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Formation of 1,1-[Bis(diphenylphosphino)ethane]-2,3-dicarba-1-nickela-*closo*-heptaborane via the Intermediacy of 4,5-(μ-Halogeno[bis(diphenylphosphino)ethane]nickel)-2,3-dicarba-*nido*-hexaborane(8)

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The reaction between $[(C_6H_5)_2PCH_2]_2NiX_2$ (X = Cl, Br) and $K[C_2B_4H_7]$ has been examined between −35 and −80 °C. When the bromo reagent is used, the only product observed is 1,1-[bis(diphenylphosphino)ethane]-2,3-dicarba-1-nickela-*closo*-heptaborane (I), even at −80 °C. ^1H NMR and other data are reported for I. If the chloro reagent is used, evidence for the intermediate nido species 4,5-(μ-chloro[bis(diphenylphosphino)ethane]nickel)-2,3-dicarba-*nido*-hexaborane(8) (II) is observed from ^1H NMR spectra when the reaction mixture is maintained at −80 °C. On warming, the nido species (II) loses HCl to afford the closo product (I). It is suggested that this type of mechanism is general for the insertion of ligated metal moieties into *nido*-borane cages to afford *closo*-metallaboranes.

Introduction

The application of electron-counting rules[1] for clusters has proved to be a most useful predictive tool in inorganic chemistry. Such applications span the range of cluster systems including transition-metal clusters, metallaboranes, boranes, carbocations, and other main-group clusters. Of interest to us are examples of transformations of metallaboranes from one cluster type to another. Although there are well-documented examples of this phenomenon for larger metallaboranes[2] and smaller metal cluster systems,[3] examples involving small metallaboranes or metallacarboranes are quite rare. The first such example, prepared by Grimes et al.,[4] involved the nido species $[(\eta^5\text{-}C_5H_5)Fe(CO)_2C_2B_4H_7]$. UV irradiation of the species results in loss of CO and formation of the closo species $[(\eta^5\text{-}C_5H_5)Fe^{III}C_2B_4H_6]$ or $[(\eta^5\text{-}C_5H_5)Fe^{II}(H)C_2B_4H_6]$. Related work by Stone et al.[5] involved pyrolysis of $[$*nido*-4,5-(μ-*trans*-$(Et_3P)_2Pt(H)$)-5,6-(μ-H)-2,3-Me_2-2,3-$C_2B_4H_6]$ to afford the related *closo*-species $[1,1\text{-}(Et_3P)_2\text{-}2,3\text{-}Me_2\text{-}1,2,3\text{-}PtC_2B_4H_6]$ and H_2. In both cases the reactions involve the formal loss of one polyhedral skeletal electron pair from the *nido*-μ-metallocarborane to afford the pentagonal-bipyramidal closo species with the metal moiety in the 1-position. Grimes et al.[4,6] have prepared directly a series of closo metallo derivatives of $C_2B_4H_8$. Of interest to us is whether these syntheses involve the intermediacy of *nido*-μ-metallocarboranes. For most of these examples prepared by Grimes et al., it is possible to write a reaction scheme in which an edge-bonded *nido*-metalloborane is precursor to the closo product. Often the reaction procedure maximizes the yield of closo product and minimizes the possibility of isolation of the less stable nido species. This was the case in the preparation[6] of $[(dppe)NiC_2B_4H_6]$ from $[(dppe)NiCl_2]$ and $K[C_2B_4H_7]$ at 26 °C. (dppe = 1,2-bis(diphenylphosphino)ethane). It is probable that this reaction proceeds via the formation of a nido species analogous to the series of (dppe)MX derivatives of B_5H_9[7] and B_6H_{10}[8] (M = Ni, Pd, Pt; X = halide). The work presented herein is part of our continuing study of (dppe)-ligated metallaboranes and carboranes,[9] and it describes our attempts to isolate the nido species $[4,5\text{-}(\mu\text{-}(dppe)NiX)\text{-}2,3\text{-}C_2B_4H_7]$ (X = Cl, Br) and to study its conversion to the previously prepared $[1,1\text{-}(dppe)NiC_2B_4H_6]$. We also report additional NMR data for this latter species.

Experimenal Section

Materials. 2,3-Dicarbahexaborane(8) was prepared from B_5H_9 by published methods[10-12] and $[(dppe)NiX_2]$ (X = Cl, Br) was prepared from dppe and NiX_2.[13] dppe (Strem) was used without purification as were $NiCl_2{\cdot}6H_2O$ (Mallinckrodt) and $NiBr_2{\cdot}xH_2O$ (Alfa), and B_5H_9 (Callery Chemical) was distilled on the vacuum line prior to use. KH (Alfa), obtained as a mineral oil suspension, was washed with C_5H_{12} on the vacuum line until it was a free-flowing white powder. Its activity, as measured by H_2 evolution on reaction with methanol at low temperatures, was 94–98%. All solvents were reagent grade and were dried and distilled before use and stored in Pyrex vessels with Teflon stopcocks.

Spectra. Boron-11 NMR spectra at 96.3 MHz and ^1H NMR spectra at 300.1 MHz were obtained on a Nicolet NT 300 spectrometer. ^{11}B chemical shifts are reported relative to $BF_3{\cdot}O(C_2H_5)_2$, positive shifts indicate deshielding, and proton chemical shifts are reported relative to $(CH_3)_4Si$ (δ = 0). IR spectra were obtained on a Perkin-Elmer 337 spectrometer and X-ray data on a Nicolet XRD P3 diffractometer. Samples were placed in 0.1-mm thin-wall capillaries, which were sealed with silicone grease under argon. Intensity data were collected at room temperature by using graphite-monochromated Mo Kα radiation at 0.71069A. Data reduction was done with the Enraf-Nonius structure determination package modified by B. A. Frenz and Associates on a VAX 11/780 computer.

Preparation of *closo*-$[(dppe)NiC_2B_4H_6]$. The procedure used by Grimes et al.[6] was modified slightly. $K[C_2B_4H_7]$, prepared from KH and $C_2B_4H_8$ in THF at −35 °C, was allowed to react with $[(dppe)NiCl_2]$ at −35 °C. The resulting violet-brown solution was warmed to 25 °C and filtered and the product extracted with C_6H_6 in the drybox. Recrystallization from CH_2Cl_2 at 0 °C afforded red needles, which melted at 81 °C with decomposition. The presence of a resonance at 5.32 ppm in the proton NMR spectrum suggested a CH_2Cl_2 adduct. Analysis also suggested the presence of one CH_2Cl_2 molecule of solvation. Anal. Calcd for $C_{29}H_{32}B_4Cl_2NiP_2$: C, 56.62; H, 5.24. Found: C, 53.28; H 5.74). IR (KBr) (cm^{-1}): 3080 (m), 3070 (m), 3060 (m), 2980 (m), 2950 (m), 2570 (s), 2560 (s), 2530 (s), 2500 (w), 2490 (s), 1430 (s), 1270 (m), 1110 (s), 830 (s), 760 (m), 750 (m), 720 (m), 710 (m), 700 (m), 540 (m), 530 (m), 495 (m).

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(1) For pertinent reviews see: Williams, R. E. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 67. Rudolph R. W. *Acc. Chem. Res.* **1976**, *9*, 446. O'Neill, M. E.; Wade, K. In "Metal Interactions with Boron Clusters"; Grimes, R. N., Ed., Plenum Press: New York, 1982; Chapter 2. Barton, L. *Top. Curr. Chem.* **1982**, *100*, 169. Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311. Greenwood, N. N. *Chem. Soc. Rev.* **1984**, *13*, 353.

(2) For example see: Doi, J. A.; Teller, R. G.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1980**, 80. Bould, J.; Crook, J. E.; Greenwood, N. N.; Kennedy, J. D.; McDonald, W. S. *J. Chem. Soc., Chem. Commun.* **1982**, 346.

(3) Eady, C. R.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1976**, 302.

(4) Sneddon, L. G.; Beer, D. C.; Grimes, R. N. *J. Am. Chem. Soc.* **1973**, *95*, 6622.

(5) Barker, G. K.; Green, M.; Stone, F. G. A.; Welch, A. J.; Onak, T. P.; Siwapanyoyos, G. *J. Chem. Soc., Dalton Trans.* **1979**, 1687.

(6) Grimes, R. N.; Beer, D. C.; Sneddon, L. G.; Miller, V. R.; Weiss, R. *Inorg. Chem.* **1974**, *13*, 1138.

(7) Greenwood, N. N.; Staves, J. *J. Chem. Soc., Dalton Trans.* **1977**, 1788. Greenwood, N. N.; Kennedy, J. D.; Staves, J. *J. Chem. Soc., Dalton Trans.* **1978**, *1146*. Kennedy, J. D.; Staves, J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 808.

(8) Greenwood, N. N. *Pure Appl. Chem.* **1977**, *49*, 791. Barton, L.; Shore, S. G., unpublished observations.

(9) Barton, L.; Rush, P. K. *Inorg. Chem.* **1985**, *24*, 3413. Rush, P. K.; Barton, L. *Polyhedron* **1985**, *24*, 1741.

(10) Shapiro, I.; Keilin, B.; Williams, R. E.; Good, C. D. *J. Am. Chem. Soc.* **1963**, *85*, 3167.

(11) Onak, T. P.; Drake, R.; Dunks, G. *Inorg. Chem.* **1964**, *3*, 1686.

(12) Hosmane, N. S.; Grimes, R. N. *Inorg. Chem.* **1979**, *18*, 3294.

(13) Booth, G.; Chatt, J. *J. Chem. Soc.* **1965**, 3238.

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Table I. 300-MHz Proton NMR Data in CD_2Cl_2 at −78 °C

	C_6H_5	CH_2	H_{apex}	H(2) H(3)	H(4) H(5)	H(6)	μ-H
$(dppe)NiC_2B_4H_6$	7.67 7.43	2.03	1.14	5.13	3.62 2.90	3.62	
$(dppe)Ni(X)C_2B_4H_7$	7.67 7.43	2.16	*a*	~5.57 5.32[b]	2.79	3.64	−1.25

[a] Not observed. [b] Estimated value, obscured by $CHCl_2$ resonance.

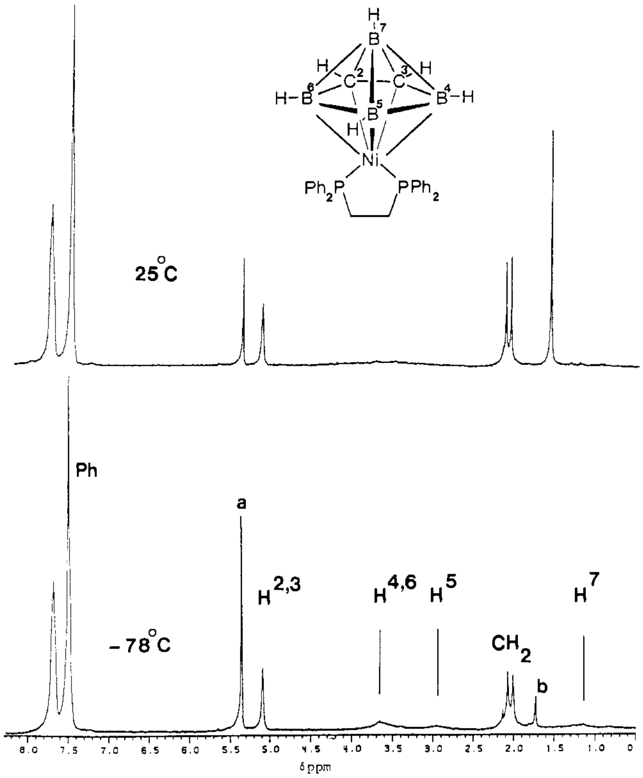

Figure 1. 300.1-MHz ^1H NMR spectra of 1,1-$(dppe)NiC_2B_4H_6$ in CD_2Cl_2 at 25 and −78 °C. a, CH_2Cl_2; b, free dppe. H atoms are numbered the same as the B atoms to which they are bonded in the proposed structure.

Attempted Preparation of *nido*-4,5-[μ-(dppe)Ni(X)]-2,3-$C_2B_4H_7$ (X = Cl, Br). $K[C_2B_4H_7]$ (~0.5 mmol) was prepared at −78 °C from the reaction between $C_2B_4H_8$ and KH in $(CH_3)_2O$ on the vacuum line. After H_2 had been removed at −190 °C, an equimolar quantity of $[(dppe)NiX_2]$ was added and CH_2Cl_2 (3 mL) was condensed into the reaction vessel. The reaction mixture was slowly warmed to −78 °C and stirred overnight. The product mixture, which contained a chocolate brown precipitate and brown needles, was evacuated at −78 °C for several days to remove CH_2Cl_2 and $(CH_3)_2O$. CD_2Cl_2 was added to the solid residue, which was stirred and tipped into a NMR tube side arm. The temperature of the system was not allowed to rise above −78 °C during this procedure. NMR tubes were sealed off with a torch at −196 °C and stored at that temperature until spectra could be obtained. Alternative methods using $CHCl_3$ as solvent in order to simplify ^1H NMR spectra were unsuccessful. $CHCl_3$ freezes at −63 °C, and running the reaction above this temperature resulted in formation of *closo*-$[(dppe)NiC_2B_4H_6]$ only as indicated by ^1H NMR spectra. The crystals obtained in these reactions were similarly identified as the closo species. Attempts to isolate the solid products by removal of solvent at −78 °C prior to warming to ambient temperatures were unsuccessful; the only identifiable solid product obtained in these reactions was *closo*-$[(dppe)NiC_2B_4H_6]$.

Results and Discussion

The reaction between $[(dppe)NiX_2]$ (X = Cl, Br) and $K[C_2B_4H_7]$ in ether/CH_2Cl_2 at −35 °C affords only the closo species $[(dppe)NiC_2B_4H_6]$, which has been prepared previously by Grimes et al.[6] at higher temperatures. In the reaction involving $[(dppe)NiBr_2]$, even at −78 °C, the only product observed is the closo species, identified by spectral data. The species was isolated as red crystalline needles, melts at 81 °C with decomposition, and exhibits an infrared spectrum essentially identical with that obtained previously.[6] As previously noted, the ^{11}B NMR spectrum[6] exhibits a very broad featureless hump at ~20 ppm ($W_{1/2}$ ~ 800 Hz); however, we were able to observe more detail in the proton spectrum. Analysis suggested that the species crystallized as a CH_2Cl_2 adduct and this was supported by the proton NMR spectrum, which exhibits a strong resonance at 5.32 ppm. Spectra are shown in Figure 1. At 25 °C only the H–C resonances are observed at 7.67 and 7.43 (phenyl), 5.13 (carborane H–C), and 2.03 ppm ($J_{^{31}P-^1H}$ = 19 Hz; a doublet arising from the methylene protons on the ligand). A single resonance at 1.73 ppm ($J_{^{31}P-^1H}$ ~ 4.5 Hz) arises from the methylene protons on the free ligand. It is well established that phenyl phosphines are labile ligands[14] in complexes of the late transition metals and especially in metallaboranes. There is also a very weak broad hump centered at ~3.55 ppm. When the same sample is cooled to −78 °C, new features appear in the spectrum. Weak broad resonances appear at 3.62 and 2.90 ppm in approximate area ratios 2:1, respectively, and another appears at 1.14 ppm with approximate area ratio 1 as seen in Figure 1. These resonances fall in the chemical shift range expected for protons bonded to cage borons in *closo*-carboranes[15] and are tentatively assigned to the protons on B(4,6), B(5), and B(1); respectively. Presumably these protons, which would be observed as 1:1:1:1 quartets, are partially thermally decoupled[16] and merge with the base line at 25 °C. Only at the low temperature where the decoupling is almost complete are they seen as two broad resonances. The spectral data are listed in Table I.

If the preparation is carried out at −78 °C and the reaction mixture is maintained at that temperature for subsequent workup and spectral measurements, different products are observed when the two reagents $[(dppe)NiBr_2]$ and $[(dppe)NiCl_2]$ are used. When the bromo reagent is used, the same product, *closo*-$[(dppe)NiC_2B_4H_6]$, is observed as is the case when the reaction is carried out at −35 °C and warmed to room temperature. ^{11}B and ^1H NMR data indicate the presence of only this species, which is ultimately isolated as dark red needles that melt at 81 °C and exhibit an IR spectrum identical with that reported by Grimes et al.[6] Attempts to solve the crystal structure of the species were unsuccessful due to decomposition; however, we can report some preliminary data. Lattice parameters determined from a least-squares refinement of the angular setting for 15 reflections are a = 15.33 Å, b = 15.35 Å, c = 13.57 Å, β = 106.6°, and V = 3060 Å^3. Systematic extinctions in $0k0$ for $k = 2n + 1$ and $h0l$ for $h + l = 2n + 1$ uniquely determined the space group to be $P2_1/n$. Final structure determination was not possible due to decomposition in the X-ray beam. A possible solution would be a low-temperature structure determination.

The reaction between $[(dppe)NiCl_2]$ and $K[C_2B_4H_7]$ at −78 °C results in a different product mixture. The ^1H NMR spectrum is complicated due to the presence of residual solvent not removed at the low temperatures. The product mixture exhibits resonances that can be assigned neither to *closo*-$[(dppe)NiC_2B_4H_6]$ nor to starting materials. A multiplet at 2.16 ppm is assigned to the methylene protons of the ligand, but it falls at neither the position expected for *closo*-$[(dppe)NiC_2B_4H_6]$ nor that for free dppe. The latter is seen in the reaction mixture at 1.73 ppm. Resonances at 2.79 and 3.64 ppm, which are in area ratio of 2:1 respectively, appear at frequencies similar to those reported[17] for basal B–H in $[C_2B_4H_7]^-$ and the equatorial B–H protons in *closo*-$[(dppe)NiC_2B_4H_6]$. The areas ratios, as seen in Figure 2, are the reciprocal of those observed for $[C_2B_4H_7]^-$ and for *closo*-$[(dppe)NiC_2B_4H_6]$. We believe that these resonances arise from hydrogens on basal borons in an intermediate species *nido*-

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(14) Muetterties, E. L.; Allegranti, C. W. *J. Am. Chem. Soc.* **1970**, *92*, 4144. Lippard, S. J.; Mayerle, J. J. *Inorg. Chem.* **1972**, *11*, 753. Fife, D. J.; Moore, W. M.; Morse, K. W. *Inorg. Chem.* **1984**, *23*, 1684.

(15) Miller, V. R.; Grimes, R. N. *Inorg. Chem.* **1977**, *16*, 15.

(16) Bacon, J.; Gillespie, R. J.; Quail, J. W. *Can. J. Chem.* **1963**, *41*, 3063. Beall, H.; Bushweller, C. H. *Chem. Rev.* **1973**, *73*, 465.

(17) Onak, T. P.; Lockman, B.; Haran, G. *J. Chem. Soc., Dalton Trans.* **1975**, 2115.

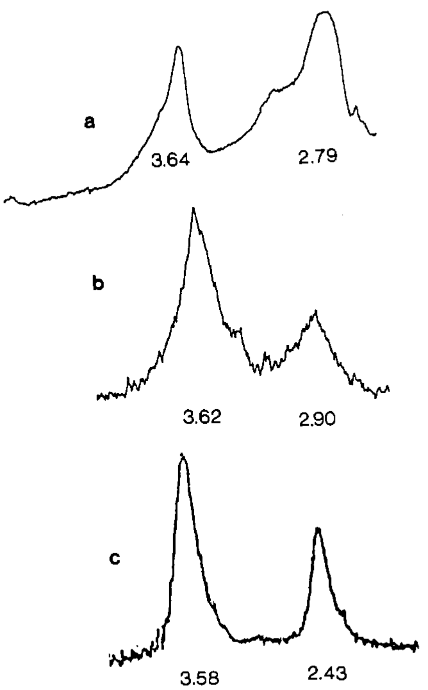


Figure 2. 300.1-MHz ^1H NMR spectra in the basal B–H region of (a) (dppe)Ni(Cl)$C_2B_4H_7$, (b) (dppe)$NiC_2B_4H_6$, and (c) K[$C_2B_4H_7$] in CD_2Cl_2 Chemical shifts are given in δ.

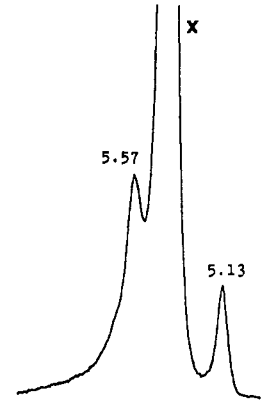
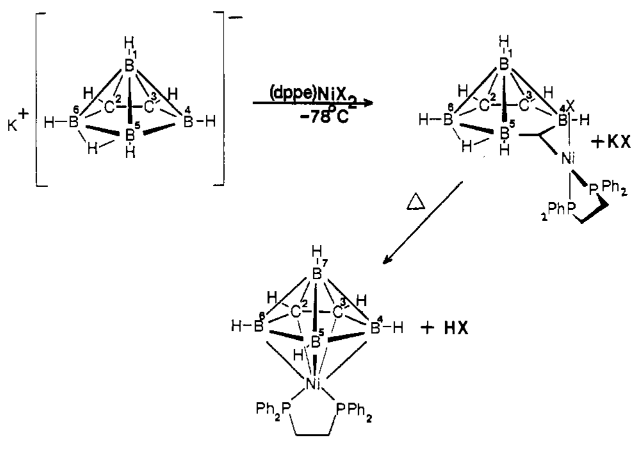


Figure 3. 300.1-MHz ^1H NMR spectrum at −78 °C in the CH cage region of the reaction mixture for the preparation of (dppe)Ni(Cl)$C_2B_4H_7$ (CD_2Cl_2 solvent), X = CH_2Cl_2.

[(dppe)Ni(Cl)$C_2B_4H_7$] and we assign the pair overlapping at 2.79 ppm to H(4) and H(5) and that at 3.64 ppm to H(6). The resonance at 5.57 ppm is unique to the reaction mixture. Figure 3 shows this resonance as a shoulder on the CH_2Cl_2 resonance. The spectra also exhibit a resonance at 5.13 ppm, which we assign to the equivalent C–H protons on the carborane cage of *closo*-[(dppe)$NiC_2B_4H_6$]. If the resonance at 5.57 ppm arises from a cage C–H hydrogen from the nido species, then there is one resonance missing. A nido metallo derivative of $C_2B_4H_6$ should show resonances arising from the two inequivalent C–H groups. Spectra of 4,5-(μ-metallo)-2,3-dicarbahexaboranes(8)[4,18] show two resonances in this region. Presumably the second resonance is obscured by the intense CH_2Cl_2 peak. As the sample is warmed to −35 °C, the resonance at 5.13 increases in intensity irreversibly while the resonance at 5.57 ppm is lost. The high-field region of the spectrum is also informative. *closo*-[(dppe)$NiC_2B_4H_6$] possesses no bridging hydrogens so resonances upfield of 1.14 ppm are not observed. The spectrum of the reaction mixture shows a broad resonance at −1.25 ppm, which we tentatively assign to the unique bridge hydrogen of *nido*-[(dppe)Ni(Cl)$C_2B_4H_7$]. A resonance observed at 0.05 ppm is common to all spectra of these samples and is presumed to be an impurity, perhaps arising from silicone grease. A sharp resonance arising from the apical hydrogen of a nido species would not be expected at low temperatures since they have longer relaxation times[19] and are thus not expected to be thermally decoupled. In the spectrum of the low-temperature reaction mixture, some broad weak peaks are observed, which may comprise part of a weak 1:1:1:1 quartet due to the apical hydrogen. Chemical shifts assigned to the ^1H NMR spectrum of the intermediate *nido*-[(dppe)Ni(Cl)$C_2B_4H_7$] are given in Table I.

Scheme I



These results indicate that although the final product of the reaction between (dppe)NiX_2 and K[$C_2B_4H_7$] is *closo*-[(dppe)$NiC_2B_4H_6$], in the case where X = Cl and the reaction is carried out at −78 °C, the nido species [(dppe)Ni(Cl)$C_2B_4H_7$] is observed as an intermediate. We suggest that the reaction between (dppe)NiX_2 and K_2[$C_2B_4H_7$] proceeds according to Scheme I.

The intermediate nido species is initially formed by insertion of the (dppe)NiX^+ moiety into the vacant bridging site of $C_2B_4H_7^-$, and KX is eliminated. In the case where X = Br, subsequent elimination of HBr from the nido species is very facile, even at low temperatures, and thus only the closo product is observed. Our results indicate that elimination of HCl from *nido*-[4,5-(μ-(dppe) Ni(Cl))$C_2B_4H_7$] proceeds less easily, and thus at −78 °C, the product mixture from the reaction between [(dppe)$NiCl_2$] and K[$C_2B_4H_7$] contains both *nido*-[4,5-(μ-(dppe)Ni(Cl))$C_2B_4H_7$] and *closo*-[(dppe)$NiC_2B_4H_6$]. As the reaction mixture is warmed, HCl is eliminated and the closo product is formed from the intermediate nido species. The insertion of (dppe)NiX^+ into the basal B–B bond of $C_2B_4H_7^-$ may be considered in terms of (dppe)NiX^+ serving the role of a proton, thus not changing the polyhedral skeletal electron count in this 16-electron nido cluster. On the other hand, it is perhaps more informative to regard the Ni atom as a seventh vertex, supplying 2 electrons to afford an 18-electron cluster. Loss of HX, i.e. 2 electrons, and movement of the Ni atom to an axial vertex completes the transformation to the 16-electron closo cluster with seven vertices. This mechanism for the formation of closed polyhedra from the insertion of ligated metal moieties into *nido*-borane or -carborane cages is probably a general one, and identification of intermediate nido species in other such processes should be possible. We are currently pursuing such investigations.

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[18] Thompson, M. L.; Grimes, R. N. *Inorg. Chem.* **1972**, *11*, 1925. Tabereaux, A.; Grimes, R. N. *Inorg. Chem.* **1973**, *12*, 792.

[19] Weiss, R.; Grimes, R. N. *J. Am. Chem. Soc.* **1978**, *100*, 1401.