Inorg. Chem. **1992**, *31*, 2889-2892 **2889**

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Synthesis of Monosubstituted Derivatives of *closo*-Decahydrodecaborate(2−). X-ray Crystal Structures of [*closo*-2-$B_{10}H_9CO$]$^-$ and [*closo*-2-$B_{10}H_9NCO$]$^{2-}$

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Received January 7, 1992

The *closo*-decahydrodecaborate(2−) ion, [*closo*-$B_{10}H_{10}$]$^{2-}$, reacts with oxalyl chloride to produce the equatorially monosubstituted species [*closo*-2-$B_{10}H_9CO$]$^-$ (**1**) in high yield. The triphenylmethylphosphonium salt, [Ph_3PMe]·**1**, crystallizes in the triclinic space group $P\bar{1}$ with $a = 11.945$ (1) Å, $b = 14.509$ (1) Å, $c = 16.455$ (1) Å, $\alpha = 106.436$ (3)°, $\beta = 95.446$ (3)°, $\gamma = 111.786$ (3)°, $V = 2475$ Å^{-3}, and $Z = 4$. Data were collected using Cu Kα radiation, to a maximum $2\theta = 115°$, giving 6782 unique reflections, and the structure was solved by direct methods (SHELX86). The final discrepancy indices were $R = 0.060$ and $R_w = 0.086$ for 5627 independent reflections with $I > 3\sigma(I)$. The borane ion contains an equatorial carbon monoxide ligand with an essentially linear B–C–O array. The chemistry of **1** is similar to that previously observed for other borane carbonyls, thereby allowing the synthesis of several other derivatives. In aqueous solvent mixtures, **1** is hydrated to form [*closo*-2-$B_{10}H_9CO_2H$]$^{2-}$ (**2**). Reaction of **1** with azide ion affords [2-$B_{10}H_9NCO$]$^{2-}$ (**3**). The triethylammonium salt, [Et_3NH]$_2$·**3**, crystallizes in the monoclinic space group $P2_1/m$ with $a = 8.980$ (1) Å, $b = 13.314$ (2) Å, $c = 10.073$ (1) Å, $\beta = 95.099$ (4)°, $V = 1199$ Å^{-3}, and $Z = 2$. Data were collected using Cu Kα radiation, to a maximum $2\theta = 115°$, giving 1731 unique reflections, and the structure was solved by direct methods (SHELX86). The final discrepancy indices were $R = 0.078$ and $R_w = 0.117$ for 1390 independent reflections with $I > 3\sigma(I)$. The versatile [2-$B_{10}H_9CO$]$^-$ ion is also readily converted into amides and esters by reaction with amines and alcohols.

Introduction

The polyhedral [*closo*-$B_{10}H_{10}$]$^{2-}$ and [*closo*-$B_{12}H_{12}$]$^{2-}$ ions[1a-c] occupy a special position in the development of borane cluster chemistry. The apparent stabilization of these species by three-dimensional electron delocalization provides unusual oxidative, hydrolytic, and thermal stabilities that are atypical of the boron hydrides.[1b-d] The aromatic character of these electron-rich anions makes them susceptible to electrophilic attack, and their derivative chemistry has been extensively studied.[2-20]

The utility of the rich derivative chemistry of [*closo*-$B_{10}H_{10}$]$^{2-}$ and [*closo*-$B_{12}H_{12}$]$^{2-}$ is, however, limited by several factors. The well-known substitution of these ions by monovalent or saturated ligands (e.g. halogens[3] and Me_2S[4]) generally precludes further reaction of the substituent for the purpose of conjugation to substrates such as biomolecules. Electrophilic substitution reactions with these anions is usually difficult to control and may yield mono-, di-, and polysubstituted mixtures of products or result in mixtures of isomers that are difficult to separate.[3-8] Finally, the syntheses of potentially useful derivatives often employ severe reaction conditions and give only low yields of products.[7-13]

Carbon monoxide is one of the most versatile substituents known in polyhedral borane anion chemistry (e.g. in *closo*-1,10-$B_{10}H_8(CO)_2$).[8,9] Some common transformations of the carbonyl group are its reaction with nucleophiles to produce acyl derivatives (amides, esters),[8,14] substitution to form an amine,[15] reduction to a methyl[8] or hydroxymethyl[16,17] group, and rearrangement upon reaction with azide ion to form an isocyanate.[15] Unfortunately the synthesis of the dicarbonylborane precursors requires severe conditions (high pressures and temperature) and produces a low yield of product.[8,9] On the other hand, monocarbonyl derivatives of ligand-substituted [*closo*-$B_{10}H_{10}$]$^{2-}$ ions (e.g. [*closo*-2-$B_{10}H_9NMe_3$]$^-$) have been produced in more reasonable quantities,[14,15] but the substituted borane precursors are available in only low to moderate yields.[4,7,10]

Our interest in the production of a variety of stable and water-soluble borane species for possible use in boron neutron capture therapy (BNCT)[21] has led us to investigate derivatives of the *closo*-decahydrodecaborate(2−) ion and related species. The results reported here are based on the new observation that oxalyl chloride reacts with [*closo*-$B_{10}H_{10}$]$^{2-}$ under mild conditions to produce a single monosubstituted product, [*closo*-2-$B_{10}H_9CO$]$^-$ (**1**), in good yield. This carbonyl species exhibits reactivity similar to that previously reported for other polyhedral borane carbonyls, thereby allowing the synthesis of other desired monosubstituted [*closo*-$B_{10}H_{10}$]$^{2-}$ derivatives. Also presented is the structure of **1**, the first polyhedral borane carbonyl to be characterized by X-ray crystallography, as well as the structure of the corresponding isocyanate derivative, [*closo*-2-$B_{10}H_9NCO$]$^{2-}$ (**3**).

Results and Discussion

Synthesis and Characterization of [*closo*-2-$B_{10}H_9CO$]$^-$ (1) and [*closo*-2-$B_{10}H_9CO_2H$]$^{2-}$ (2). Oxalyl chloride reacts rapidly with [Ph_3PMe]$_2$[*closo*-$B_{10}H_{10}$] at 0 °C with the evolution of carbon monoxide. While this reaction appears to proceed most smoothly in CH_2Cl_2, it has also been observed in MeCN and THF using the cesium, tetramethylammonium, and triethylammonium salts of [*closo*-$B_{10}H_{10}$]$^{2-}$. The use of a 5-fold excess of $(COCl)_2$ does not lead to multiple substitution, nor does it increase the yield of **1**. The reaction mixture in CH_2Cl_2 exhibits an infrared stretching band typical of coordinated carbon monoxide (vide

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infra), and the ^{11}B NMR spectrum indicates a virtually quantitative conversion to carbonyl product. Although the isolated yield of $[Ph_3PMe]\cdot\mathbf{1}$ is somewhat lower, it is often unnecessary to isolate or purify this species if it is to be converted to another derivative in a subsequent reaction.

The proton-decoupled ^{11}B NMR spectrum of the product is well resolved and quite informative, clearly indicating monosubstitution of the cage at an equatorial site. The $^{11}B\{^1H\}$ spectrum of $[Ph_3PMe]\cdot\mathbf{1}$ in CH_2Cl_2 contains seven lines in the ratio 1:1:1:2:2:2:1 (with other solvents, the two low-field apical signals often overlap). Six of these signals are doublets in the proton-coupled spectrum, but the highest field resonance (−43.8 ppm relative to $BF_3{\cdot}Et_2O$) is a singlet and is assigned to the substituted equatorial boron atom. Equatorial monosubstitution of $[$*closo*-$B_{10}H_{10}]^{2-}$ by a carboxylic acid chloride has been observed previously in its reaction with benzoyl chloride.[10]

The solid-state FTIR spectrum of $[Ph_3PMe]\cdot\mathbf{1}$ exhibits an intense absorption at 2129 cm^{-1} attributable to the CO ligand. This carbonyl stretch is at a higher energy than that of nearly all known metal carbonyls, whose frequencies are significantly lowered due to back-bonding from filled d orbitals. On the other hand, the electron-deficient nature of boron compounds usually gives rise to ν_{CO} absorption frequencies for borane carbonyls which are *higher* than that of free carbon monoxide (2143 cm^{-1}). For example, ν_{CO} is 2165 cm^{-1} for BH_3CO[22] and for *closo*-polyhedral borane derivatives the values range from 2147 cm^{-1} for *closo*-1,10-$B_{10}H_8(CO)_2$ to 2263 cm^{-1} for *closo*-1,10-$B_{10}Cl_8(CO)_2$.[8] The lower stretching frequency observed for **1** may be due to its negative charge, since the previously reported borane carbonyls are all neutral species.

The salt $[Ph_3PMe]\cdot\mathbf{1}$ is air-stable and nonhygroscopic, but in aqueous solvent mixtures it is readily hydrated to form the $[$*closo*-2-$B_{10}H_9CO_2H]^{2-}$ ion (**2**). This is in accord with the previously reported aqueous equilibrium for the closo polyhedral borane carbonyl group[8]

$$[2\text{-}B_{10}H_9CO]^- + H_2O \rightleftharpoons [2\text{-}B_{10}H_9CO_2H]^{2-} + H^+ \quad (1)$$

which lies predominantly to the right in dilute solution. The transformation of the carbonyl group from $-C{\equiv}O$ to $>C{=}O$ is indicated by the appearance of an infrared stretch at 1690 cm^{-1}, as well as a C—O stretch at 1256 cm^{-1}. The $[$*closo*-2-$B_{10}H_9CO]^-$ ion can be regenerated from **2** by dehydration with $(COCl)_2$ or $SOCl_2$ in methylene chloride.

The ^{11}B spectrum of **2**, while not as informative as that of the corresponding carbonyl compound **1**, is also indicative of equatorial substitution. In the low-field region of the spectrum, where the resonances corresponding to apical boron atoms usually occur, there are doublets for two B–H vertices, and a singlet appears at −25.5 ppm due to the substituted equatorial boron atom. The remainder of the equatorial boron atom resonances are unresolved. The identity of $[Ph_3PMe]_2\cdot\mathbf{2}$ has been confirmed by crystallographic analysis, but a satisfactory refinement of the structure was prevented by disorder of the anion.

Structure of $[$*closo*-2-$B_{10}H_9CO]^-$ (1). Crystals of $[Ph_3PMe]\cdot\mathbf{1}$ were found to contain two crystallographically independent anions and two crystallographically independent cations. The structures of the two anions are quite similar. The atomic numbering scheme and the structure of one of the crystallographically independent anions are shown in Figure 1. The *closo*-borane cage is similar to others previously investigated;[23] bond distances and angles involving the carbonyl substituent are listed in Table I.

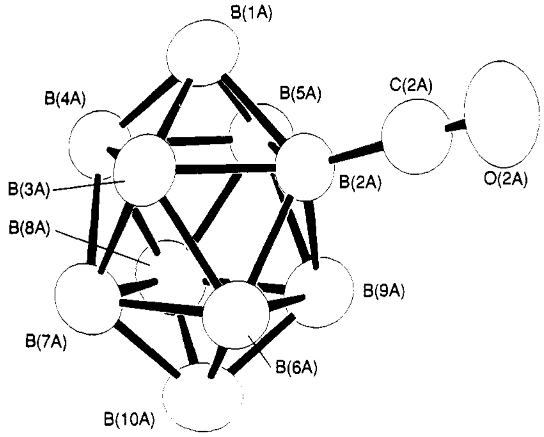

Figure 1. Structure of one of the crystallographically independent anions of $[Ph_3PMe][$*closo*-2-$B_{10}H_9CO]$ showing the atom-numbering scheme.

Table I. Selected Bond Distances and Angles for $[Ph_3PMe]\cdot\mathbf{1}^a$ and $[Et_3NH]_2\cdot\mathbf{3}$

$[Ph_3PMe]\cdot\mathbf{1}$		$[Et_3NH]_2\cdot\mathbf{3}$	
	Distances (Å)		
B(2A)–C(2A)	1.484 (6)	B(2)–N(2)	1.498 (7)
B(2B)–C(2B)	1.472 (6)	N(2)–C(2)	1.128 (7)
C(2A)–O(2A)	1.130 (5)	C(2)–O(2)	1.187 (7)
C(2B)–O(2B)	1.132 (6)		
	Angles (deg)		
B(2A)–C(2A)–O(2A)	179.2 (4)	B(2)–N(2)–C(2)	172.3 (3)
B(2B)–C(2B)–O(2B)	177.5 (5)	N(2)–C(2)–O(2)	177.8 (4)

[a] The two crystallographically independent anions are denoted as A and B; the unrefined minor occupant is included only in the complete tabulation in the supplementary material.

This structure represents the first carbonyl derivative of a polyhedral borane anion to be characterized by X-ray crystallography. Other borane carbonyls whose structures have been determined include $B_2H_4(CO)_2$,[24] B_3H_7CO[25] (low-temperature X-ray), and BH_3CO (microwave spectroscopy,[26] electron diffraction[27]). All structures involve terminal CO groups with essentially linear B–C–O arrays. The C–O distances in **1** are 1.130 (5) and 1.132 (6) Å. These bond lengths are slightly shorter than those normally found in metal carbonyls (~1.15 Å) and more closely resemble the value for free carbon monoxide (1.128 Å).[28] These differences may lack significance due to their small magnitude and the fact that bond lengths are relatively insensitive to slight changes in bond order between 2 and 3. However, the C–O bond length found for **1** is comparable to the value determined for BH_3CO; the C–O distances for the carbonyl derivatives of the boron hydrides cited above are all relatively short, ranging from 1.11 to 1.31 Å.

Another comparison that should be noted is that to be made between the present structure and $(\mu\text{-}H)_3(CO)_9Os_3BCO$, in which a linear BCO group caps a triangular metal cluster.[29] Although this compound is not a boron hydride, the electronic environment of the Os_3B cluster may more closely resemble the charged, delocalized polyhedral **1**. Like **1**, it is thermally stable and does not lose carbon monoxide at normal temperatures, which may be reflected in its short B–C distance of 1.469 (15) Å. The boron–carbon bond lengths observed in the two crystallographic forms of **1** are 1.484 (6) and 1.472 (6) Å; the distances in the borane carbonyls cited above range from 1.52 to 1.57 Å. The Os_3B cluster also exhibits an infrared carbonyl stretch at 2120 cm^{-1} (between the ranges for metal carbonyls and boron hydride carbonyls). However, the C–O distance found at the BCO vertex of the osmium cluster (1.145 (15) Å) is closer to the values found in "normal" metal carbonyls.

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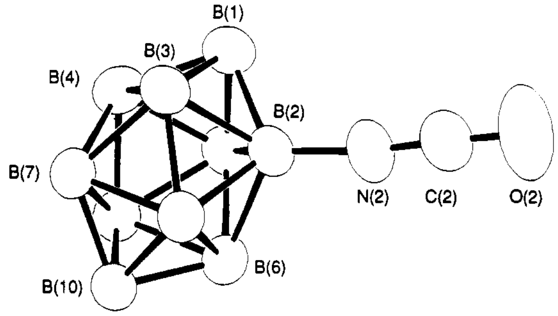

Figure 2. Structure of the $[closo\text{-}2\text{-}B_{10}H_9NCO]^{2-}$ anion (**3**) showing the atom-numbering scheme. The borane cage has a mirror plane passing through B(1), B(2), B(4), and B(10).

Synthesis and Structure of $[closo\text{-}2\text{-}B_{10}H_9NCO]^{2-}$ (3). A stirred mixture of $[Et_3NH]\cdot$**1** (prepared from the reaction of oxalyl chloride and $[Et_3NH]_2[B_{10}H_{10}]$) and NaN_3 in acetonitrile slowly evolves nitrogen gas over a period of hours. This reaction presumably proceeds[8] by the formation of an acyl azide followed by a spontaneous Curtius rearrangement to form the $[closo\text{-}B_{10}H_9NCO]^{2-}$ ion (**3**). The isocyanate function exhibits a strong infrared absorption at 2304 cm^{-1}, as well as weak NCO bending modes at 597 and 577 cm^{-1}.

The isocyanate derivative is stable in neutral aqueous solution, but acidic hydrolysis of **3** produces the known[7] $[closo\text{-}2\text{-}B_{10}H_9NH_3]^-$ ion, identified by its infrared and ^{11}B NMR spectra. Although the amine derivative has been previously synthesized by direct substitution of $[closo\text{-}B_{10}H_{10}]^{2-}$ with hydroxylamine-*O*-sulfonic acid, the multistep synthesis described here affords a much higher overall yield. Investigation into the reactivity of **3** with nucleophiles is in progress.

The structure of **3** is shown in Figure 2 along with the atomic numbering scheme. The anion has a mirror plane passing through the three atoms of the isocyanate group and four boron atoms. The structure of the borane cage resembles others previously investigated.[23] Bond distances and angles involving the isocyanate substituent are listed in Table I. The isocyanate group itself is nearly linear, as is the corresponding BNCO assembly.

Other Derivatives of $[closo\text{-}2\text{-}B_{10}H_9CO]^-$ (1). As demonstrated with the synthesis of the isocyanate described above, **1** exhibits reactivity similar to that seen with other polyhedral borane carbonyls (e.g. $closo\text{-}1,10\text{-}B_{10}H_8(CO)_2$). An extension of this chemistry is the reaction of **1** with nucleophiles to produce carboxylic acid derivatives. Spectroscopic evidence indicates that **1** reacts with amines and alcohols to produce amides and esters, respectively, in accord with eqs 2 and 3. These reactions are

$$[closo\text{-}2\text{-}B_{10}H_9CO]^- + RNH_2 \rightleftharpoons [closo\text{-}2\text{-}B_{10}H_9CONHR]^{2-} + H^+ \quad (2)$$

$$[closo\text{-}2\text{-}B_{10}H_9CO]^- + ROH \rightleftharpoons [closo\text{-}2\text{-}B_{10}H_9CO_2R]^{2-} + H^+ \quad (3)$$

analogous to the hydration equilibrium of eq 1. The conversion to an amide may be conveniently accomplished by dissolution of the carbonyl derivative in the desired amine. The proton produced in this reaction is consumed by the amine solvent. The alcoholysis shown in eq 3 is slow and incomplete unless an auxiliary base (e.g. triethylamine) is added.

Conclusion

The *closo*-decahydrodecaborate(2–) ion is substituted by a carbon monoxide ligand derived from oxalyl chloride in high yield under mild conditions. This reaction produces a single monosubstituted product, $[closo\text{-}2\text{-}B_{10}H_9CO]^-$. This borane carbonyl anion is a versatile synthon that may be used to produce a variety of other singly substituted derivatives of $[closo\text{-}B_{10}H_{10}]^{2-}$.

Experimental Section

Methods and Materials. Synthetic reactions were performed under an atmosphere of dry argon. The solvents THF and Et_2O were distilled from Na/benzophenone, and the solvents MeCN and CH_2Cl_2 were distilled from CaH_2 prior to use. Oxalyl chloride (Aldrich) was obtained as a 2.0 M solution in CH_2Cl_2. Silica gel was activated by oven-drying prior to use. The salt $[Ph_3PMe]_2[closo\text{-}B_{10}H_{10}]$ was precipitated from an aqueous solution of $[Et_3NH]_2[closo\text{-}B_{10}H_{10}]$[30] with $[Ph_3PMe]Br$, filtered, dried, and recrystallized from MeCN.

Physical Measurements. The ^{11}B FT NMR spectra were obtained with a Bruker AM-500 instrument at 160.463 MHz. Boron chemical shifts were externally referenced to $BF_3\cdot Et_2O$ in C_6D_6; peaks upfield of the reference are designated as negative. IR spectra were obtained on a Beckman FT 1100 spectrometer; only anion absorptions are given.

$[Ph_3PMe][closo\text{-}2\text{-}B_{10}H_9CO]$ ($[Ph_3PMe]\cdot$1). A mixture of $[Ph_3PMe]_2[closo\text{-}B_{10}H_{10}]$ (6.73 g, 10 mmol) in 125 mL of dry CH_2Cl_2 was chilled in an ice bath with stirring. A solution of $(COCl)_2$ in CH_2Cl_2 (5.1 mL, 10.2 mmol) was added via syringe, and the mixture was stirred at 0 °C for 30 min. The solution was allowed to warm to room temperature and stirred an additional 30 min. The volume of the solution was reduced to ~15 mL by mechanical vacuum. The resulting solution was passed through a 2.5 × 30 cm column of silica gel, eluting with CH_2Cl_2, and the effluent was evaporated in vacuo. The residue was recrystallized from CH_2Cl_2/Et_2O to yield 3.59 g (8.5 mmol, 85%) of light tan $[Ph_3PMe]\cdot$**1**. Anal. Calcd for $C_{20}H_{27}B_{10}OP$: C, 56.85; H, 6.44; B, 25.59. Found: C, 57.01; H, 6.30; B, 25.50. IR (cm^{-1}, KBr disk): 2519 (s), 2501 (s), 2129 (s). $^{11}B\{^1H\}$ NMR (ppm, CH_2Cl_2, relative areas in parentheses): 6.4 (1), 6.0 (1), –17.9 (1), –25.9 (2), –28.4 (2), –28.9 (2), –43.8 (1). The –43.8 ppm resonance was a singlet in the proton-coupled spectrum.

$[Ph_3PMe]_2[closo\text{-}2\text{-}B_{10}H_9CO_2H]$ ($[Ph_3PMe]_2\cdot$2). A mixture of $[Ph_3PMe]_2[closo\text{-}B_{10}H_{10}]$ (5.52 g, 8.2 mmol) in 100 mL of CH_2Cl_2 was allowed to react with 4.2 mL of $(COCl)_2$ as described above. After vacuum removal of the solvent, the residue was dissolved in 200 mL of hot acetone, and the solution was stirred with 3 g of activated charcoal. The mixture was filtered, and 150 mL water was added to the filtrate. The solution was neutralized by addition of 0.5 N NaOH, and acetone was allowed to evaporate from the mixture at room temperature. The resulting crystals were filtered off and dried to give 4.21 g of $[Ph_3PMe]_2\cdot$**2** (5.9 mmol, 72%). Anal. Calcd for $C_{39}H_{46}B_{10}O_2P_2$: C, 65.35; H, 6.47; B, 15.08. Found: C, 65.18; H, 6.43; B, 15.20. IR (cm^{-1}, KBr disk): 2458 (s), 1694 (m), 1256 (m). $^{11}B\{^1H\}$ NMR (ppm, CH_2Cl_2, relative areas in parentheses): –0.5 (1), –1.3 (1), –25.5 (1), –28.6 (3), –29.6 (4).

$[Et_3NH]_2[closo\text{-}2\text{-}B_{10}H_9NCO]$ ($[Et_3NH]_2\cdot$3). A solution of $[Et_3NH]_2[closo\text{-}B_{10}H_{10}]$ (3.22 g, 10 mmol) in 150 mL of MeCN was allowed to react with 5 mL of $(COCl)_2$ as described above. Solid NaN_3 (1.4 g, 21 mmol) was added, and the mixture was stirred overnight. The mixture was then filtered, 200 mL ether was added, and the solution was chilled to –20 °C overnight. The precipitate was filtered off and dried under vacuum, yielding 2.73 g of $[Et_3NH]_2\cdot$**3** (7.5 mmol, 75%). Analytical and crystallographic samples of $[Et_3NH]_2\cdot$**3** were purified further by recrystallization from acetone/pentane. Anal. Calcd for $C_{13}H_{41}B_{10}N_3O$: C, 42.94; H, 11.37; N, 11.56; B, 29.73. Found: C, 42.81; H, 11.18; N, 11.71; B, 29.50. IR (cm^{-1}, KBr disk): 2538 (s), 2505 (s), 2475 (s), 2304 (s), 1013 (m), 967 (m), 597 (w), 577 (w). $^{11}B\{^1H\}$ NMR (ppm, MeCN, relative areas in parentheses): –2.3 (2), –16.8 (1), –25.2 (2), –25.6 (2), –28.3 (2), –31.6 (1). The resonance at –16.8 ppm was a singlet in the proton-coupled spectrum.

Collection and Reduction of X-ray Data for $[Ph_3PMe]\cdot$1.[31] A pale yellow parallelepiped (0.3 × 0.2 × 0.32 mm) of $[Ph_3PCH_3]\cdot$**1** was obtained from a CH_2Cl_2/Et_2O solution. Data were collected for $(+h,\pm k,\pm l)$. No systematic absences were found. Unit cell parameters were determined from a least-squares fit of 30 accurately centered reflections ($18.3 < 2\theta < 38.2°$). These dimensions and other parameters, including conditions of data collection, are summarized in Table II. Three intense reflections $(20\bar{6})$, $(24\bar{1})$, and $(3\bar{4}0)$ were monitored every 97 reflections to check stability. Intensities of these reflections decayed 1% and had a maximum fluctuation of ±3% during the course of the experiment (87.9 h). Of the 6782 unique reflections measured, 5628 were considered observed ($I > 3\sigma(I)$) and were used in the subsequent structure analysis.

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(30) Hawthorne, M. F.; Pilling, R. L. *Inorg. Synth.* **1967**, *9*, 16.

(31) Crystals were mounted on a fiber on a Syntex $P\bar{1}$ diffractometer (Cu Kα radiation, graphite monochromator) modified by Professor C. E. Strouse of this department. Data were collected at 25 °C in the θ–2θ scan mode. Data were corrected for Lorentz and polarization effects and for extinction but not for absorption. Programs used in this work include locally modified versions of the following programs: CARESS (Broach, Coppens, Becker, and Blessing), peak profile analysis, Lorentz and polarization corrections; ORFLS (Busing, Martin, and Levy), structure factor calculation and full-matrix least-squares refinement; SHELX76 and SHELX86 (Sheldrick), crystal structure and solution packages; ORTEP (Johnson), figure plotting.

Table II. Details of the Crystallographic Data Collection for $[Ph_3PMe]\cdot\mathbf{1}$ and $[Et_3NH]_2\cdot\mathbf{3}$

compound	$[Ph_3PMe]\cdot\mathbf{1}$	$[Et_3NH]_2\cdot\mathbf{3}$
chem formula	$C_{20}H_{27}B_{10}OP$	$C_{13}H_{41}B_{10}N_3O$
fw	422.5	363.6
temp, °C	25	25
wavelength, Å	1.5418	1.5418
space group	$P\bar{1}$	$P2_1/m$
a, Å	11.945 (1)	8.980 (1)
b, Å	14.509 (1)	13.314 (2)
c, Å	16.455 (1)	10.073 (1)
α, deg	106.436 (3)	
β, deg	95.446 (3)	95.099 (4)
γ, deg	111.786 (3)	
V, Å^3	2475	1199
Z	4	2
ρ(calcd), g cm^{-3}	1.13	1.01
μ, cm^{-1}	10.3	3.8
R, R_w, GOF[a]	0.060, 0.086, 2.98	0.078, 0.117, 4.17

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w = [\sum w(|F_o - F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = 1/\sigma^2(|F_o|)$. GOF $= [\sum w(|F_o - F_c|)^2/(N_o - N_v)]^{1/2}$.

Table III. Positional and Equivalent Isotropic Thermal Parameters for the Non-Hydrogen Atoms of the Anion of $[Ph_3PMe]\cdot\mathbf{1}$[a]

atom	*x*	*y*	*z*	U_{eq}, Å^2
O(2A)	−0.427 40 (34)	1.144 49 (26)	0.236 74 (21)	0.1196
C(2A)	−0.426 91 (35)	1.073 50 (32)	0.252 13 (23)	0.0718
B(1A)	−0.443 55 (38)	0.970 21 (30)	0.370 80 (24)	0.0609
B(2A)	−0.424 87 (34)	0.980 33 (30)	0.271 79 (24)	0.0540
B(3A)	−0.307 53 (34)	0.973 12 (29)	0.344 45 (23)	0.0558
B(4A)	−0.427 33 (33)	0.856 17 (29)	0.353 34 (23)	0.0530
B(5A)	−0.545 20 (34)	0.866 10 (31)	0.282 06 (25)	0.0569
B(6A)	−0.316 55 (35)	0.935 05 (34)	0.227 03 (25)	0.0615
B(7A)	−0.318 08 (34)	0.845 22 (31)	0.285 83 (25)	0.0593
B(8A)	−0.485 87 (35)	0.768 67 (30)	0.241 06 (25)	0.0614
B(9A)	−0.486 86 (36)	0.857 21 (33)	0.182 44 (25)	0.0627
B(10A)	−0.382 37 (39)	0.803 93 (37)	0.178 10 (27)	0.0744
O(2B)	0.283 62 (33)	0.684 30 (26)	0.355 65 (23)	0.0947
C(2B)	0.241 65 (39)	0.595 02 (37)	0.326 05 (26)	0.0624
B(1B)	0.218 16 (42)	0.407 91 (42)	0.344 32 (29)	0.0787
B(2B)	0.182 57 (41)	0.478 77 (33)	0.289 48 (27)	0.0699
B(3B)	0.228 58 (41)	0.374 32 (37)	0.238 08 (28)	0.0736
B(4B)	0.112 14 (45)	0.287 31 (39)	0.278 79 (35)	0.0835
B(5B)	0.071 35 (40)	0.395 32 (37)	0.332 38 (31)	0.0739
B(6B)	0.139 12 (51)	0.415 57 (36)	0.174 23 (28)	0.0834
B(7B)	0.085 47 (46)	0.279 05 (34)	0.166 22 (32)	0.0813
B(8B)	−0.026 79 (44)	0.293 10 (36)	0.229 51 (39)	0.0935
B(9B)	0.023 89 (45)	0.430 81 (35)	0.242 41 (31)	0.0794
B(10B)	−0.010 00 (56)	0.335 02 (40)	0.144 41 (36)	0.1021
C(6B)	0.233 2	0.475 5	0.133 4	0.070*
O(6B)	0.296 3	0.514 5	0.096 6	0.100*

[a] Units of each esd, in parentheses, are those of the least significant digit of the corresponding parameter. Isotropic values are $(^1/_8\pi^2)$ times the "equivalent *B* value" as defined by Hamilton.[35] U_{eq} values with asterisks denote atoms that were refined isotropically. The occupancy factor for C(2B) and O(2B) is 80%, and that for C(6B) and O(6B) is 20%.

Solution and Refinement of the Structure of $[Ph_3PMe]\cdot\mathbf{1}$.[32] All cation hydrogens were included in calculated positions as members of rigid C_6H_5 groups (C–C = 1.395 and C–H = 1.0 Å, angles of 120°) or CH_3 groups (H–C–H = 109.5°). Anion hydrogens were included in located positions. After inclusion of all anion hydrogens, except for that on B(6B), the two highest peaks on a difference electron density map corresponded to suitable assignments for another position for CO. This second site for CO was given 20% occupancy and not refined, and C(2B) and O(2B) were included at 80% occupancy. The minor occupancy position is not from another isomer, nor is it from a doubly CO-substituted anion. With the exception of the minor occupant CO group, all non-hydrogen atoms were refined anisotropically. Anomalous dispersion terms were applied to the scattering of phosphorus. The larger peaks on a final difference electron density map were 0.2 e/Å^{-3}. Final positional and thermal parameters for non-hydrogen atoms are given in Table III.

Table IV. Positional and Equivalent Isotropic Thermal Parameters for the Non-Hydrogen Atoms of $[Et_3NH]_2\cdot\mathbf{3}$[a]

atom	*x*	*y*	*z*	U_{eq}, Å^2
O(2)	0.5164 (6)	0.2500	0.2830 (5)	0.148
C(2)	0.5869 (6)	0.2500	0.3884 (5)	0.072
N(2)	0.6580 (5)	0.2500	0.4865 (4)	0.069
B(1)	0.6276 (6)	0.2500	0.7555 (5)	0.053
B(2)	0.7330 (6)	0.2500	0.6253 (5)	0.050
B(3)	0.7475 (4)	0.1529 (3)	0.7519 (4)	0.050
B(4)	0.7636 (6)	0.2500	0.8809 (5)	0.052
B(6)	0.9057 (4)	0.1815 (3)	0.6582 (3)	0.048
B(7)	0.9264 (4)	0.1815 (3)	0.8400 (3)	0.049
B(10)	1.0388 (5)	0.2500	0.7480 (5)	0.046
N(1)	0.2196 (3)	0.0201 (2)	0.7716 (3)	0.057
C(11)	0.1345 (9)	−0.0787 (6)	0.7182 (8)	0.082
C(12)	−0.0012 (5)	−0.0976 (3)	0.7621 (4)	0.092
C(21)	0.2602 (6)	0.0032 (4)	0.9250 (5)	0.056
C(22)	0.3245 (4)	0.0979 (3)	0.9873 (4)	0.080
C(31)	0.3519 (7)	0.0370 (5)	0.7032 (7)	0.069
C(32)	0.3109 (5)	0.0777 (4)	0.5547 (5)	0.101
C(11′)	0.1645 (13)	−0.0658 (9)	0.8243 (18)	0.103
C(21′)	0.3668 (11)	0.0629 (9)	0.8390 (14)	0.102
C(31′)	0.2761 (17)	0.0049 (10)	0.6254 (12)	0.105

[a] Units of each esd, in parentheses, are those of the least significant digit of the corresponding parameter. Isotropic values are $(^1/_8\pi^2)$ times the "equivalent *B* value" as defined by Hamilton.[35] The occupancy factor for primed atoms is 40%. For unprimed atoms of the same label, the occupancy factor is 60%.

Collection and Reduction of X-ray Data for $[Et_3NH]_2\cdot\mathbf{3}$.[31] A colorless parallelepiped (0.2 × 0.12 × 0.45 mm) of $[Et_3NH]_2\cdot\mathbf{3}$ was obtained from an acetone/pentane solution. Data were collected for $(+h,+k,\pm l)$. Systematic absences were found for $0k0 \neq 2n$. Unit cell parameters were determined from a least-squares fit of 15 accurately centered reflections ($15.2 < 2\theta < 40.1°$). These dimensions and other parameters, including conditions of data collection, are summarized in Table II. Three intense reflections $(12\bar{2})$, $(2\bar{1}3)$, and $(\bar{2}21)$ were monitored every 97 reflections to check stability. Intensities of these reflections did not decay during the course of the experiment (34.9 h). Of the 1731 unique reflections measured, 1390 were considered observed ($I > 3\sigma(I)$) and were used in the subsequent structure analysis.

Solution and Refinement of the Structure of $[Et_3NH]_2\cdot\mathbf{3}$.[32] The ethyl groups of the Et_3NH cation were found to be disordered, with separable methylene carbon atom positions and overlapping methyl carbon atom positions. The methylene carbon atoms were included at 60% and 40% occupancies (unprimed and primed C(11), C(21), and C(31), respectively). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of ethyl groups, for the major occupant only, were included in calculated positions (C–H = 1.0 Å, H–C–H = 109.5°). All other hydrogens were included in located positions. The larger peaks on a final difference electron density map were 0.25 e/Å^{-3}. Final positional and thermal parameters for non-hydrogen atoms are given in Table IV.

Acknowledgments. This research was conducted as part of the BNCT program of the Idaho National Engineering Laboratory (INEL) and was performed under the auspices of the U.S. Department of Energy, Office of Energy Research, under DOE Field Office, Idaho, Contract No. DE-AC07-76ID01570.

Supplementary Material Available: For $[Ph_3PMe]\cdot\mathbf{1}$ and $[Et_3NH]_2\cdot\mathbf{3}$, Tables 1S–5S, giving details of the crystallographic data collection, final positional and thermal parameters, and bond distances and angles, and, for $[Ph_3PMe]\cdot\mathbf{1}$, a packing diagram with shortest nearest neighbor contacts (10 pages); Tables 6S and 7S, listing calculated and observed structure factors (41 pages). Ordering information is given on any current masthead page.

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(32) Atoms were located by use of direct methods (SHELX86). All calculations were performed on the VAX 3100 computer in the J. D. McCullough X-ray Crystallography Laboratory. Hydrogen atoms were assigned isotropic thermal parameter values based approximately on the value for the attached atom. Scattering factors for H were obtained from Stewart et al.[33] and for other atoms were taken from ref 34. Because of the disorder of the anion of $[Ph_3PMe]\cdot\mathbf{1}$, refinement was attempted in the space group *P*1, without success. The successful refinement of $[Et_3NH]_2\cdot\mathbf{3}$ was assumed to confirm its space group.

(33) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

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