New Derivatives of [NHMe₃][7-Me-µ-(9,10-HMeC)-*nido*-7-CB₁₀H₁₀]

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 $[NHMe_3][7-Me_{\mu}-(9,10-HMeC)-nido-7-CB_{10}H_{10}]$ (1) reacts with $[PdCl_2(PPh_3)_2]$ in refluxing ethanol solutions to afford four compounds which are the result of PPh₃ addition. Three of the products are structural isomers, viz. $[5-PPh_3-7-Me_{\mu}-(9,10-HMeC)-nido-7-CB_{10}H_9]$ (2), $[6-PPh_3-7-Me_{\mu}-(9,10-HMeC)-nido-7-CB_{10}H_9]$ (3), and $[2-Me-3-\{CHMe(PPh_3)\}-closo-2-CB_{10}H_9]$ (4), and the fourth is $[7-Me-8-OEt-9-\{CHMe(PPh_3)\}-nido-7-CB_{10}H_{10}]$ (5). The compounds were characterized by NMR spectrometry, high-resolution mass spectrometry, and single-crystal X-ray diffraction studies and are the first derivatives of the "unreactive" $[7-R-\mu-(9,10-HRC)-nido-7-CB_{10}H_{10}]^-$ anion (R = Me) not involving degradation.

Introduction

It is well-known that the isomeric 1,2-*closo*- $C_2B_{10}H_{12}$, 1,7- and 1,12- carboranes, and some of their derivatives undergo a two-electron-reduction reaction with sodium¹ to form $[C_2B_{10}H_{12}]^{2-}$ carborane ions. Protonation of this dianion makes possible the formation of two monoanions of the formula $[C_2B_{10}H_{13}]^{-.2}$ One of them is the kinetic compound $[7,9-R_2$ -*nido*- $C_2B_{10}H_{11}]^{-}$ (**I**; R = R' = H), also



known as the "reactive" form. Its dianionic $[7,9-R_2-nido-7,9-C_2B_{10}H_{10}]^{2-}$ form features an open six-membered face,^{2c} and it has proven to be a versatile ligand for f-block and early-transition-metal elements.³ The second

isomer, which is the most stable, is the thermodynamic product $[7\text{-}R-\mu-(9,10\text{-}HR'C)-nido-7\text{-}CB_{10}H_{11}]^-$, known as the "unreactive" form since it is inert in the usual reactions leading to metallacarboranes.^{4,5} Recent studies verified this affirmation by theoretical calculations. It was found that, at the MP2/6-31G*/3-21G+ZPE level, the "unreactive" isomer is 6.7 kcal/mol more stable than the reactive one.⁶ The kinetic isomer undergoes thermal rearrangement^{2b.7} to the second isomer [7-R- μ -(9,10-HR'C)-*nido*-7-CB₁₀H₁₁]⁻ (**II**; R = R' = H). Recently, a



more convenient, direct, high-yield route⁸ to alkylated derivatives of the thermodynamic isomer has been developed, thus prompting us to attempt to further investigate its chemistry.

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Results and Discussion

Reflux of ethanol solutions of the anionic cluster species [NHMe₃][7-Me-μ-(9,10-HMeC)-*nido*-7-CB₁₀H₁₀] (1) and $[PdCl_2(PPh_3)_2]$ in a 1:1 molar ratio followed by thin-layer chromatographic separation of the products affords low yields of two new zwitterionic non-metalcontaining isomeric cluster species, [5-PPh₃-7-Me-*µ*-(9,10-HMeC)-nido-7-CB₁₀H₉] (compound 2, 10%) and [6-PPh₃-7-Me-μ-(9,10-HMeC)-*nido*-7-CB₁₀H₉] (compound **3**, 16%), in which there has been an effective replacement of an exo-cluster hydrogen vertex by a PPh₃ unit. The reaction is shown in Scheme 1. The compounds were characterized by a combination of ¹¹B, ¹H, and ³¹P NMR spectrometry, high-resolution mass spectrometry (HRMS), and single-crystal X-ray diffraction studies. The structures of compounds 2 and 3 are shown in Figures 1 and 2, respectively, and crystallographic data and selected distances and angles are given in Tables 1 and 2.

The ¹¹B spectrum of **2** shows a 2:1:1:2:2:2 relative intensity pattern appropriate for a molecule with C_s symmetry, and **3** shows 10 resonances of unit intensity resulting from the breaking of the pseudo-mirror-plane symmetry by the phosphonium group bonded to B(6). Both spectra contain a resonance of unit intensity coupled to phosphorus (¹J(³¹P-¹¹B) = 140 Hz (**2**), 153 Hz (**3**)). A stick diagram illustrating the ¹¹B{¹H} NMR spectra of **2** and **3** and relating them to the previously assigned^{7a} spectrum for [μ -(9,10-H₂C)-*nido*-7-CB₁₀H₁₁]⁻ is given in Figure 3. The data reveal that PPh₃ has replaced a terminal hydrogen on the lower belt of boron atoms in the *nido*-11-vertex monocarbaundecaborane cluster. Substitution of terminal hydrogen atoms by Lewis base groups is a very common motif in borane



Figure 1. Molecular structure of $[5-PPh_3-7-Me_{\mu}-(9,10-HMeC)-nido-7-CB_{10}H_{10}]$ (2).

and heteroborane chemistry,⁹ where the electrons in the exo cluster $B-L \sigma$ -bond arise from the Lewis base group. Thus, the exo cluster substituent brings an "extra" electron to the cluster, subrogating either a bridging hydrogen atom or a delocalized electronic charge in anionic clusters such as in compounds **2** and **3** reported here.

The detailed interatomic dimensions of **2** show little difference within experimental error from those of the unsubstituted anion 1,¹⁰ with the largest difference being that for the bridged B9–B10 edge, which is only 0.030 Å longer (from 1.847(2) Å in **2** to 1.879(3) Å in **1**) and which produces an attendant increase in the B9–C12–B10 angle from 68.3(1) to 69.78(14)°. The different positions of phosphine substitution make little difference in dimensions for compounds **2** and **3**. The asymmetric unit in **3** contains two independent molecules,

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Figure 2. One of the two independent molecules in the unit cell of $[6-PPh_3-7-Me-\mu-(9,10-HMeC)-$ *nido* $-7-CB_{10}H_{10}]$ **(3)**, shown with 50% probability ellipsoids.



Figure 3. Stick diagrams of the ¹¹B{¹H} NMR spectra for (bottom) [6-PPh₃-7-Me- μ -(9,10-HMeC)-*nido*-7-CB₁₀H₁₀] (**3**), (middle) [5-PPh₃-7-Me- μ -(9,10-HMeC)-*nido*-7-CB₁₀H₁₀] (**2**), and (top) [μ -(9,10-H₂C)-*nido*-7-CB₁₀H₁₁]⁻ (**1**).³

one of which featured an incompletely resolved disorder involving the phosphine group. However, the HRMS and NMR data fully support the structure shown in Figure 2.

The compounds are stable at room temperature, although in performing ¹¹B NMR measurements of **2** in $C_6D_5CD_3$ solution at 90 °C we noted that a slow $2 \rightarrow 3$ isomerization process occurs. This implies a vertex exchange mechanism. Vertex isomerization by a triangular face rotation has been invoked in [1,2-*closo*- $C_2B_{10}H_{12}$] clusters,¹¹ and this could also account for the



Figure 4. Molecular structure of $[2-Me-3-\{CHMe(PPh_3)\}-closo-2-CB_{10}H_9]$ (4), with 50% probability ellipsoids.

observation here. A related thermal rearrangement of the Me₂S substituent in [7-(Me₂S)-*nido*-B₁₁H₁₃] from a position on the upper open face to the lower pentagonal belt and thence to the B1 position has been noted previously.¹²

These compounds represent the first derivatives of the "unreactive" $[7-R-\mu-(9,10-HRC)-nido-7-CB_{10}H_{10}]^{-}$ anion (R = Me) which do not involve degradation of the cluster. The course of the reaction reported here, which adds phosphine to the cluster, is unclear. Phosphine migration from a metal center to a boron atom in metallacarborane and metallaborane species is well established.¹³ For example, a related phosphine transfer has been previously reported in (phosphino)metallacarboranes with Rh,14 Ni,15 Pd,16 and Pt.17 In these examples a metal-bonded PPh3 unit migrates and forms a B–PPh₃ bond^{14,15,17} with the former B(10) in the free $[-nido-7, 8-C_2B_9H_{11}]^{2-}$ ligand or a B-PPh₂ bond with the former B(11) in the free nido-o-carboranyl monophosphines^{16a,c} and *nido-o*-carboranyl monothioethers.^{16b} In an attempt to investigate whether the palladium species might have a catalytic behavior in the phosphine addition possibly through Pd metal released during the reaction the procedure was repeated using 1/2 equiv of the palladium complex and excess triphenylphosphine. The result was a reduced yield of the compounds **2** and **3**. However, two further interesting minor products were

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	2	3	4	5
empirical formula	C ₂₂ H ₃₁ B ₁₀ P	$C_{22}H_{31}B_{10}P$	$C_{22}H_{31}B_{10}P$	C24.25H38.50B10O1.50P
formula wt	434.54	434.54	434.54	493.12
temp/K	120(2)	120(2)	120(2)	120(2)
cryst syst	monoclinic	trigonal	monoclinic	monoclinic
space group	$P2_1/c$	$R\overline{3}$	$P2_1/n$	$P2_1/c$
a/Å	9.6187(8)	32.3006(3)	10.457(3)	13.5326(1)
b/Å	22.952(2)	32.3006(3)	14.955(4)	17.2277(2)
c/Å	11.9724(9)	14.9362(3)	15.893(4)	24.9167(3)
$\alpha, \beta, \gamma/\text{deg}$	90, 111.677(5), 90	90, 90, 120	90, 91.82(2), 90	90, 91.4360(10), 90
$V/Å^{-3}$	2456.2(3)	13495.6(3)	2484.1(11)	5807.2(1)
Ζ	4	21	4	8
cryst size/mm	$0.22\times0.20\times0.06$	0.22 imes 0.20 imes 0.20	$0.28\times0.22\times0.20$	0.28 imes 0.20 imes 0.20
θ range for data collcn/deg	1.77 - 27.49	2.18 - 24.99	1.87 - 25.68	1.51 - 25.00
no. of rflns collected	21 776	62 698	24 003	73 224
F(000)	912	4788	912	2088
no. of indep rflns	5610 ($R_{\rm int} = 0.08$)	5268 ($R_{\rm int} = 0.11$)	$4724 \ (R_{\rm int} = 0.17)$	$10\ 210\ (R_{\rm int}=0.17)$
no. of data/restraints/params	5610/0/362	5268/21/325	4724/0/346	10 210/6/631
goodness of fit	1.005	1.075	0.998	1.010
final <i>R</i> indices $(I > 2\sigma(I))$				
R1	0.046	0.067	0.079	0.105
$wR2(F^2)$	0.112	0.187	0.229	0.323
largest diff peak and hole/e ${\rm \AA^{-3}}$	0.37 and -0.25	0.56 and -0.52	0.59 and -0.54	0.98 and -0.90

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for [5-PPh₃-7-Me-μ-(9,10-HMeC)-*nido*-7-CB₁₀H₉] (2) and [6-PPh₃-7-Me-μ-(9,10-HMeC)-*nido*-7-CB₁₀H₉] (3)

	2	3		2	3
B-P1	1.950(2)	1.944(4)	B5-B9	1.809(3)	1.781(6)
B5-B1	1.786(3)	1.776(5)	B6-B10	1.741(3)	1.783(5)
B5-B10	1.808(3)	1.785(5)	B6-B11	1.798(3)	1.740(5)
B5-B6	1.768(3)	1.803(5)	B6-B2	1.794(3)	1.773(5)
C7-C71	1.526(3)	1.525(5)	B9-B10	1.879(3)	1.842(5)
C7-B8	1.634(3)	1.645(5)	B9-C12	1.644(3)	1.640(6)
C7-B11	1.623(3)	1.644(5)	B10-C12	1.641(3)	1.651(5)
B8-B9	1.872(3)	1.869(6)	C12-C13	1.527(3)	1.511(5)
B1_B6_D1		120 6(2)	B1_B5_D1	118 49(14)	

B1-B6-P1 120.6(2) B1-B5-P1 118.42(14 B9-C12-B10 69.78(14) 68.1(2)

isolated and characterized by NMR spectroscopy, HRMS, and single-crystal X-ray diffraction studies as [2-Me-3- $\{CHMe(PPh_3)\}$ -*closo*-2-CB₁₀H₉] (compound **4**, Scheme 1, 4%) and [7-Me-8-OEt-9- $\{CHMe(PPh_3)\}$ -*nido*-7-CB₁₀H₁₀] (compound **5**, Scheme 1, <1%).

The structures of compounds 4 and 5 are shown in Figures 4 and 5, respectively, with selected distances and angles given in Tables 3 and 4. The ¹¹B{¹H} NMR spectrum of **4** shows a 1:1:3:3:2 pattern rather than the expected 1:1:1:1:2:2:2 pattern, indicating a coincidental overlap of four resonances. The low-field singlet in the ¹¹B NMR spectrum at +19.6 ppm indicates the presence of a substituent on boron. Indeed, the cluster hydrogen atoms overlapping peaks in the ¹H{¹¹B} NMR spectrum are all contained between +1.45 and +1.61 ppm. Features in the ¹H NMR spectrum due to the -CHMe- (PPh_3) moiety are a doublet of doublets at +1.78 ppm for the Me group and two overlapping quartets at +3.58ppm for the H atom, which collapse to a doublet and quartet, respectively, with ³¹P decoupling (${}^{3}J({}^{31}P-{}^{1}H)$) = 20.4 Hz). The doublet and quartet are mutually coupled with ${}^{3}J({}^{1}H-{}^{1}H) = 7.4$ Hz.

A single-crystal X-ray diffraction study of compound **4** reveals a *closo*-monocarbaundecaborane cluster in which the phosphine substituent now resides on an organic side chain arising, presumably, from addition to the bridging { μ -HMeC} group in the starting carborane cluster and resulting in a zwitterionic alkylidene-triphenylphosphorane derivative. The group acts as a



Figure 5. Molecular structure of one of the two independent molecules in the unit cell of $[7-Me-8-OEt-9-\{CHMe-(PPh_3)\}-nido-7-CB_{10}H_{10}]$ (5), shown with 50% probability ellipsoids and with phenyl rings, except for ipso carbon atoms, and noncage hydrogen atoms omitted to aid clarity.

two-electron donor to the cluster, comparable to the PPh₃ substituent in compounds **2** and **3**, so that, together with the cluster carbon vertex, the cage achieves an overall 2n + 2 skeletal electron pair count required for a closo 11-vertex cluster.¹⁸ Only one other alkylidene-triphenylphosphorane-substituted borane cluster, CH₂-(PPh₃)B₃H₇, has been characterized previously, made directly from $-CHR(PPh_3)$ (R = H, Me, Ph) and B₃H₇.thf.¹⁹ A structural characterization has been car-

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Table 3. Selected Interatomic Distances (Å) and Angles (deg) for [2-Me-3-{CHMe(PPh₂)}-close-2-CB₁₀H₂] (4)

B1-C2	1.646(7)	B1-B3	1.768(7)		
B1-B4	2.026(7)	B1-B5	2.005(7)		
B1-B6	2.020(7)	B1-B7	2.074(7)		
C(2) - C(3)	1.520(7)	C2-B4	1.575(7)		
C2-B5	1.577(7)	C2-B8	1.673(7)		
B3-C119	1.617(6)	C119-C120	1.547(6)		
P1-C101	1.802(4)	P1-C113	1.798(4)		
P1-C107	1.804(4)	P1-C119	1.806(4)		
C120-C119-B3	112.4(4)	C120-C119-P1	111.2(3)		
B3-C119-P1	113.8(3)	C113-P1-C119	109.8(2)		
C101-P1-C119	110.99(19)	C107-P1-C119	112.2(2)		
C3-C2-B1	124.0(4)	C119-B3-B9	135.5(4)		
C3-C2-B8	126.2(4)				

 Table 4. Selected Interatomic Distances (Å) and

 Angles (deg) for

 [7] M. 8 OFt 0. (CUMe(DBb.)) mide 7 CB. Hall (5)

[/-Me-9-OEI-	9-{CHMe(P	Ph ₃)}- <i>mao</i> -7-CB	$[10H_{10}](3)$
B9'-C1'	1.607(9)	B9'-B10'	1.917(10)
C1'-P1'	1.810(6)	C1'-C2'	1.588(9)
B8'-B9'	1.917(10)	C7'-C21'	1.472(12)
B8'-C7'	1.661(11)	B11'-01'	1.463(9)
C7'-B11'	1.665(10)	B10'-B11'	1.851(12)
C9'-C1'-D1'	107 7(4)	C2'-C1'-B0'	113 9(5)
P1-C1-B9	113.0(4)	C1'-B9'-B5'	121.6(6)
C1'-B9'-B4'	117.2(5)	C1'-B9'-B8'	125.1(5)
C21'-C7'-B2'	112.6(8)	C1'-B9'-B10'	130.0(5)
C21'-C7'-B3'	120.1(7)	C21'-C7'-B8'	124.1(7)
C21'-C7'-B11'	115.1(7)		

ried out for $R = H^{20}$ The P–B distances are essentially equal at 1.632(8) Å in the triborane adduct and 1.607-(9) Å in compound **4**. The geometry of **4** is comparable to that of the neutral *closo*-monocarbaundecaborane cluster with a Lewis base ligand [2-(Me₃Si)₂-6-Me₂S-2-CB₁₀H₉] **(6**), and related compounds,²¹ and also to the *closo*-[PhCB₁₀H₁₀]⁻ anion **(7)**.²² The most notable features for all these compounds are the distances for the apical six-connected B1 vertex to the lower belt B4–B7 vertexes. These range from 2.005(7) to 2.074(7) Å in **4**, and although they are somewhat long for interboron distances, they are comparable to those in **6** (1.747(3)– 2.040(7) Å) and **7** (2.015(4)–2.057(4) Å) and are somewhat shorter than in [B₁₁H₁₁]²⁻ itself, where they range from 1.959(7) to 2.159(7) Å.²³

The syntheses of compounds **2** or **3** and **4** highlight the process of converting a nonclassical into a classical carbon atom. The sequence is shown in Scheme 2. Initially, in 1,2-R₂-*closo*-1,2-C₂B₁₀H₁₀ both carbon atoms are nonclassical (see Scheme 3) and contribute three atomic orbitals to the cluster molecular orbitals. The connectivity of these carbon atoms is 5. The species at the left in Scheme 2 corresponds to the "kinetic" isomer, [7,9-R₂-*nido*-7,9-C₂B₁₀H₁₁]⁻. One of the two carbon atoms invests three atomic orbitals to generate a 3-fold connectivity. In the "thermodynamic" isomer [7-R- μ -(9,10-HRC)-*nido*-7-CB₁₀H₁₁]⁻ (**1**), the endo carbon atom invests two atomic orbitals to produce a 2-fold connectivity. Finally, in **4**, the carbon atom invests one atomic orbital for a σ -bond. The exo cluster disposition of the -CHMe(PPh₃) group in **4** clearly proves the classical nature of this carbon. However, the endo nature of the bridging $\{\mu$ -HMeC $\}$ group in **1** and **2** or **3** may balance the fact that the number of orbitals invested parallels the number of connectivities. The endo feature supports a nonclassical carbon, while the number of orbitals/number of connectivities suggests the contrary. We feel that the synthesis of **4** indicates that in 1-3 the bridging carbon in the { μ -HMeC} group has more nonclassical than classical character. The incoming PPh₃ requires an atomic orbital for the C-P coupling, which is available after disconnecting one C-B connectivity. Then, the original endo configuration of the former bridging $\{\mu$ -HMeC $\}$ group is switched to an exo disposition. Our view is that if the bridging $\{\mu$ -HMeC} group had not been an integral part of the cluster, relocation of the -CHMe(PPh₃) moiety to an exo cluster position would not have been necessary. A further argument that supports this view is that once the C–B connectivity is broken and in order to preserve the cluster integrity new B-B connectivities are generated that ultimately produce the closo species 4 (see Scheme 4).

Compound 5 is related to 4, but with an additional two bridging hydrogen atoms, giving it a nido 11-vertex structure. ¹¹B NMR spectrometry shows a 1:1:2:1:1:2: 1:1 pattern with two singlet resonances of unit intensity, corresponding to the presence of two substituents on boron. The ${}^{1}H{}^{11}B{}$ NMR spectrum showed two sets of the doublet of doublets, which are characteristic for the methyl group in the methyltriphenylphosphorane substituent, and the ${}^{31}P{}^{1}H$ spectrum showed two singlet resonances at +34.8 and +35.3 ppm, indicating the presence of two closely related species in solution. We were unable to chromatographically separate them, but slow evaporation of a CH₂Cl₂/hexane solution gave crystals of a single species suitable for a single-crystal X-ray study. The data reveal two unique molecules in the unit cell with -CHMe(PPh₃) and ethoxy substituents on two boron vertexes in a nido-monocarbaundecaborane cluster (Figure 4). The B-OEt and C-Me positions were disordered, as was one phenyl group on the triphenylphosphine moiety. The B11'-O1' distance of 1.463(9) Å is similar to the C7'- C21' distance, 1.472-(12) Å, and is somewhat longer than a range of cage B-OR separations (1.371-1.409 Å),²⁴ although this is probably an artifact of the disorder. The bridging hydrogen atoms evident in the proton spectrum were also located in the X-ray structure determination. The molecular formulation shown is supported by the HRMS data, which exhibits a signal group pattern centered at m/z 478.3421 (478.3429 calculated) for P⁺ - H₂ on C₂₄H₃₇B₁₀PO. The ethoxy substituent clearly comes from the ethanol solvent, and it may also supply the two extra hydrogen atoms required to achieve the observed nido cluster.

The EtO- substitution is not rare in boron chemistry clusters. Upon reaction of $[MCl_2(PPh_3)_2]$ (M = Pd, Pt) with borate anions in refluxing alcohols as solvent,

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Scheme 2. Fate of a Nonclassical Carbon in the "Kinetic" Isomer [7,9-R₂-*nido*-7,9-C₂B₁₀H₁₁]- to a Classical One in [2-Me-3-{CHMe(PPh₃)}-*closo*-2-CB₁₀H₉] (4) through the "Thermodynamic" [7-R-μ-(9,10-HRC)-*nido*-7-CB₁₀H₁₀]- Isomer (1)



Scheme 3. Synthesis of the "Thermodynamic" Isomer [7-R-μ-(9,10-HRC)-*nido*-7-CB₁₀H₁₀]- (1), Produced Directly from the Reaction of 1,2-R₂-*closo*-1,2-C₂B₁₀H₁₀ with Magnesium Metal



Scheme 4. Suggested Pathway to Convert One Nonclassical Carbon Atom from [7-R-μ-(9,10-HRC)-*nido*-7-CB₁₀H₁₀]- (1) into a Classical One in

 $[2-Me-3-{CHMe(PPh_3)}-closo-2-CB_{10}H_9]$ (4)



alkoxy group substitution to occupy terminal positions has been observed. $^{\rm 25}$

The synthesis of compounds 2-5, although obtained in low yield, opens a way to explore the derivative chemistry of the "thermodynamic" isomer, [7-R- μ -(9,10-HRC)-*nido*-7-CB₁₀H₁₁]⁻ (**1**), considered up to now a nonreactive species. The diversity of generated com-

pounds and the low yields are indicative of the difficulty of the $[7-R-\mu-(9,10-HRC)-nido-7-CB_{10}H_{11}]^-$ (1) to react, but it fulfills the objective of this work, which potentially demonstrates that routes to monocarbaundecaboranes through the readily available [NHMe₃][7-Me- μ -(9,10-HMeC)-*nido*-7-CB₁₀H₁₀] (1) may be attainable.

Experimental Section

General Considerations. Experiments were carried out under a dry nitrogen atmosphere, with subsequent isolation and characterizations being carried out in air. Solvents were dried by conventional methods. [NHMe3][7-Me-µ-(9,10-HMeC)nido-7-CB₁₀H₁₀] and [PdCl₂(PPh₃)₂] were prepared by the literature methods.^{8,26} ¹H and ¹H{¹¹B} NMR (300.13 MHz), ¹³C-{¹H} NMR (75.47 MHz), and ¹¹B NMR (96.29 MHz) spectra were recorded with a Bruker ARX 300 instrument equipped with the appropriate decoupling accessories. All NMR spectra were recorded from CDCl₃ solutions at 298 K. Chemical shift values for ¹¹B NMR spectra were referenced to external BF₃. $OEt_2,\ ^{31}P\{^1H\}$ NMR spectra were referenced to external 85% H_3PO_4 (minus values upfield), and those for ¹H, ¹H{¹¹B}, and ¹³C{¹H} NMR spectra were referenced to Si(CH₃)₄. Chemical shifts are reported in units of parts per million downfield from the reference, and all coupling constants are reported in hertz. The mass spectra were measured in the FAB mode on a JEOL MStation JMS-70 spectrometer using 3-nitrobenzyl alcohol (3-NBA, or 3-NBA/CsI).²⁷ Thin-layer chromatography (TLC) plates were individually crafted from aqueous slurries of Aldrich standard grade TLC silica gel with a fluorescent indicator and dried at ambient temperature.

[5-PPh₃-7-Me-µ-(9,10-HMeC)-nido-7-CB₁₀H₉] (2) and [6-PPh₃-7-Me-µ-(9,10-HMeC)-nido-7-CB₁₀H₉] (3). [NHMe₃]-[7-Me-µ-(9,10-HMeC)-*nido*-7-CB₁₀H₁₀] (57 mg, 0.244 mmol) and [PdCl₂(PPh₃)₂] (175 mg, 0.25 mmol) were stirred at reflux overnight in ethanol. After it was cooled, the dark solution was filtered through a plug of silica gel and the filtrate was reduced in volume (rotary evaporator, ca. 40 °C) and subjected to preparative TLC (75/25 CH₂Cl₂/hexane). A colorless band observed under UV irradiation, A ($R_f = 0.8$), and B, a rusty brown band ($R_f = 0.2$), were obtained. Band B did not contain boron and was not further investigated. Band A was redeveloped (20/80 CH₂Cl₂/hexane), giving two further UV-active bands at $R_f = 0.3$ (C), 0.2 (D). Crystals suitable for singlecrystal X-ray diffraction studies were grown for each compound by slow evaporation of layered hexane/CDCl₃ solutions of the compound. The bands were identified by NMR spectrometry, high-resolution mass spectrometry, and single-crystal X-ray diffraction analyses.

Band C: [5-PPh₃-7-Me- μ -(9,10-HMeC)-*nido*-7-CB₁₀H₉] (compound **2**, 10.3 mg, 24 μ mol, 10%). ¹H NMR: δ 7.75–7.52 (m,

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15H, H_{aryl}), 3.64 (quartet, ${}^{3}J({}^{1}\text{H}{}^{-1}\text{H}) = 6.3$, 1H, C12–*H*), 3.69– 1.33 (br m, 9H, B–*H*), 1.81 (s, 3H, C7–*Me*), 1.42 (d, ${}^{3}J({}^{1}\text{H}{}^{-1}\text{H}) = 6.3$, 3H, C12-*Me*). ${}^{1}\text{H}\{{}^{11}\text{B}\}$ NMR: δ 7.75–7.52 (m, 15H, H_{aryl}), 3.64 (quartet, ${}^{3}J({}^{1}\text{H}{}^{-1}\text{H}) = 6.3$, 1H, C12–H), 3.69 (br s, 2H, B8–*H* and B11–*H*), 2.92 (br s, 1H, B1–*H*), 1.96 (br s, 2H, B2–*H* and B3–*H*), 1.49 (br s, 2H, B9–*H* and B10–*H*), 1.33 (br s, 2H, B4–*H* and B6–*H*), 1.81 (s, 3H, C7–*Me*), 1.42 (d, ${}^{3}J({}^{1}\text{H}{}^{-1}\text{H}) = 6.3$, 3H, C12–*Me*). ${}^{11}\text{B}\{{}^{1}\text{H}\}$ NMR: δ +19.3 (s, 2B, B8 and B11), 0.0 (d, ${}^{1}J({}^{11}\text{B}{}^{-31}\text{P}) = 140$, 1B, B5), -0.6 (s, 1B, B1), -5.3 (s, 2B, B2 and B3), -12.8 (s, 2B, B9 and B10), -21.6 (s, 2B, B4 and B6). ${}^{31}\text{P}\{{}^{1}\text{H}\}$ NMR: δ +5.7 (quartet, ${}^{1}J({}^{31}\text{P}{}^{-11}\text{B}) = 140$). Mass spectrometry shows two envelopes centered at *m*/*z* 433.3121 and 419.2982, within 7.6 and 12 ppm of the calculated peak profile for (P⁺ + H) – H₂ and (P⁺ + H) – CH₄ in C₂₂H₃₁B₁₀P.

Band D: [6-PPh₃-7-Me- μ -(9,10-HMeC)-*nido*-7-CB₁₀H₉] (compound **3**, 16.6 mg, 40.2 μ mol, 16%). ¹H NMR: δ 7.75–7.52 (m, 15H, *H*_{aryl}), 4.06 (quartet, ³*J*(¹H–¹H) = 6.0, 1H, C12–*H*), 1.74 (s, 3H, C7–*Me*), 1.48 (d, ³*J*(¹H–¹H) = 6.0, 3H, C12–*Me*). ¹¹B-{¹H} NMR: δ +21.0 (s, 1B, B8 or B11), +14.7 (s, 1B, B11 or B8), +3.9 (s, 1B, B1 or B5), -1.6 (s, 1B, B5 or B1), -5.5 (s, 1B, B2 or B3), -6.6 (s, 1B, B3 or B2), -12.4 (s, 1B, B9 or B10), -15.2 (s, 1B, B10 or B9), -20.4 (s, 1B, B4), -23.2 (d, ¹*J*(³¹P–¹¹B) = 153, 1B, B6). ³¹P{¹H} NMR: δ +6.2 (quartet, ¹*J*(³¹P–¹¹B) = 153). Mass spectrometry showed two envelopes centered at *m*/*z* 433.3057 (433.3099 calcd) and 419.2936 (419.2942 calcd) within 9.6 and 1.4 ppm, respectively, of that calculated for (P⁺ + H) – H₂ and (P⁺ + H) – CH₄ in C₂₂H₃₁B₁₀P.

[2-Me-3-{CHMe(PPh₃)}-closo-2-CB₁₀H₉] (4) and [7-Me-8-OEt-9-{CHMe(PPh₃)}-nido-7-CB₁₀H₁₀] (5). In a similar experiment [NHMe3][7-Me-µ-(9,10-HMeC)-nido-7-CB10H10] (72 mg, 0.31 mmol) and $[PdCl_2(PPh_3)_2]$ (111 mg, 0.16 mmol) with added PPh₃ (161 mg, 0.61 mmol) were refluxed in ethanol for 24 h, and after cooling the solution was filtered, giving a sandy colored, non-boron-containing solid (yield 61 mg). The filtrate was reduced in volume and subjected to preparative TLC as described above (80/20 CH₂Cl₂/hexane), giving colorless bands observed under UV illumination at $R_f = 0.8, 0.7, \text{ and } 0.2$. The first band contained a mixture of compounds 2 and 3 (5 mg). The second band was characterized as [2-Me-3-{CHMe(PPh₃)}*closo*-2-CB₁₀H₉] (compound **4**, 5.0 mg, 12 µmol, 4%). ¹H NMR: δ 7.75–7.52 (m, 15H, $\mathit{H}_{\mathrm{aryl}}$), 3.58 (overlapping doublet of quartets, ${}^{3}J({}^{1}H-{}^{1}H) = 7.4$, ${}^{3}J({}^{3}P-{}^{1}H) = 20.4$, 1H, C(119)- \hat{H} , 1.78 (doublet of doublets, ${}^{3}J({}^{1}H-{}^{1}H) = 7.3$, ${}^{3}J({}^{3}P-{}^{1}H) =$ 20.4, 3H, C119-Me), 1.61-1.45 (br m, 9H, B-H), 1.28 (s, 3H, C2-Me). ${}^{1}H{}^{11}B{}$ NMR: δ 7.75-7.52 (m, 15H, H_{arvl}), 3.58 (overlapping doublet of quartets, ${}^{3}J({}^{1}H-{}^{1}H) = 7.4$, ${}^{3}J({}^{3}P-{}^{1}H)$ = 20.4, 1H, C(119)-H), 1.78 (doublet of doublets, ${}^{3}J({}^{1}H-{}^{1}H)$ = 7.3, ${}^{3}J({}^{3}P-{}^{1}H) = 20.4$, 3H, C119–*Me*), 1.61 (br s, 3H, B–H), 1.51 (br s, 3H, B-H), 1.45 (br s, 3H, B-H), 1.28 (s, 3H, C2-*Me*). ¹¹B{¹H} NMR: δ +19.6 (s. 1B), -6.4 (s. 1B), -12.1 (s. 3B), -14.3 (s, 3B), -20.2 (s, 2B). ${}^{31}P{}^{1}H{}$ NMR: δ +32.2 (s). Mass spectrometry ((NBA/CsI)) shows an peak envelope centered at m/z 567.2216 within -2.8 ppm of that calculated for the peak profile of P⁺ in C₂₂H₃₁PB₁₀Cs (567.2232). Colorless cubic single crystals were obtained by slow evaporation of a CH₂Cl₂/hexane solution of the compound.

The third band (ca. 1 mg) contained two very closely related species. The mixture was crystallized by slow evaporation of a CH₂Cl₂/hexane solution. The compound was characterized by a single-crystal X-ray diffraction study, together with NMR and HRMS, as [7-Me-8-OEt-9-{CHMe(PPh₃)-*nido*-7-CB₁₀H₁₀] (compound **5**). ¹¹B{¹H} NMR: δ +7.9 (s, 1B, B9'), -6.3 (s, 1B), -8.6 (s, 2B), -11.6 (s, 1B), -16.5 (s, 1B, B11'), -26.9 (s, 2B), -32.6 (s, 1B), -35.1 (s, 1B). ³¹P{¹H} NMR: δ +34.8, +35.3 in ca. 2:1 ratio, respectively. ¹H{¹¹B} NMR: overlapping peaks for both species A and species B in a ca. 2:1 ratio at δ 7.80–8.00 (m, 15H, H_{aryl}), 3.5 (1H, C9–*H*), two sets of doublets of doublets for isomers A and B at δ +1.62 (³J(¹H-¹H) = 7.3, ³J(³¹P-¹H) = 20.5, CHPPh₃-CH₃), 1.49 (³J(¹H-¹H) = 7.6, ³J(³¹P-¹H) = 20.5, CHPPh₃-CH₃), 1.38 (s, 3H, C7'-CH₃); B-H

atoms show overlapping peaks for the two species at δ +2.38, +2.27, +1.91, +1.73, +1.22, +0.88, +0.75, -0.38, -0.30 (μ -H(9'-10')), -2.34 (μ -H(10'-11')), -3.42, -3.70. Mass spectrometry shows a peak envelope centered at m/z 478.3421 within -1.6 ppm of that calculated for the peak profile of P⁺-H₂ in C₂₄H₃₇B₁₀PO (478.3412).

X-ray Crystallography. Crystals of appropriate dimensions were mounted on glass fibers in a random orientation. Preliminary examination and data collection was performed using a Brüker SMART charge coupled device (CCD) detector system single-crystal X-ray diffractometer using graphitemonochromated Mo K α radiation ($\lambda = 0.710$ 73 Å) equipped with a sealed-tube X-ray source at 120 K. Preliminary unit cell constants were determined with a set of 45 narrow frames $(0.4^{\circ} \text{ in } \varpi)$ scans. A typical data set consisted of 3636 frames with a frame width of 0.3° in ϖ and typical counting time of 15-30 s/frame at a crystal to detector distance of 4.900 cm. The double-pass method of scanning was used to exclude any noise. The collected frames were integrated using an orientation matrix determined from the narrow frame scans. SMART and SAINT software packages²⁸ were used for data collection and data integration. Analysis of the integrated data did not show any decay. Final cell constants were determined by a global refinement of xyz centroids. Collected data were corrected for systematic errors using SADABS²⁹ based on the Laue symmetry using equivalent reflections.

Crystal data and intensity data collection parameters are listed in Table 1.

Structure solution and refinement for compounds **2**, **4**, and **5** were carried out using the SHELXTL-PLUS software package.³⁰ The structures were solved by direct methods and refined successfully in the monoclinic space groups $P2_1/c$, $P2_1/c$, $P2_1/c$, respectively. Full-matrix least-squares refinement was carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$. The nonhydrogen atoms were refined anisotropically to convergence. The cage hydrogen atoms for all three compounds were located from difference Fourier syntheses and refined freely for compounds **2** and **4**. The cage H's for compound **5** were located but not refined. All other hydrogen atoms were treated using the appropriate riding model (AFFIX m3).

Refinement for compound 3 was carried out using SHELX-97.28 The asymmetric unit of compound 3 contains one ordered molecule and one-sixth of a disordered molecule. There are two neighboring equivalent positions for the disordered molecule, although only one can be present in either position. The phosphorus atom and the boron atom connected to the phosphorus atom of the disordered molecule lie on a 3-fold axis, and the rest of the non-hydrogen atoms are in the vicinity of the 3-fold axis. Each phenyl group of the disordered molecule assumes two orientations. Owing to the disorder and low occupancy of the disordered molecule, the Me and μ -HMeC groups could not be accurately located or the cage carbon atom reliably identified. Therefore, all non-hydrogen atoms of the disordered cage were treated as boron atoms in the final calculations. The H atoms of the disordered cage were not located. EADP constraints and DFIX restraints were utilized in order to keep bond parameters reasonable for the disordered cage. All non-hydrogen atoms of the ordered molecule and the phosphorus atom of the disordered molecule were refined anisotropically, but the atoms of the disordered cage were refined with isotropic thermal displacement parameters. Hydrogen atoms were placed at calculated distances from their host atoms and treated as riding atoms using the SHELX97 default parameters.³¹ Refinements of the structure in the lower symmetry space groups also resulted in a partially disordered structure.

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The asymmetric unit of compound **5** contains two unique molecules, and both exhibit disorder. A phenyl group was disordered in one of the two molecules and shows large thermal motion. Rigid-body refinement (AFFIX 66) and thermal ellipsoid constraints (EADP) were used to model this disorder. In the second molecule, the C–Me and B–Et positions are disordered. These two positions were modeled with partial occupancy of all the involved atoms, and positional and thermal parameter restraints (EXYZ and EADP) were used to model the disorder.

Structure refinement parameters are listed in Table 1. Drawings of the molecules were made with $ORTEP^{32}$ with nonhydrogen atoms represented by 50% probability ellipsoids. **Acknowledgment.** We thank the MCyT (Grant No. MAT01-1575) for partial support of this research and the Generalitat de Catalunya (Grant No. 2001/SGR/00337). J.B. thanks the Ministerio de Educación, Cultura y Deporte, for a stay of foreign researchers in Spain (Grant No. SAB2000-0293).

Supporting Information Available: Tables giving complete X-ray data for compounds **2**–**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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