P ($\delta(H_3PO_4)$ = 0.00 ppm) NMR spectra were obtained on a Bruker MSL-300 NMR spectrometer. Infrared spectra were obtained on a Mattson Cygnus 25 spectrometer. Mass spectra were obtained on VG 70-250S and Kratos MS-30 mass spectrometers.

X-ray diffraction data were collected with an Enraf-Nonius CAD4 diffractometer. Crystallographic parameters are given in Table I. Computations were carried out on a PDP 11/44 computer using the SDP structure determination package. All data were corrected for Lorentz and polarization effects, and the structures were solved by a combination of the direct-method MULTAN 11/82 and difference Fourier techniques with analytical atomic scattering factors used throughout. Full-matrix least-squares refinements were employed.

$[B_{11}H_{13}]^{2-}$. From the reaction of NaH with B_5H_9 in glyme $Na[B_{11}H_{14}]$ (10.35 mmol) was prepared according to a previously reported procedure.[2] Then, in the glovebox, NaH (282.3 mg, 88% activity, 10.53 mmol of active NaH) was added to a tip tube attached to the reaction vessel containing the $Na[B_{11}H_{14}]$. Glyme (20 mL) was condensed into the flask at −196 °C. The vessel was allowed to warm to room temperature until all the $Na[B_{11}H_{14}]$ had dissolved. Then the tip tube was tilted so as to introduce the NaH into the solution. The resulting slurry was stirred for

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Table I. Crystallographic Data for *closo*-1-$P(CH_3)B_{11}H_{11}$ and *nido*-7-$P(CH_3)B_{10}H_{12}$

chemical formula	$CH_{14}B_{11}P$	$CH_{15}B_{10}P$
mol wt	176.03	166.23
color of cryst	colorless	colorless
space group	*Pc*	*Cc*
molecules/unit cell	2	8
temp, °C	−40	−50
a, Å	6.979	12.188
b, Å	10.562	8.142
c, Å	10.036	21.425
β, deg	136.05	101.49
vol of unit cell, $Å^3$	513.4	2083.5
cryst dimens, mm	0.38 × 0.30 × 0.25	0.50 × 0.43 × 0.38
density (calcd), g cm^{-3}	1.139	1.060
radiation	Mo Kα (0.710730 Å)	Mo Kα (0.710730 Å)
abs coeff, cm^{-1}	1.9	1.9
scan mode	ω−2θ	ω−2θ
data collcn limits (2θ), deg	4–50	4–45
no. of unique reflcns	1109	2500
no. of reflcns used in struct refin (>3σ(*I*))	953	1553
$R_F = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.066	0.046
$R_{wF} = (\sum w(\|F_o\| - \|F_c\|)^2/\sum w\|F_o\|^2)^{1/2}$	0.086	0.053
$w = (\sigma(I)^2 + (kI)^2)^{-1}$	$k = 0.04$	$k = 0.04$

48 h at room temperature. A white precipitate formed during this period. The vessel was cooled to −196 °C and the evolved H_2 gas (10.08 mmol, 97%) was measured. In the glovebox, the vessel was attached to an extractor, and the slurry was filtered. $Na_2[B_{11}H_{13}]$ (only slightly soluble in glyme) was collected on the frit. The product was extracted three times with glyme until all the yellow color was gone, and then the volatiles were removed under dynamic vacuum for 1 h. The apparatus was taken into the glovebox and a new 100-mL collection flask attached to the extractor. The product was dissolved in 15 mL of THF and filtered (leaving any unreacted NaH on the frit). The volatiles were removed under dynamic vacuum for 1 h, leaving a white solid in the collection flask. Then the flask was heated to 90 °C, while additional volatiles were removed under dynamic vacuum for 20 h. The product, $Na_2[B_{11}H_{13}]$, was scraped from the vessel and stored in the glovebox until use (1.36 g, 7.64 mmol). $K_2[B_{11}H_{13}]$ was prepared in a similar manner, excluding the THF extraction since $K_2[B_{11}H_{13}]$ is insoluble in THF. To ensure that no KH was present in the $K_2[B_{11}H_{13}]$, a slight deficiency of hydride was used during the deprotonation of $K[B_{11}H_{14}]$.

$B_{11}H_{11}PCH_3$. $Na_2[B_{11}H_{13}]$ (631.9 mg, 3.56 mmol) was loaded into a 100-mL reaction vessel containing a magnetic stir bar. THF (15 mL) and PCH_3Cl_2 (3.56 mmol, measured as a gas) were condensed into the vessel at −196 °C. The vessel was covered with aluminum foil to exclude light, and the reaction mixture was stirred for 5 days at room temperature. During this time period 0.52 mmol of H_2 gas was formed. The THF was removed under dynamic vacuum until a gel remained in the vessel. Then the vessel, under vacuum, was heated to 80–90 °C for 12 h in order to sublime $B_{11}H_{11}PCH_3$ to the air-cooled neck of the flask. This crude material was then transfered (in the glovebox) to a sublimation apparatus and resublimed in vacuum at 55 °C to a water-cooled cold finger. The yield of $B_{11}H_{11}PCH_3$ was 24.5 mg (0.14 mmol, 3.9% based upon $Na_2[B_{11}H_{13}]$). The ^{11}B NMR spectrum indicated that the sample contained a small amount of 7-methylphosphaundecaborane(13), $B_{10}H_{12}PCH_3$, which could be removed by fractional crystallization from toluene. Crystals of $B_{11}H_{11}PCH_3$ suitable for X-ray diffraction were obtained by vapor diffusion of hexane into a toluene solution. ^{11}B NMR (CD_2Cl_2, 25 °C) with assignments based on 2D ^{11}B–^{11}B: −1.07 (d, *J* = 150 Hz, boron atom 12), −6.72 (d, *J* = 150 Hz, boron atoms 7–11), −14.4 ppm (d, *J* = 164 Hz, boron atoms 2–6). IR (Nujol): 3010 (w), 2922 (w), 2581 (s), 2563 (s), 2544 (s), 1391 (w), 1285 (w), 1023 (w), 913 (w), 888 (w), 795 (w), 784 (w), 722 (w) cm^{-1}. MS: calculated for $^{11}B_{11}{}^{1}H_{14}{}^{31}P^{12}C$, 178; observed, 178.19.

$B_{10}H_{12}PCH_3$. $K_2[B_{11}H_{13}]$ (555 mg, 2.64 mmol), prepared as above, was loaded into a 100-mL reaction vessel containing a magnetic stir bar, and diethyl ether (20 mL) and $P(CH_3)Cl_2$ (317 mg, 2.71 mmol) were condensed into the vessel at −196 °C. The vessel was covered with aluminum foil to exclude light and allowed to stir for 7 days at room temperature. Then the vessel was cooled to −196 °C, and the H_2 evolved (0.53 mmol) was measured. The vessel was warmed to room temperature, and in the glovebox, it was attached to an extractor and the solution was filtered. The diethyl ether was removed under dynamic vacuum, and the receiving flask was attached to a sublimator. $B_{10}H_{12}PCH_3$ sublimed at 60 °C to a dry ice cooled sublimation probe (53.0 mg, 0.32 mmol, 12% based upon $K_2[B_{11}H_{13}]$). Crystals of $B_{10}H_{12}PCH_3$ were obtained by slow (7 days) sublimation of the compound at 35 °C to the air-cooled walls of a sealed tube. Similar results were obtained with $Na_2[B_{11}H_{13}]$. MS: parent mass *m/e* calculated for $^{11}B_{10}{}^{12}C^{1}H_{15}{}^{31}P$, 168; found, 167.2. ^{11}B NMR (CD_3CN): 3.3 (d, *J* = 145 Hz), −7.2 (d, *J* = 160 Hz), −11.7 (d, *J* = 161 Hz), −16.9 (d, *J* = 149 Hz), and −24.5 ppm (d, *J* = 148 Hz) in relative areas of 1:2:2:2:3, respectively. $^{1}H\{^{11}B\}$ NMR (CD_3CN): 2.61, 2.30, 1.72, 1.59 (br), 1.14 ppm (terminal BH); −4.04 ppm (J_{PH} = 22.7 Hz), bridge BHB); 2.12 ppm (d, J_{PH} = 12.0 Hz, CH_3). $^{31}P\{^{1}H\}$ NMR (CD_3CN): −85.6 ppm (br).

Discussion

Several icosahedral heteroboranes have been prepared[5-7] directly from $[B_{11}H_{13}]^{2-}$ or from reactions in which this dianion was prepared in situ from $[B_{11}H_{14}]^{-}$. From the reaction between $Na_2[B_{11}H_{13}]$ and $P(CH_3)Cl_2$ in THF, was isolated $B_{11}H_{11}PCH_3$ as the main phosphaborane product, while from the reaction in diethyl ether $B_{10}H_{12}PCH_3$ was isolated as the main product. Although the yields of phosphaboranes are low, they are consistent with the reports of yields for the only other reported icosahedral phosphaboranes, $B_{11}H_{11}PC_6H_5$,[5] 1,2-$P_2B_{10}H_{10}$, and 1,7-$P_2B_{10}H_{10}$,[5] and for $B_{10}H_{12}PCH_3$ which has been prepared through a different reaction route,[4] the reaction of $[B_{10}H_{12}]^{2-}$ with $P(CH_3)Cl_2$.

$B_{11}H_{11}PCH_3$ is air-sensitive but thermally very stable, not decomposing until 220 °C in a sealed capillary. It is soluble in toluene, methylene chloride, chloroform, and acetonitrile and slightly soluble in pentane and hexane. The ^{11}B NMR spectrum of $B_{11}H_{11}PCH_3$ (Experimental Section) is consistent with an icosahedral $B_{11}P$ framework in solution. A single-crystal X-ray analysis shows the molecular structure to be a slightly distorted icosahedron in the solid state due to the larger size of the phosphorus atom than the boron atom (Figure 1). The structure is consistent with that[8] of $[B_{12}H_{12}]^{2-}$. Positional parameters are given in Table IIA; selected bond distances and bond angles are given in Tables IIIA and IVA.

The angle between the P–C bond and the B2–B3–B4–B5–B6 plane is 98.21°. This deviation from perpendicularity is probably due to crystal packing forces. The intermolecular contacts are 3.01 Å or longer with the exception of one distance, 2.33 Å between one C–H hydrogen and one B–H hydrogen on neighboring molecules. If the angle between the P–C bond and the B2–B3–B4–B5–B6 plane were 90°, the C–H, B–H hydrogen intermolecular contact would be 2.01 Å, and the distance between the C and the hydrogen of the B–H bond would be reduced from 3.01 to 2.80 Å.

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Table II. Positional Parameters (Esd's) and Isotropic Equivalent Thermal Parameters for *closo*-1-$P(CH_3)B_{11}H_{11}$ and *nido*-7-$P(CH_3)B_{10}H_{12}$[a]

atom	*x*	*y*	*z*	*B*, Å^2
	A. *closo*-1-$P(CH_3)B_{11}H_{11}$			
P1	0.095	0.2426 (1)	0.936	2.95 (3)
C1	0.446 (1)	0.1952 (6)	1.1115 (8)	3.5 (2)
B2	−0.150 (1)	0.2094 (7)	0.9636 (8)	3.4 (2)
B3	−0.186 (1)	0.1080 (6)	0.7958 (9)	3.5 (2)
B4	−0.153 (1)	0.2080 (7)	0.6595 (8)	3.2 (2)
B5	−0.098 (2)	0.3773 (9)	0.747 (1)	5.0 (3)
B6	−0.102 (2)	0.3748 (9)	0.930 (1)	5.0 (3)
B7	−0.432 (1)	0.3197 (8)	0.8165 (8)	3.3 (2)
B8	−0.477 (1)	0.1614 (7)	0.7388 (8)	3.2 (2)
B9	−0.478 (1)	0.1616 (7)	0.5607 (8)	3.4 (2)
B10	−0.435 (1)	0.3203 (8)	0.5274 (8)	3.5 (2)
B11	−0.405 (1)	0.4206 (7)	0.6846 (9)	3.4 (2)
B12	−0.627 (1)	0.2889 (7)	0.5737 (9)	3.2 (2)
H2	−0.11 (1)	0.174 (7)	1.08 (1)	4.4
H3	−0.09 (1)	−0.001 (9)	0.821 (8)	4.5
H4	−0.06 (1)	0.184 (5)	0.627 (6)	4.2
H5	0.07 (1)	0.434 (8)	0.755 (8)	6.0
H6[b]	0.022	0.447	1.055	6.0
H7	−0.53 (1)	0.345 (6)	0.864 (7)	4.3
H8	−0.60 (1)	0.108 (9)	0.718 (8)	4.2
H9	0.40 (1)	0.090 (6)	0.450 (7)	4.4
H10	−0.52 (1)	0.344 (8)	0.380 (9)	4.5
H11	−0.49 (1)	0.516 (6)	0.641 (7)	4.4
H12	−0.84 (1)	0.299 (5)	0.479 (6)	4.2
H13[b,c]	0.497	0.166	1.050	4.5
H14[c,d]	0.470	0.128	1.187	4.5
H15[b,c]	0.559	0.265	1.193	4.5
	B. *nido*-7-$P(CH_3)B_{10}H_{12}$[e] (Molecule 1)			
C	−0.0534 (4)	−0.0160 (7)	0.4900 (2)	3.4 (1)
B1	0.2466 (5)	−0.095 (1)	0.6493 (3)	3.7 (1)
B2	0.1676 (6)	−0.1611 (9)	0.5784 (3)	3.6 (1)
B3	0.1168 (5)	−0.0052 (9)	0.6234 (3)	3.5 (1)
B4	0.7314 (6)	−0.622 (1)	1.1577 (3)	3.8 (1)
B5	0.3511 (5)	0.0393 (9)	0.6340 (3)	3.6 (1)
B6	0.3134 (6)	−0.1350 (9)	0.5834 (3)	3.6 (1)
P7	0.090	0.0288 (2)	0.529	2.84 (2)
B8	0.1415 (6)	0.2083 (9)	0.5903 (3)	3.7 (1)
B9	0.2960 (6)	0.2218 (9)	0.6009 (3)	4.0 (2)
B10	0.3481 (5)	0.055 (1)	0.5521 (3)	3.7 (1)
B11	0.2295 (5)	−0.0684 (9)	0.5102 (3)	3.5 (1)
H1	−0.230 (5)	0.673 (7)	0.192 (3)	5 (1)
H2	−0.375 (4)	0.774 (5)	0.066 (2)	2 (1)
H3	0.024 (4)	−0.007 (6)	0.639 (2)	3 (1)
H4[d]	−0.256	0.334	0.207	6
H5	0.438 (4)	0.960 (6)	0.162 (2)	3 (1)
H6[d]	0.357	−0.245	0.594	6
H8	0.079 (4)	0.310 (5)	0.597 (2)	2 (1)
H9	0.340 (4)	0.345 (6)	0.611 (2)	4 (1)
H10	0.412 (4)	0.051 (5)	0.527 (2)	2 (1)
H11	0.215 (5)	−0.133 (7)	0.466 (2)	5 (1)
H12[c,d]	−0.062	−0.149	0.495	4
H13[c,d]	−0.105	0.040	0.510	4
H14[c,d]	−0.055	0.019	0.445	4
H(8,9)	−0.277 (5)	−0.256 (6)	−0.441 (2)	4 (1)
H(10,11)	0.277 (4)	0.076 (6)	0.510 (2)	4 (1)

[a] Values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameters defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$. $B(H) = B(B \text{ or } C) + 1$ in *closo*-1-$P(CH_3)$-$B_{11}H_{11}$, but H atoms were isotropically refined in *nido*-7-$P(CH_3)$-$B_{10}H_{12}$. [b] Position calculated. [c] Methyl H. [d] Located but not refined. [e] Only data for molecule 1 are given. Data for independent molecule 2 are given in the supplementary material.

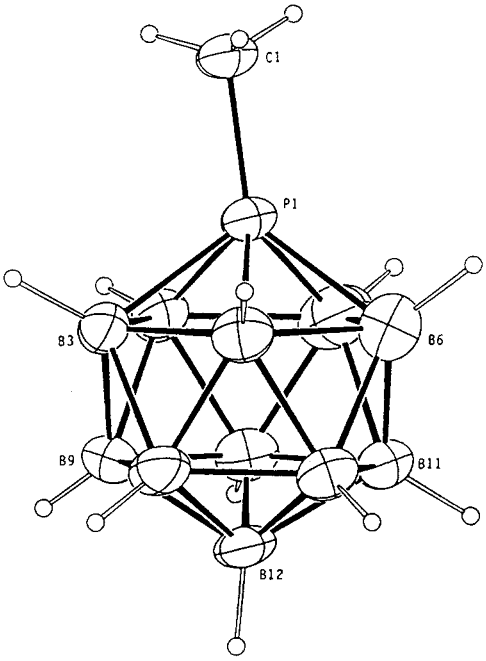

Figure 1. Molecular structure of $B_{11}H_{11}PCH_3$ (ORTEP plot with 50% probability ellipsoids).

Table III. Selected Bond Distances (Å) and Esd's for *closo*-1-$P(CH_3)B_{11}H_{11}$ and *nido*-7-$P(CH_3)B_{10}H_{12}$

	A. *closo*-1-$P(CH_3)B_{11}H_{11}$		
P1–C1	1.774 (4)	B5–B6	1.855 (9)
P1–B2	1.954 (5)	B5–B10	1.813 (7)
P1–B3	1.966 (4)	B5–B11	1.807 (8)
P1–B4	1.978 (5)	B6–B7	1.783 (8)
P1–B5	1.940 (5)	B6–B11	1.808 (7)
P1–B6	1.927 (6)	B7–B8	1.775 (6)
B2–B3	1.858 (7)	B7–B11	1.813 (6)
B2–B6	1.857 (7)	B7–B12	1.766 (6)
B2–B7	1.794 (6)	B8–B9	1.782 (7)
B2–B8	1.770 (5)	B8–B12	1.776 (6)
B3–B4	1.869 (7)	B9–B10	1.775 (6)
B3–B8	1.761 (7)	B9–B12	1.763 (6)
B3–B9	1.767 (5)	B10–B11	1.783 (6)
B4–B5	1.905 (7)	B10–B12	1.740 (7)
B4–B9	1.771 (6)	B11–B12	1.760 (6)
B4–B10	1.813 (6)		
	B. *nido*-7-$P(CH_3)B_{10}H_{12}$[a] (Molecule 1)		
P7–C	1.814 (4)	B4–B5	1.770 (8)
P7–B2	2.001 (6)	B4–B8	1.777 (8)
P7–B3	1.996 (5)	B4–B9	1.775 (9)
P7–B8	1.978 (6)	B5–B6	1.789 (9)
P7–B11	1.996 (6)	B5–B9	1.724 (9)
B1–B2	1.714 (8)	B5–B10	1.753 (8)
B1–B3	1.732 (8)	B6–B10	1.769 (8)
B1–B4	1.790 (10)	B6–B11	1.778 (8)
B1–B5	1.760 (8)	B8–B9	1.854 (8)
B1–B6	1.793 (8)	B9–B10	1.900 (9)
B2–B3	1.778 (8)	B10–B11	1.839 (8)
B2–B6	1.772 (8)	B8–H(8,9)	1.34 (5)
B2–B11	1.926 (8)	B9–H(8,9)	1.15 (5)
B3–B4	1.774 (8)	B10–H(10,11)	1.13 (5)
B3–B8	1.924 (9)	B11–H(10,11)	1.31 (8)

[a] Only data for molecule 1 are given. Data for independent molecule 2 are given in the supplementary material.

The X-ray analysis confirms the proposed[4,9] structure of $B_{10}H_{12}PCH_3$. There are two independent molecules in the asymmetric unit. Their structural parameters are very similar. Positional parameters for molecule 1 are given in Table IIB; selected bond distances and bond angles are given in Tables IIIB and IVB. This *nido*-phosphaborane has a structure (Figure 2) which is based upon that of an icosahedron with one vertex removed. It has pseudo-C_s symmetry. The phosphorus atom occupies a vertex site on the open face of the structure. It is 0.08 Å above the least-squares plane of the open face. The least-squares plane of the open face is nearly parallel to that of the least-squares plane defined by B2–B3–B4–B5–B6 with a dihedral angle of 1°. Four of the borons on the face are hydrogen-bridged. Hydrogen bridges are asymmetric with the short ends averaging 1.14 Å and the long ends

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(9) Wright, W. F.; Garber, A. R.; Todd, L. J. *J. Magn. Reson.* **1978**, *30*, 595.

Table IV. Selected Bond Angles (deg) and Esd's Involving Cage Atoms for *closo*-1-$P(CH_3)B_{11}H_{11}$ and *nido*-7-$P(CH_3)B_{10}H_{12}$

			A. *closo*-1-$P(CH_3)B_{11}H_{11}$				
C1-P1-B2	122.3 (2)	B4-B3-B8	107.6 (3)	B5-B6-B11	59.1 (3)	B10-B9-B12	58.9 (3)
C1-P1-B3	117.3 (2)	B4-B3-B9	58.2 (2)	B7-B6-B11	60.6 (3)	B4-B10-B5	63.4 (3)
C1-P1-B4	121.9 (2)	B8-B3-B9	60.7 (3)	B2-B7-B6	62.6 (3)	B4-B10-B9	59.1 (3)
C1-P1-B5	131.9 (2)	P1-B4-B3	61.4 (2)	B2-B7-B8	59.5 (2)	B4-B10-B11	111.6 (3)
C1-P1-B6	132.8 (2)	P1-B4-B5	59.9 (2)	B2-B7-B11	110.7 (3)	B4-B10-B12	108.8 (3)
B2-P1-B3	56.6 (2)	P1-B4-B9	108.0 (3)	B2-B7-B12	108.4 (3)	B5-B10-B9	109.4 (3)
B2-P1-B4	101.3 (2)	P1-B4-B10	107.2 (3)	B6-B7-B8	109.0 (3)	B5-B10-B11	60.3 (3)
B2-P1-B5	102.1 (3)	B3-B4-B5	106.5 (3)	B6-B7-B11	60.4 (3)	B5-B10-B12	108.4 (4)
B2-P1-B6	57.2 (2)	B3-B4-B9	58.0 (2)	B6-B7-B12	107.4 (3)	B9-B10-B11	108.9 (3)
B3-P1-B4	56.6 (2)	B3-B4-B10	105.2 (3)	B8-B7-B11	108.1 (3)	B9-B10-B12	60.2 (3)
B3-P1-B5	101.5 (2)	B5-B4-B9	105.6 (3)	B8-B7-B12	60.2 (2)	B11-B10-B12	60.0 (3)
B3-P1-B6	100.5 (2)	B5-B4-B10	58.3 (3)	B11-B7-B12	58.9 (2)	B5-B11-B6	61.7 (3)
B4-P1-B5	58.2 (2)	B9-B4-B10	59.4 (2)	B2-B8-B3	63.5 (3)	B5-B11-B7	108.7 (3)
B4-P1-B6	101.9 (2)	P1-B5-B4	61.9 (2)	B2-B8-B7	60.8 (2)	B5-B11-B10	60.7 (3)
B5-P1-B6	57.3 (3)	P1-B5-B6	61.0 (2)	B2-B8-B9	110.5 (3)	B5-B11-B12	107.8 (3)
P1-B2-B3	62.0 (2)	P1-B5-B10	108.9 (3)	B2-B8-B12	109.0 (3)	B6-B11-B7	59.0 (3)
P1-B2-B6	60.7 (2)	P1-B5-B11	109.8 (4)	B3-B8-B7	111.3 (3)	B6-B11-B10	108.7 (3)
P1-B2-B7	108.7 (3)	B4-B5-B6	107.5 (4)	B3-B8-B9	59.8 (2)	B6-B11-B12	106.5 (3)
P1-B2-B8	109.0 (3)	B4-B5-B10	58.3 (3)	B3-B8-B12	108.4 (3)	B7-B11-B10	106.8 (3)
B3-B2-B6	107.4 (3)	B4-B5-B11	106.5 (3)	B7-B8-B9	108.2 (3)	B7-B11-B12	59.2 (3)
B3-B2-B7	106.1 (3)	B6-B5-B10	105.5 (4)	B7-B8-B12	59.6 (2)	B10-B11-B12	58.8 (3)
B3-B2-B8	58.0 (2)	B6-B5-B11	59.2 (3)	B9-B8-B12	59.4 (3)	B7-B12-B8	60.1 (3)
B6-B2-B7	58.4 (3)	B10-B5-B11	59.0 (3)	B3-B9-B4	63.8 (3)	B7-B12-B9	109.4 (3)
B6-B2-B8	105.9 (3)	P1-B6-B2	62.2 (2)	B3-B9-B8	59.5 (3)	B7-B12-B10	110.8 (3)
B7-B2-B8	59.7 (2)	P1-B6-B5	61.7 (3)	B3-B9-B10	111.4 (3)	B7-B12-B11	61.9 (3)
P1-B3-B2	61.4 (2)	P1-B6-B7	110.4 (3)	B3-B9-B12	108.8 (3)	B8-B12-B9	60.4 (2)
P1-B3-B4	62.0 (2)	P1-B6-B11	110.3 (3)	B4-B9-B8	111.1 (3)	B8-B12-B10	109.9 (3)
P1-B3-B8	108.8 (3)	B2-B6-B5	109.3 (3)	B4-B9-B10	61.5 (2)	B8-B12-B11	110.4 (3)
P1-B3-B9	108.7 (3)	B2-B6-B7	59.0 (3)	B4-B9-B12	109.7 (3)	B9-B12-B10	60.9 (3)
B2-B3-B4	109.4 (3)	B2-B6-B11	108.1 (3)	B8-B9-B10	108.1 (3)	B9-B12-B11	110.5 (3)
B2-B3-B8	58.5 (3)	B5-B6-B7	107.9 (4)	B8-B9-B12	60.1 (3)	B10-B12-B11	61.2 (3)
B2-B3-B9	107.3 (3)						
			B. *nido*-7-$P(CH_3)B_{10}H_{12}$[a] (Molecule 1)				
B2-B1-B3	62.1 (3)	B2-B3-B4	108.1 (4)	B6-B5-B10	59.9 (3)	B3-B8-P7	61.5 (3)
B2-B1-B4	110.3 (4)	B2-B3-P7	63.7 (3)	B9-B5-B10	66.3 (4)	B3-B8-B9	103.8 (4)
B2-B1-B5	109.2 (4)	B2-B3-B8	110.4 (4)	B1-B6-B2	57.5 (3)	B4-B8-P7	108.0 (4)
B2-B1-B6	60.7 (3)	B4-B3-P7	107.3 (3)	B1-B6-B5	58.9 (3)	B4-B8-B9	58.5 (3)
B3-B1-B4	60.5 (4)	B4-B3-B8	57.3 (3)	B1-B6-B10	108.8 (4)	P7-B8-B9	108.0 (4)
B3-B1-B5	109.0 (4)	P7-B3-B8	60.6 (2)	B1-B6-B11	111.6 (4)	B4-B9-B5	60.7 (4)
B3-B1-B6	110.7 (4)	B1-B4-B3	58.2 (3)	B2-B6-B5	105.4 (4)	B4-B9-B8	58.6 (3)
B4-B1-B5	59.8 (4)	B1-B4-B5	59.3 (4)	B2-B6-B10	113.2 (4)	B4-B9-B10	106.9 (4)
B4-B1-B6	109.2 (4)	B1-B4-B8	111.7 (4)	B2-B6-B11	65.7 (3)	B5-B9-B8	107.6 (4)
B5-B1-B6	60.4 (3)	B1-B4-B9	108.4 (4)	B5-B6-B10	59.0 (3)	B5-B9-B10	57.6 (3)
B1-B2-B3	59.4 (3)	B3-B4-B5	106.7 (4)	B5-B6-B11	109.0 (4)	B8-B9-B10	109.4 (4)
B1-B2-B6	61.9 (3)	B3-B4-B8	65.6 (3)	B10-B6-B11	62.5 (3)	B5-B10-B6	61.1 (3)
B1-B2-P7	110.4 (4)	B3-B4-B9	113.8 (4)	C-P7-B2	113.6 (3)	B5-B10-B9	56.2 (3)
B1-B2-B11	108.3 (4)	B5-B4-B8	109.1 (4)	C-P7-B3	113.1 (2)	B5-B10-B11	107.9 (4)
B3-B2-B6	109.5 (4)	B5-B4-B9	58.2 (3)	C-P7-B8	127.4 (3)	B6-B10-B9	106.6 (4)
B3-B2-P7	63.4 (3)	B8-B4-B9	62.9 (3)	C-P7-B11	127.3 (2)	B6-B10-B11	59.0 (3)
B3-B2-B11	111.3 (4)	B1-B5-B4	60.9 (4)	B2-P7-B3	52.9 (2)	B9-B10-B11	110.0 (4)
B6-B2-P7	107.8 (4)	B1-B5-B6	60.7 (3)	B2-P7-B8	99.7 (3)	B2-B11-B6	57.0 (3)
B6-B2-B11	57.3 (3)	B1-B5-B9	112.1 (4)	B2-P7-B11	57.6 (3)	B2-B11-P7	61.3 (3)
P7-B2-B11	61.1 (2)	B1-B5-B10	111.1 (4)	B3-P7-B8	57.9 (3)	B2-B11-B10	103.4 (4)
B1-B3-B2	58.4 (3)	B4-B5-B6	110.3 (4)	B3-P7-B11	100.1 (2)	B6-B11-P7	107.8 (3)
B1-B3-B4	61.4 (3)	B4-B5-B9	61.1 (4)	B8-P7-B11	104.7 (3)	B6-B11-B10	58.5 (3)
B1-B3-P7	109.9 (3)	B4-B5-B10	114.0 (4)	B3-B8-B4	57.1 (3)	P7-B11-B10	107.8 (4)
B1-B3-B8	107.5 (4)	B6-B5-B9	113.7 (4)				

[a] Only data for molecule 1 are given. Data for independent molecule 2 are given in the supplementary material.

averaging 1.33 Å. Bridge hydrogens are probably fluxional. They spin couple with ^{31}P. The ^{11}B NMR spectrum obtained at 96.3 MHz (Experimental Section) is consistent with that obtained at 70.6 MHz.[9] The 2D ^{11}B–^{11}B COSY experiment does not allow an unambiguous assignment of the spectrum; however, it is in agreement with the previous assignment.[9]

Interestingly, there is no cross peak observed between the resonances assigned to B(8,11) and B(2,3). This is consistent with certain thiaborane[10] systems where no cross peak is observed between boron atoms that are bridged by a sulfur atom. The sites B(8,11) and B(2,3) are all adjacent to the phosphorus atom and can be considered to be "bridged" by the PCH_3 group. It should be noted that cross peaks have been observed between boron sites that are adjacent to phosphorus atoms in 1,2-$P_2B_{10}H_{10}$ and 1,7-$P_2B_{10}H_{10}$.[5b] A cross peak has also been observed between boron sites that are adjacent to both sulfur and cobalt in *nido*-3,10-$(\eta\text{-}C_5(CH_3)_5)_2Co_2$-7,9-$S_2B_7H_7$.[10b]

$B_{10}H_{12}PCH_3$ is isoelectronic and isostructural with the $[B_{11}H_{13}]^{2-}$ dianion,[11] both having 26 skeletal electrons. Their open pentagonal faces are isolobal, both having two bridging hydrogen atoms. The $[B_{11}H_{13}]^{2-}$ dianion can be readily protonated to form the $[B_{11}H_{14}]^-$ anion,[3] which contains an endo H atom[1a] as well as the bridge hydrogens. The phosphorus atom of $B_{10}H_{12}PCH_3$ is expected to have an unshared pair of electrons available for

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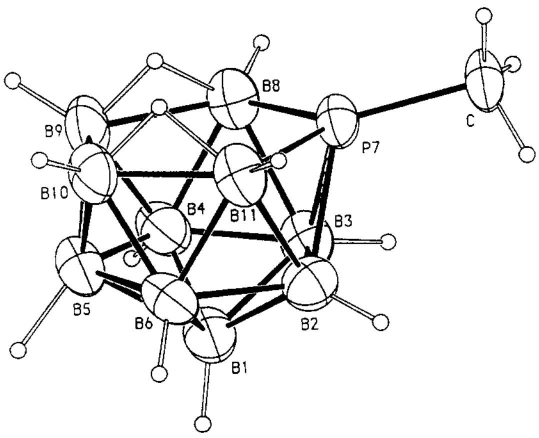

Figure 2. Molecular structure of $\mathrm{B_{10}H_{12}PCH_3}$ (ORTEP plot with 50% probability ellipsoids).

protonation to form the $\mathrm{[B_{11}H_{14}]^-}$ analogue $\mathrm{[B_{10}H_{12}PHCH_3]^+}$. However, attempts to protonate the phosphaborane molecule by HCl, $\mathrm{HBF_4}$, and $\mathrm{HCl\text{-}BCl_3}$ were unsuccessful.

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Registry No. $\mathrm{Na_2[B_{11}H_{13}]}$, 55624-52-7; $\mathrm{K_2[B_{11}H_{13}]}$, 122213-27-8; $\mathrm{B_{11}H_{11}PCH_3}$, 119203-72-4; $\mathrm{B_{10}H_{12}PCH_3}$, 57108-87-9; $\mathrm{Na[B_{11}H_{14}]}$, 52261-23-1.

Supplementary Material Available: Full listings of positional parameters, bond distances, bond angles, and anisotropic thermal parameters (18 pages); tables of calculated and observed structure factor amplitudes (26 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
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Facile Synthesis of $\mathrm{M_3(CO)_9(\mu_3\text{-}Te)_2}$ (M = Ru, Os) and the Synthesis and Characterization of the Novel Cluster $\mathrm{Fe_2Os_3(CO)_{17}(\mu_4\text{-}Te)(\mu_3\text{-}Te)}$

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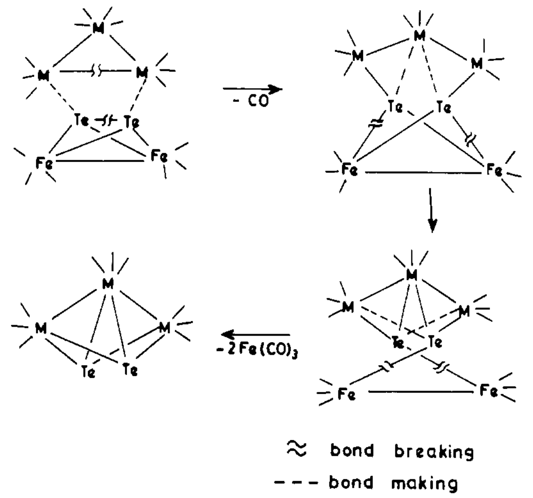
Received February 22, 1989

Scheme I. Proposed Mechanism of Formation of $\mathrm{Me_3Te_2(CO)_9}$



Cluster compounds incorporating single-atom ligands have received considerable attention recently, largely because of their utility in the synthesis of high-nuclearity clusters.[1,2] The ligands act as the initial point of contact when treated with coordinatively unsaturated metal fragments. Numerous sulfido-osmium and -ruthenium clusters have been synthesized and characterized, demonstrating the potential of this synthetic approach.[3-9] The lone pair of electrons on the triply bridging sulfido ligands in $\mathrm{Os_3(CO)_9(\mu_3\text{-}S)_2}$ have been used to coordinate to an additional metal atom, thereby providing a facile first step in cluster-growth sequences.[10-13] The molecule $\mathrm{Os_4(CO)_{12}(\mu_3\text{-}S)_2}$, obtained from $\mathrm{Os_3(CO)_9(\mu_3\text{-}S)_2}$ and $\mathrm{Os(CO)_5}$,[10] is one of several examples highlighting the ability of the sulfido ligands to aid cluster growth. Synthesis of the selenido-osmium carbonyl cluster $\mathrm{Os_4(CO)_{12}(\mu_3\text{-}Se)_2}$ from $\mathrm{Os_3(CO)_9(\mu_3\text{-}Se)_2}$ and $\mathrm{Os(CO)_5}$ suggests that selenium behaves in a manner similar to that of sulfur in cluster-growth reactions.[14]

Reports by Rauchfuss and co-workers[15,16] and recent work in our laboratory[17-19] suggest that the much larger tellurium is markedly different from sulfur or selenium in reactions of the above type, and it is expected that the tellurium-containing clusters may exhibit unusual bonding properties and reactivity. Herein, we report a new route for the synthesis of the compounds $\mathrm{Os_3(CO)_9(\mu_3\text{-}Te)_2}$ (**1**) and $\mathrm{Ru_3(CO)_9(\mu_3\text{-}Te)_2}$ (**2**) and the synthesis and characterization of the new trimetallic cluster $\mathrm{Fe_2Os_3(CO)_{17}(\mu_4\text{-}Te)(\mu_3\text{-}Te)}$ (**3**). It is significant that they have been made at room temperature from the readily available compounds $\mathrm{Fe_2Te_2(CO)_6}$, $\mathrm{M_3(CO)_{10}(NCMe)_2}$ (M = Ru, Os), and $\mathrm{Os_3(CO)_{11}(NCMe)}$.

Results

Room-temperature stirring of a benzene solution of $\mathrm{Os_3(CO)_{10}(CH_3CN)_2}$ and $\mathrm{Fe_2Te_2(CO)_6}$ (**4**) formed the cluster **1** along with a maroon compound, which in solution slowly converted to **1**. When the maroon compound was refluxed in benzene solvent for 3 h, it converted to the yellow **1**. UV irradiation of a benzene solution of the maroon compound for 30 min also led to a conversion to **1**. The conversion of the maroon compound to **1** by photolysis or thermolysis was always found to be accompanied by the formation of traces of $\mathrm{Fe_3(CO)_9(\mu_3\text{-}Te)_2}$, suggesting that the maroon compound is a mixed-metal intermediate. The ruthenium analogue **2** was obtained similarly from the reaction of $\mathrm{Ru_3(CO)_{10}(CH_3CN)_2}$ and **4**. Both **1** and **2** have been obtained previously from the high-temperature and high-CO-pressure reactions of $\mathrm{M_3(CO)_{12}}$ (M = Ru, Os) and tellurium.[20] Our method provides an ambient-pressure route for an improved-yield synthesis of $\mathrm{M_3(CO)_9(\mu_3\text{-}Te)_2}$ (M = Ru, Os). It has been amply demon-

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