(4) Surface coverage by the Prussian blue can be as high as 2×10^{-7} mol/cm^2 and will tenaciously adhere for several thousand oxidation–reduction cycles over the entire redox-active potential range from 0 to +1.2 V in neutral aqueous medium.

(5) Experimental evidence suggests that it is the soluble form of Prussian blue, $KFeFe(CN)_6$, that adheres to the electrode, presumably through cyanide bridges to the iron sites on the plasma polymer (or deposit) surface modified electrode.

(6) Further evidence was presented to show that Prussian blue may be reduced to form Everitt's salt, $M_2Fe^{2+}Fe^{II}(CN)_6$, and partially oxidized to Berlin green, $M_{1/2}Fe^{3+}(Fe^{III}(CN)_6)_{1/2}(Fe^{II}(CN)_6)_{1/2}$ ($M = K^+, Na^+$).

(7) The kinetics of these oxidation–reduction processes at the electrode surface are controlled by diffusion of the electrolyte cation in and out of the Prussian blue lattice.

(8) Both K^+ and Na^+ migrate in and out of the film and produce well-defined cyclic voltammograms whose E_{av} values are alkali metal cation dependent. Cyclic voltammograms obtained in mixed electrolytic solutions establish the following order of cation selectivity in aqueous medium: $K^+ > Na^+ >> Li^+$.

The method of surface preparation and several key features (e.g., points 3, 5, 7, and 8) of the Prussian blue adherent surface modified graphite electrode reported here are different from those in recent reports in the literature where polymeric Prussian blue is deposited on a electrode by chemical precipitation[12] or electroplating.[14] Itaya and co-workers present evidence to suggest that in their case the insoluble form of Prussian blue is attached to the electrode surface.[14] The permeability of the film to both Na^+ and K^+ ions is in contrast to previous workers who have investigated the redox behavior of Prussian blue films deposited on other substrates by different means and who report no activity in the presence of Na^+.[12,14]

Acknowledgment. We gratefully acknowledge David F. Natschke, who obtained the atomic adsorption spectra. This work was made possible by NSF Grant No. CPE-8006805.

Registry No. $Fe(CO)_5$, 13463-40-6; $K_3Fe(CN)_6$, 13746-66-2; $KFe^{3+}(Fe(CN)_6)$, 25869-98-1; $Na_3Fe(CN)_6$, 14217-21-1; $K_2Fe^{2+}(Fe(CN)_6)$, 15362-86-4; $K_{1/2}Fe^{3+}(Fe^{III}(CN)_6)_{1/2}(Fe^{II}(CN)_6)_{1/2}$, 87371-33-3; K, 7440-09-7; Na, 7440-23-5; graphite, 7782-42-5; ethane, 74-84-0.

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Simultaneous Conversion of Ni–PR$_3$ and B–H to Ni–H and B–PR$_3$ Linkages by Thermal Rearrangement of d^8 *closo*-Bis(triarylphosphine)nickelacarboranes. Crystal and Molecular Structure of [*closo*-3-(μ-CO)-8-PPh$_3$-3,1,2-NiC$_2$B$_9$H$_{10}$]$_2$: A Dimeric Nickelacarborane Complex Containing a Metal–Metal Bond

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The reaction of L_2NiCl_2 ($L = PR_3$) species with *nido*-7,8-, *nido*-7,9-, or *nido*-2,9-$C_2B_9H_{11}^{2-}$ ions led to the formation of the corresponding icosahedral bis(phosphine)nickelacarboranes in high yield. Heating members of the *closo*-3,3-(triarylphosphine)$_2$-3,1,2-$NiC_2B_9H_{11}$ series at 80 °C in benzene solution led to the formation of the corresponding [*closo*-3,8-(triarylphosphine)$_2$-3-H-3,1,2-$NiC_2B_9H_{11}$] by interchange of phosphine and hydrido ligands. No intermediates were observed, and the reaction was specific for the bis(triarylphosphine)–3,1,2-NiC_2 icosahedral system among those investigated. The dimeric nickelacarborane carbonyl [*closo*-(3-(μ-CO)-8-PPh$_3$-3,1,2-$NiC_2B_9H_{11}$)$_2$] was prepared by a variety of routes such as the reaction of [*closo*-3,3-(PPh$_3$)$_2$-3,1,2-$NiC_2B_9H_{11}$] (**1a**) with CO in benzene at 80 °C. A variety of ligand substitution reactions were carried out with **1a**. The mechanism of the phosphine–hydride ligand interchange is discussed. The dimeric nickelacarborane complex was characterized by an X-ray diffraction study. Amber crystals were triclinic, space group $P\bar{1}$, with $a = 13.319$ (4) Å, $b = 10.039$ (3) Å, $c = 9.813$ (3) Å, $\alpha = 80.00$ (1)°, $\beta = 82.91$ (1)°, $\gamma = 110.32$ (1)°, and $Z = 1$. The structure was solved by conventional heavy-atom methods to a final discrepancy index of $R = 0.057$ for 2233 independent observed reflections. The complex contains a metal–metal bond (2.477 (2) Å) and two metal–bridging carbon monoxide groups.

We have previously reported the formation of the *closo*-hydridonickelacarborane complex **1b** through an unusually facile thermolysis of the *closo*-bis(triphenylphosphine)nickelacarborane complex **1a**.[1] The reaction involved the interchange of a nickel-bound phosphine with the hydrogen atom of an adjacent boron vertex of the dicarbollide ligand, thereby forming B–P and Ni–H bonds, respectively (Figure 1). This type of ligand-interchange reaction has also been demonstrated with (phosphine)rhodacarborane[2] and (phosphine)ruthenacarborane[3] complexes in these laboratories and with (phosphine)platinacarborane[4] complexes elsewhere. In an attempt to establish the possible mechanism and scope of these reactions, a series of *closo*-bis(phosphine)nickelacarboranes was prepared and characterized (Figure 2).

Results and Discussion

Reaction of the respective *nido*-7,8-, *nido*-7,9-, or *nido*-2,9-$C_2B_9H_{11}^{2-}$ ions[5] with the appropriate bis(phosphine)nickel dihalide in dichloromethane (Tl_2 salt) or tetrahydrofuran (Na_2 salt) afforded the bis(phosphine)nickelacarborane complexes **1**–**6**, **9**, and **10** in high yield. Of the bis(phosphine)nickela-

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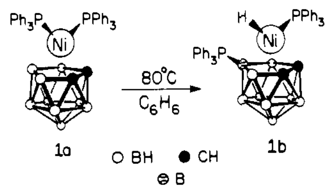

Figure 1. Ligand migration reaction.

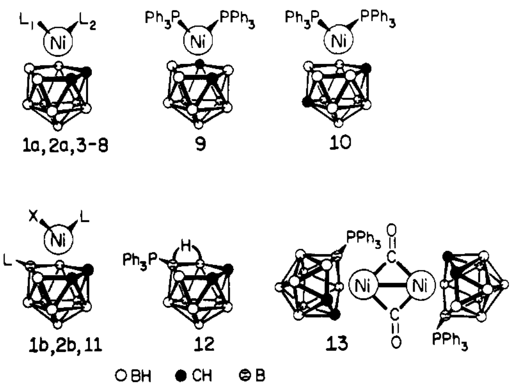

Figure 2. Numbering scheme for the nickelacarborane complexes prepared: **1a**, $L_1 = L_2 = PPh_3$; **2a**, $L_1 = L_2 = P(p\text{-tol})_3$; **3**, $L_1 = L_2 = PEt_3$; **4**, $L_1 = L_2 = PPh_2Me$; **5**, $L_1 = L_2 = PPhMe_2$; **6**, $L_1 = L_2 = PPh_2(CH_2)_3PPh_2$; **7**, $L_1 = PPh_3$, $L_2 = CO$; **8**, $L_1 = PPh_3$, $L_2 = C_5H_5N$; **1b**, $L = PPh_3$, $X = H$; **2b**, $L = P(p\text{-tol})_3$, $X = H$; **11**, $L = PPh_3$, $X = Cl$.

carborane complexes prepared, only the bis(tricyclohexylphosphine)nickelacarborane complex was unstable, yielding $HPCy_3^+[\textit{commo}\text{-}3,1,2\text{-}Ni(C_2B_9H_{11})_2]^-$[6] (Cy = cyclohexyl, C_6H_{11}) and nickel metal via a disproportionation reaction.

Ligand Dissociation and Substitution Reactions with Bis(triarylphosphine)nickelacarboranes. It was observed in $^{31}P\{^1H\}$ NMR experiments performed at −23 °C that dichloromethane solutions of the bis(triarylphosphine)nickelacarboranes **1a**, **2a**, **9**, and **10** exhibited not only their characteristic resonance(s) but also those of free triarylphosphine. With **1a** and **2a**, two additional resonances were observed downfield from the parent complex as well, and at temperatures higher than 30 °C, these downfield resonances broadened as the resonance due to free PPh_3 disappeared into the base line. Addition of a fractional molar equivalent of the respective triarylphosphine ligand resulted in the immediate disappearance of the two downfield resonances, which presumably correspond to mono(phosphine)nickelacarborane complexes. The remaining nickelacarborane complexes **3–8** did not exhibit a similar ligand dissociation process.

Ligand substitution reactions utilizing [*closo*-3,3-$(PPh_3)_2$-3,1,2-$NiC_2B_9H_{11}$] (**1a**) resulted in the preparation of the monosubstituted complexes [*closo*-3-CO-3-PPh_3-3,1,2-$NiC_2B_9H_{11}$] (**7**) ($\nu(CO) = 2050\ cm^{-1}$) and [*closo*-3-C_5H_5N-3-PPh_3-3,1,2-$NiC_2B_9H_{11}$] (**8**) ($\nu(C_5H_5N) = 1610\ cm^{-1}$) by reacting dichloromethane solutions of **1a** with carbon monoxide or pyridine, respectively. Mixed triarylphosphine complexes could be generated in situ by the addition of 2.2 molar equiv of $P(p\text{-tol})_3$ to dichloromethane solutions of **1a**. The resonances observed suggested the presence of $[(P(p\text{-tol})_3)(PPh_3)NiC_2B_9H_{11}]$, $[(PPh_3)_2NiC_2B_9H_{11}]$, and $[(P(p\text{-tol})_3)_2NiC_2B_9H_{11}]$ in an equilibrium mixture of approximately 1:1:1 (along with free PPh_3 and $P(p\text{-tol})_3$). The equilibria could be shifted in either direction by the addition of an excess of the respective phosphine ligand. Attempts to isolate the mixed tertiary phosphine complex by either column chromatography or fractional crystallizations were unsuccessful. Strongly basic ligands such as triethylphosphine quantitatively displaced the triphenylphosphine ligands from the nickel vertex of **1a**.

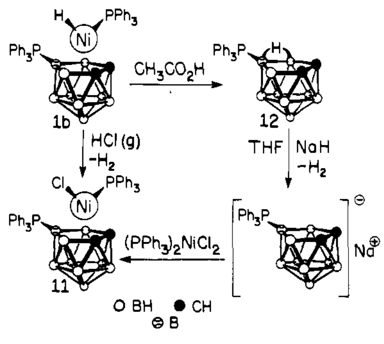

Figure 3. Derivative chemistry of **1b**.

Thermal Rearrangement of Bis(triarylphosphine)nickelacarboranes. The complexes **1–10** were heated in benzene at the reflux temperature for up to 3 days to determine their ability to undergo the ligand-interchange reaction (Figure 1). The surprising result was that only those icosahedral nickelacarboranes that had the 3,1,2-NiC_2 configuration and two triarylphosphine ligands at the formal Ni(+2) vertex were subject to the ligand-interchange reaction under the conditions employed here.

In another set of experiments the progress of the phosphine–hydride migration reaction was monitored by $^{31}P\{^1H\}$ FTNMR at 80 °C in benzene solutions of **1a**. The resonances assigned to the product were observed to grow in smoothly at the expense of the resonance assigned to the starting material. Other resonances that might be associated with the buildup of an intermediate species were not observed. The final spectrum showed two distinctly different resonances that could be easily distinguished as Ni–P (sharp singlet) and B–P (broad quartet) linkages, respectively. The solubility of **1a** in aromatic solvents was limited and precluded the possibility of performing meaningful kinetic experiments.

Reactivity of the Nickel–Hydride Complex 1b. The nickel–hydrogen bond in complex **1b** reacted, as expected, with chlorinating agents.[7] Dichloromethane solutions of **1b** reacted immediately with dry hydrogen chloride to give [*closo*-3,8-$(PPh_3)_2$-3-Cl-3,1,2-$NiC_2B_9H_{11}$] (**11**). Thermolysis of **1b** in chlorinated solvents such as dichloromethane or chloroform also gave **11**. The $^{11}B\{^1H\}$ NMR spectrum of **11** clearly showed the B–P coupling (127 Hz); unfortunately, the positional assignment of the phosphorus-substituted boron atom could not be obtained from this spectrum and the structure of **11** was proven by syntheses described below.

Degradation of the nickel–hydride complex, **1b**, in hot glacial acetic acid gave PPh_3, $Ni(OAc)_2$, and the phosphine-substituted carborane [*nido*-10-PPh_3-7,8-$C_2B_9H_{11}$] (**12**) in high yield. The B–P coupling (J = 125 Hz) was observed in the $^{11}B\{^1H\}$ NMR spectrum, and the ratio of the resonances suggested that the formation of the B–P bond had occurred on a plane of molecular symmetry. Similar ligand-substituted carboranes have been obtained by the oxidative substitution of nitrogen, oxygen, and phosphorus donor ligands to [*nido*-7,8-$C_2B_9H_{12}]^-$ carborane ions in the presence of $FeCl_3$.[8] It should be noted that the overall transformation of the [*nido*-7,8-$C_2B_9H_{11}]^{2-}$ ion to **12** occurs in high yield and is regiospecific, in contrast to the oxidative substitution reaction with $FeCl_3$, which produces mixtures of ligand-substituted carborane isomers. The neutral ligand-substituted carborane reacted quickly with strong bases such as sodium hydride to liberate

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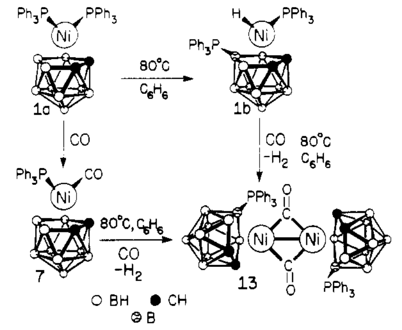

Figure 4. Derivative chemistry of **1a**.

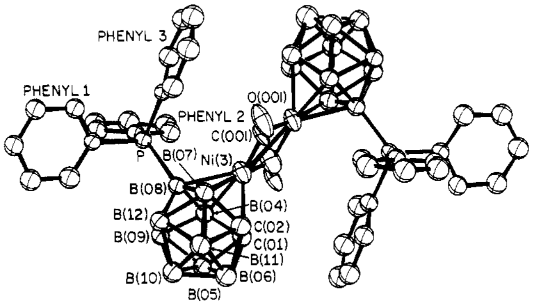

Figure 5. Structure of $[closo\text{-}3\text{-}(\mu\text{-CO})\text{-}8\text{-PPh}_3\text{-}3,1,2\text{-NiC}_2B_9H_{10}]_2$. Thermal ellipsoids are at 50% probability. Hydrogen atoms have been omitted for clarity.

hydrogen and form the $[nido\text{-}10\text{-PPh}_3\text{-}7,8\text{-C}_2B_9H_{10}]^-$ ion. The latter ion reacted with $(PPh_3)_2NiCl_2$, affording **11** in high yield (Figure 3).

Complex **1b** reacted with carbon monoxide at 80 °C to produce H_2 and a compound formulated as $[Ni(CO)(PPh_3)C_2B_9H_{10})_2]$ (**13**) (ν(CO) = 1850 cm^{-1}). Alternatively, **13** could also be prepared by heating benzene solutions of **1a**, or **7**, in the presence of carbon monoxide (Figure 4). Since the B–P coupling (120 Hz) observed in the $^{11}B\{^1H\}$ NMR spectrum was uninformative with respect to the assignment of the site of PPh_3 substitution, an X-ray crystallographic investigation of the dimeric nickelacarborane complex **13** was performed.

The molecular structure of $[closo\text{-}3\text{-}(\mu\text{-CO})\text{-}8\text{-PPh}_3\text{-}3,1,2\text{-NiC}_2B_9H_{10}]_2$ (**13**) is shown in Figure 5, from which the boron atom attached to the triphenylphosphine ligand is identified as the unique boron atom, B(08), in the bonding face of the carborane cage. The metal–metal bond in **13** is most reasonably interpreted as a single bond on the basis of its distance and the effective atomic number of 18 for the metal center. The nickel–nickel bond is also supported by two bridging carbon monoxide molecules related by a crystallographic center of symmetry. The formal nickel(I) vertex is a d^9 metal center, and therefore asymmetric nickel–carborane bonding was expected as observed with other electron-rich metallacarborane complexes.[9] However, the Ni atom is symmetrically bound to the bonding face of the carborane ligand. On the basis of calculations by Mingos,[10] icosahedral metallacarborane complexes containing metal centers that are considered to be electron rich should have distorted polyhedra. In addition, a variety of crystallographic investigations on metallacarboranes with electron-rich metal vertices clearly show deformations of the carborane cage.[11] This seeming contradiction can be most easily rationalized by recognizing that the carbon monoxide molecules bonded to the two nickel atoms are available as excess electron density sinks via back-bonding. This has been observed with another electron-rich metallacarborane complex which contained carbon monoxide as a ligand.[12]

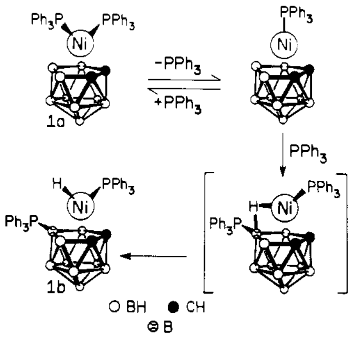

Figure 6. Possible mechanism for the migration reaction.

In a structural sense, the nickelacarborane dimer (**13**) is more closely related to the isoelectronic species $[(\eta\text{-}C_5H_4CH_3)(\mu\text{-CO})Ni]_2$ than to the unsubstituted analogue $[(\eta\text{-}C_5H_5)(\mu\text{-CO})Ni]_2$.[13] The CH_3Cp dimer and **13** each have a coplanar arrangement of the Ni atoms and the carbonyl groups. This planarity is missing in the unsubstituted Cp dimer, where the carbonyl oxygen atoms deviate greatly from the plane.[13] In **13**, the oxygen atom of each bridging carbonyl group is only 0.040 (7) Å from the Ni–C–Ni–C plane. The $[(CH_3Cp)NiCO]$ dimer was observed to have a Ni–Ni bonding distance of 2.390 (1) Å, in comparison to 2.477 (1) Å in the nickelacarborane dimer. This structure determination also confirms the position of PPh_3 substitution seen in **11** and **12**, above.

Mechanism of the Ligand-Interchange Reaction. In the absence of kinetic data any discussion of the mechanism of the phosphine–hydride interchange reaction lacks precision. However, the fact that this reaction is only observed with icosahedral nickelacarboranes of the $3,1,2\text{-NiC}_2$ configuration and only with triarylphosphine ligands attached to the metal vertex suggests that phosphine dissociation is an important initial equilibrium, which is followed by attack of the free phosphine upon the BH vertex (vertex 8). This scheme is presented in Figure 6. The reason for the peculiar susceptibility of this particular boron atom in the 3,1,2-isomer is presently obscure. Although the ligand-interchange reaction is shown as a concerted process in Figure 6, it is possible that a $Ph_3PB\text{–}H\text{–}BH$ bridge array could be present in the open face of a nido intermediate produced by nucleophilic attack of free PPh_3 at vertex 8 of $[hyper\text{-}closo\text{-}3\text{-}(PPh_3)\text{-}3,1,2\text{-NiC}_2B_9H_{11}]$[14,15] formed by the initial phosphine dissociation. Formation of this nido intermediate could be accompanied by elimination of formal Ni(0) which, in turn, could oxidatively add to the B–H–B bridge bond of the nido species. These schemes may also be applicable to the mechanisms of the ligand-interchange reactions observed with other metals.[2-4] Further work of a mechanistic sort is clearly warranted.

Experimental Section

Methods and Materials. The infrared spectra were measured as Nujol mulls on sodium chloride plates with a Perkin-Elmer 137 spectrophotometer. The ^1H (200.133 MHz) and $^{31}P\{^1H\}$ (81.02 MHz) nuclear magnetic resonance spectra were recorded on a Bruker WP200 Fourier transform instrument. The signal at δ 5.28, corresponding

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(15) Callahan, K. P.; Evans, W. J.; Lo, F. Y.; Strouse, C. E.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1975**, *97*, 296. Jung, C. W.; Baker, R. T.; Knobler, C. B.; Hawthorne, M. F. *Ibid.* **1980**, *102*, 5782.

to CHDCl$_2$ (Merck), was used as an internal reference for proton NMR spectra. The ^{31}P{^{1}H} NMR spectra were referenced externally to H$_3$PO$_4$; shifts were then corrected for the deuterated solvent used, and the chemical shift of PPh$_3$ was taken as −6.0 ppm. The ^{11}B and ^{11}B{^{1}H} (126.7 MHz) NMR spectra were measured on an instrument designed and built by F. A. L. Anet of this department with BF$_3$·OEt$_2$ as an external standard. Microanalyses were performed by Schwarzkopf Microanalytical Laboratories (Woodside, NY).

Reactions were carried out under an argon (Liquid Carbonic) atmosphere with use of standard techniques for handling air-sensitive materials, and all solvents (Mallinckrodt) were dried, deoxygenated, and distilled from appropriate drying agents[16] before use.

Literature methods were used to prepare [*closo*-7,8-(TlC$_2$B$_9$H$_{11}$)Tl],[17] (CH$_3$)$_3$NH$^+$[*nido*-7,9-C$_2$B$_9$H$_{12}$]$^-$, and (CH$_3$)$_3$NH$^+$[*nido*-2,9-C$_2$B$_9$H$_{12}$]$^-$.[5] (PPh$_3$)$_2$NiCl$_2$ and (P(*p*-tol)$_3$)$_2$NiCl$_2$ were prepared by boiling NiCl$_2$:6H$_2$O and a fourfold excess of the respective phosphine ligand in *n*-butanol for 4 h. The black crystalline product was separated from the mother liquor by filtration while the solution was warm, washed generously with ethanol, heptane, and diethyl ether, and dried under vacuum overnight. (PEt$_3$)$_2$NiCl$_2$, (PPh$_2$Me)$_2$NiCl$_2$, and (PPhMe$_2$)$_2$NiCl$_2$ and (DPPP)NiCl$_2$ (DPPP = PPh$_2$(CH$_2$)$_3$PPh$_2$) were prepared by reacting a warm ethanolic solution of NiCl$_2$·6H$_2$O with the appropriate phosphine ligand under an inert atmosphere. The red crystalline products were separated by Schlenk filtration, washed liberally with heptane and diethyl ether, and dried under vacuum overnight.

Reagents such as NiCl$_2$·6H$_2$O and glacial acetic acid (Mallinckrodt), PPh$_3$, PEt$_3$, PPh$_2$Me, PPhMe$_2$, and P(*p*-tol)$_3$ (Aldrich), PCy$_3$ and 1,3-bis(diphenylphosphino)propane (Strem), and NaH (Alfa) were all commercially available and used without further purification.

Carbon monoxide (Liquid Carbonic) and hydrogen chloride (Matheson) were purified by passing the reagent gases through H$_2$SO$_4$ and then over KOH/CaSO$_4$. Pyridine (Aldrich) was distilled from KOH.

General Procedure for the Precipitation of [*closo*-3,3-(phosphine)$_2$-3,1,2-NiC$_2$B$_9$H$_{11}$] Complexes. Stirring the appropriate bis(phosphine)nickel dichloride complex (2.00 mmol) and thallous dicarbollide (1.08 gm, 2.00 mmol) in dichloromethane (200 mL) gave dark green solutions while the white TlCl precipitated from the reaction mixture. Schlenk filtration and dilution with heptane afforded crystalline product. Reactions were usually complete within 2 h. Two recrystallizations from dichloromethane/heptane gave analytically pure complexes as large, nonsolvated, crystalline blocks.

[*closo*-3,3-(PPh$_3$)$_2$-3,1,2-NiC$_2$B$_9$H$_{11}$] (1a). With use of (PPh$_3$)$_2$NiCl$_2$ (1.31 g, 2.00 mmol) and the procedure described above, the product was isolated as olive green plates (1.13 g, 1.58 mmol, 79%): ^{1}H NMR (CD$_2$Cl$_2$) δ 7.2–7.5 (envelope); ^{11}B{^{1}H} NMR (CD$_2$Cl$_2$) −19.44, −12.68, −9.11 ppm (2:2:5); ^{31}P{^{1}H} NMR (20% CD$_2$Cl$_2$/CH$_2$Cl$_2$) 30.6 (s) ppm Anal. Calcd for C$_{38}$H$_{41}$B$_9$P$_2$Ni: C, 63.77; H, 5.77; B, 13.59; P, 8.65; Ni, 8.20. Found: C, 63.64; H, 6.28; B, 12.79; P, 7.95; Ni, 8.92.

[*closo*-3,3-(P(*p*-tol)$_3$)$_2$-3,1,2-NiC$_2$B$_9$H$_{11}$] (2a). With use of (P(*p*-tol)$_3$)$_2$NiCl$_2$ (1.48 g, 2.00 mmol) and the procedure described above, the product was isolated as an olive green crystalline solid (1.28 g, 1.60 mmol, 80%): ^{1}H NMR (CD$_2$Cl$_2$) δ 6.9–7.4 (envelope, 24 H), 2.29 (s, 18 H); ^{11}B{^{1}H} NMR (CD$_2$Cl$_2$) −19.84, −7.91 ppm (2:7); ^{31}P{^{1}H} NMR (20% CD$_2$Cl$_2$/CH$_2$Cl$_2$) 28.7 (s) ppm. Anal. Calcd for C$_{44}$H$_{53}$B$_9$P$_2$Ni: C, 66.06; H, 6.68; B, 12.17; P, 7.74; Ni, 7.34. Found: C, 66.30; H, 6.75; B, 12.33; P, 7.60; Ni, 7.59.

[*closo*-3,3-(PEt$_3$)$_2$-3,1,2-NiC$_2$B$_9$H$_{11}$] (3). With use of (PEt$_3$)$_2$NiCl$_2$ (0.73 g, 2.00 mmol) and the procedure described above, the product was isolated as bright green crystals (0.80 g, 1.86 mmol, 93%): ^{1}H NMR (CD$_2$Cl$_2$) δ 1.68 (m, 12 H), 1.18 (m, 18 H), 1.88 (br s, 2 H); ^{11}B{^{1}H} NMR (CD$_2$Cl$_2$) −19.84, −13.08, −9.11, −4.73 ppm (2:2:4:1); ^{31}P{^{1}H} NMR (20% CD$_2$Cl$_2$/CH$_2$Cl$_2$) 2.8 (s) ppm. Anal. Calcd for C$_{14}$H$_{41}$B$_9$P$_2$Ni: C, 39.34; H, 9.67; B, 22.76; P, 14.49; Ni, 13.74. Found: C, 39.03; H, 9.75; B, 22.48; P, 14.78; Ni, 13.52.

[*closo*-3,3-(PPh$_2$Me)$_2$-3,1,2-NiC$_2$B$_9$H$_{11}$] (4). With use of (PPh$_2$Me)$_2$NiCl$_2$ (1.06 g, 2.00 mmol) and the procedure described above, the product was isolated as dark green crystals (1.06 g, 1.80 mmol, 90%): ^{1}H NMR (CD$_2$Cl$_2$) δ 7.22–7.5 (envelope, 20 H), 1.70 (t, 6 H, J = 4.4 Hz); ^{11}B{^{1}H} NMR (CD$_2$Cl$_2$) −19.04, −12.29, −8.71, −6.32, −2.75 ppm (2:2:3:1:1); ^{31}P{^{1}H} NMR (20% CD$_2$Cl$_2$/CH$_2$Cl$_2$) 14.6 (s) ppm. Anal. Calcd for C$_{28}$H$_{37}$B$_9$P$_2$Ni: C, 56.84; H, 6.30; B, 16.46; P, 10.47; Ni, 9.92. Found: C, 56.56; H, 6.38; B, 16.10; P, 10.53; Ni, 10.10.

[*closo*-3,3-(PPhMe$_2$)$_2$-3,1,2-NiC$_2$B$_9$H$_{11}$] (5). With use of (PPhMe$_2$)$_2$NiCl$_2$ (0.81 g, 2.00 mmol) and the procedure described above, the product was isolated as dark green crystals (0.86 g, 1.84 mmol, 92%): ^{1}H NMR (CD$_2$Cl$_2$) δ 7.43–7.63 (envelope, 10 H), 1.76 (br s, 2 H), 1.43 (t, 12 H, J = 4.9 Hz); ^{11}B{^{1}H} (CD$_2$Cl$_2$) −18.65, −11.89, −7.91, −2.75 ppm (2:2:4:1); ^{31}P{^{1}H} NMR (20% CD$_2$Cl$_2$/CH$_2$Cl$_2$) 17.1 (s) ppm. Anal. Calcd for C$_{18}$H$_{33}$B$_9$P$_2$Ni: C, 46.26; H, 7.12; B, 20.82; P, 13.25; Ni, 12.56. Found: C, 46.21; H, 7.07; B, 21.27; P, 12.92; Ni, 13.47.

[*closo*-3,3-(DPPP)-3,1,2-NiC$_2$B$_9$H$_{11}$] (6). With use of (DPPP)NiCl$_2$ (1.08 g, 2.00 mmol) and the procedure described above, the product was isolated as light green plates (1.01 g, 1.68 mmol, 84%): ^{1}H NMR (CD$_2$Cl$_2$) δ 7.32–7.7 (envelope, 20 H), 0.84–2.55 (envelope, 6 H), 1.74 (br s, 2 H); ^{31}P{^{1}H} NMR (20% CD$_2$Cl$_2$/CH$_2$Cl$_2$) 14.8 (s) ppm. (The complex is almost insoluble in most solvents and only slightly soluble in dichloromethane.) Anal. Calcd for C$_{29}$H$_{37}$B$_9$P$_2$Ni: C, 57.70; H, 6.18; B, 16.12; P, 10.26; Ni, 9.73. Found: C, 57.59; H, 6.28; B, 16.53; P, 10.33; Ni, 10.07.

[*closo*-2,2-(PPh$_3$)$_2$-2,1,7-(or 2,1,12)-NiC$_2$B$_9$H$_{11}$]. The addition of 2.5 equiv of NaH (0.12 g, 5.00 mmol) to a tetrahydrofuran solution (250 mL) of the appropriate (CH$_3$)$_3$NH$^+$[*nido*-7,9- (or 2,9)-C$_2$B$_9$H$_{12}$]$^-$ carborane salt (0.39 g, 2.00 mmol) resulted in the evolution of hydrogen gas. The solution was stirred while it was refluxed for 6 h and filtered under argon onto the (PPh$_3$)$_2$NiCl$_2$ complex (1.31 g, 2.00 mmol). The reaction mixture was then stirred overnight at room temperature. Schlenk filtration was used to remove NaCl, and dilution with heptane afforded the crystalline product. Three recrystallizations from dichloromethane/heptane gave analytically pure product.

[*closo*-2,2-(PPh$_3$)$_2$-2,1,7-NiC$_2$B$_9$H$_{11}$] (9). With use of (CH$_3$)$_3$NH$^+$[*nido*-7,9-C$_2$B$_9$H$_{12}$]$^-$ and the procedure described above, the product was isolated as red-orange crystals (0.93 g, 1.30 mmol, 65%): ^{1}H NMR (CD$_2$Cl$_2$) δ 7.03–7.72 (envelope, 30 H), 2.68 (br s, 2 H); ^{11}B{^{1}H} NMR (CD$_2$Cl$_2$) −19.84, −15.74, −10.70, −2.75 ppm (3:1:4:1); ^{31}P{^{1}H} NMR (20% CD$_2$Cl$_2$/CH$_2$Cl$_2$) 40.6 (d, J = 29 Hz), 25.7 (d) ppm. Anal. Calcd for C$_{38}$H$_{41}$B$_9$P$_2$Ni: C, 63.77; H, 5.77; B, 13.59; P, 8.65; Ni, 8.20. Found: C, 63.18; H, 5.71; B, 14.30; P, 8.82; Ni, 8.34. **[*closo*-2,2-(PPh$_3$)$_2$-2,1,12-NiC$_2$B$_9$H$_{11}$] (10).** With use of (CH$_3$)$_3$NH$^+$[*nido*-2,9-C$_2$B$_9$H$_{12}$]$^-$ and the procedure described above, the product was isolated as dull green crystals (0.86 g, 1.20 mmol, 60%): ^{1}H NMR (CD$_2$Cl$_2$) δ 7.11–7.47 (envelope, 30 H), 2.34 (br s, 1 H), 2.27 (br s, 1 H); ^{11}B{^{1}H} NMR (CD$_2$Cl$_2$) −20.01, −14.85, −10.11, −8.12 ppm (4:2:2:1); ^{31}P{^{1}H} NMR (20% CD$_2$Cl$_2$/CH$_2$Cl$_2$) 32.8 (s) ppm. Anal. Calcd for C$_{38}$H$_{41}$B$_9$P$_2$Ni: C, 63.77; H, 5.77; B, 13.59; P, 8.65; Ni, 8.20. Found: C, 63.53; H, 6.05; B, 13.59; P, 8.78; Ni, 8.64.

General Procedure for the Preparation of [*closo*-3,8-(P(aryl)$_3$)$_2$-3-H-3,1,2-NiC$_2$B$_9$H$_{11}$] Complexes. A 300-mL Schlenk flask was charged with [*closo*-3,3-(P(aryl)$_3$)$_2$-3,1,2-NiC$_2$B$_9$H$_{11}$] (2.0 mmol) and a magnetic stirring bar. It was then fitted with a reflux condenser, vacuum evacuated, and then refilled with argon. Freshly distilled benzene (200 mL) was added via syringe. The migration reaction began when the solution was brought to the reflux temperature. The progress of the reaction was monitored by thin-layer chromatography using Kodak fluorescent thin-layer silica gel plates and benzene. The red product has a higher R_f value than the green starting material. Addition of heptane via syringe and volume reduction of the solution by vacuum evaporation afforded a red microcrystalline material. Further addition of heptane and volume reduction precipitated the product quantitatively. Three recrystallization from dichloromethane/heptane gave the analytically pure product.

[*closo*-3,8-(PPh$_3$)$_2$-3-H-3,1,2-NiC$_2$B$_9$H$_{11}$] (1b). Thermolysis of **1a** (1.43 g, 2.00 mmol), as described above, gave a red-orange crystalline product (0.84 g, 1.18 mmol, 59%): ^{1}H NMR (CD$_2$Cl$_2$) δ 7.30–7.84 (envelope, 30 H), −8.40 (dd, J_1 = 91.6 Hz, J_2 = 7.3 Hz); ^{11}B{^{1}H} NMR (CD$_2$Cl$_2$) −23, −15 ppm (7:2); ^{31}P{^{1}H} NMR (20% CD$_2$Cl$_2$/CH$_2$Cl$_2$) 24.4 (s), 2.7 (br g) ppm. Anal. Calcd for C$_{38}$H$_{41}$B$_9$P$_2$Ni: C, 63.77; H, 5.77; B, 13.59; P, 8.65; Ni, 8.20. Found: C, 63.61; H, 5.84; B, 13.92; P, 8.60; Ni, 8.13.

[*closo*-3,8-(P(*p*-tol)$_3$)$_2$-3-H-3,1,2-NiC$_2$B$_9$H$_{10}$] (2b). Thermolysis of **2a** (1.60 g, 2.00 mmol) gave an orange-red crystalline product (0.96 g, 1.22 mmol, 61%): ^{1}H NMR (CD$_2$Cl$_2$) δ 7.05–7.55 (envelope, 24

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(17) Spencer, J. L.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1972**, 1178.

Table I. Crystallographic Data for the Nickelacarborane Dimer [*closo*-3-(μ-CO)-8-PPh_3-3,1,2-$NiC_2B_9H_{10}$]$_2$

cryst syst: triclinic, $P\bar{1}$, $Z = 1$
unit cell: $a = 13.319$ (4) Å
$b = 10.039$ (3) Å
$c = 9.813$ (3) Å
$\alpha = 80.00$ (1)°
$\beta = 82.91$ (1)°
$\gamma = 110.32$ (1)°
obsd density (298 K): 1.265 g cm^{-3}
data collected at 298 K
collection limit (2θ): 50° (Mo Kα)
agreement factors:[a] $R = 0.057$
$R_w = 0.061$
goodness of fit (GOF):[b] 1.60

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [b] $\mathrm{GOF} = [\Sigma w(|F_o| - |F_c|)^2/(N_{\mathrm{observns}} - N_{\mathrm{parameters}})]^{1/2}$.

Table II. Positional Parameters (Fractional Coordinates) and Isotropic Thermal Parameters for the Non-Hydrogen Atoms of the Nickel Dimer

atom	*x*	*y*	*z*	*B*, Å^2
C(01)	0.0281 (6)	0.1431 (8)	0.1793 (7)	3.25 (15)
C(02)	0.0570 (5)	0.2724 (7)	0.2571 (7)	2.99 (14)
B(04)	0.1213 (7)	0.0625 (9)	0.1811 (9)	2.81 (16)
B(05)	0.1167 (7)	0.1816 (10)	0.0281 (9)	3.59 (18)
B(06)	0.0732 (7)	0.3169 (10)	0.0752 (10)	3.90 (19)
B(07)	0.1767 (6)	0.2993 (8)	0.3182 (8)	2.47 (15)
B(08)	0.2251 (6)	0.1678 (8)	0.2632 (8)	2.22 (14)
B(09)	0.2429 (6)	0.2028 (8)	0.0774 (8)	2.60 (15)
B(10)	0.2134 (7)	0.3615 (9)	0.0135 (9)	3.02 (16)
B(11)	0.1689 (7)	0.4174 (9)	0.1642 (9)	3.29 (17)
B(12)	0.2778 (6)	0.3515 (8)	0.1623 (8)	2.41 (15)
C(1)	0.3826 (5)	0.2079 (7)	0.4737 (7)	2.28 (12)
C(2)	0.4940 (6)	0.2710 (8)	0.4685 (7)	3.33 (15)
C(3)	0.5304 (6)	0.3486 (8)	0.5723 (8)	4.32 (17)
C(4)	0.4587 (7)	0.3619 (9)	0.6715 (9)	4.56 (18)
C(5)	0.3481 (6)	0.3023 (8)	0.6784 (8)	4.36 (17)
C(6)	0.3088 (6)	0.2219 (7)	0.5781 (8)	3.35 (15)
C(7)	0.2641 (5)	−0.0889 (7)	0.4484 (7)	2.44 (13)
C(8)	0.2110 (6)	−0.1975 (8)	0.3822 (8)	3.67 (16)
C(9)	0.1655 (6)	−0.3453 (8)	0.4566 (8)	4.12 (17)
C(10)	0.1732 (6)	−0.3824 (8)	0.5940 (8)	4.15 (17)
C(11)	0.2243 (6)	−0.2786 (8)	0.6616 (8)	4.03 (16)
C(12)	0.2702 (6)	−0.1298 (8)	0.5906 (8)	3.47 (15)
C(13)	0.4449 (5)	0.1085 (7)	0.2281 (7)	2.25 (12)
C(14)	0.4795 (5)	−0.0063 (7)	0.2388 (7)	2.77 (14)
C(15)	0.5723 (6)	0.0039 (7)	0.1487 (7)	3.17 (14)
C(16)	0.6300 (6)	0.1286 (8)	0.0468 (7)	3.34 (15)
C(17)	0.5958 (6)	0.2444 (8)	0.0324 (8)	3.84 (16)
C(18)	0.5037 (6)	0.2355 (7)	0.1229 (7)	3.22 (15)
C(001)	0.0160 (6)	0.1229 (8)	0.5641 (8)	*a*
O(001)	0.0347 (5)	0.2247 (6)	0.6099 (6)	*a*
Ni(3)	0.0596 (1)	0.0797 (1)	0.3870 (1)	*a*
P(08)	0.3273 (1)	0.1004 (2)	0.3497 (2)	*a*

[a] Anisotropic thermal parameters are given for these atoms in the supplementary material.

Table III. Selected Distances (Å) in [*closo*-3-(μ-CO)-8-PPh_3-3,1,2-$NiC_2B_9H_{10}$]$_2$

atom 1	atom 2	dist	atom 1	atom 2	dist
C(02)	Ni(3)	2.138 (7)	B(12)	B(8)	1.780 (10)
C(01)	Ni(3)	2.163 (7)	B(12)	B(9)	1.784 (11)
B(8)	Ni(3)	2.175 (8)	B(4)	C(01)	1.701 (10)
B(7)	Ni(3)	2.141 (8)	B(4)	B(5)	1.771 (12)
B(4)	Ni(3)	2.144 (8)	B(4)	B(9)	1.776 (11)
C(0001)	O(001)	1.149 (8)	B(4)	B(8)	1.799 (11)
Ni(3)	Ni(3)	2.477 (2)	B(5)	C(01)	1.672 (11)
C(001)	Ni(3)	1.870 (8)	B(5)	B(9)	1.758 (12)
C(001)	Ni(3)	1.932 (8)	B(5)	B(6)	1.759 (12)
			B(6)	C(01)	1.718 (11)
C(1)	P(08)	1.821 (6)	B(6)	C(02)	1.730 (11)
C(13)	P(08)	1.816 (6)	B(7)	C(02)	1.722 (10)
C(7)	P(08)	1.818 (7)	B(7)	B(8)	1.791 (10)
B(8)	P(08)	1.938 (8)	B(8)	B(9)	1.765 (11)
B(10)	B(6)	1.762 (12)	C(01)	C(02)	1.576 (9)
B(10)	B(5)	1.785 (12)	C(01)	H(01)	1.023
B(10)	B(12)	1.788 (11)	C(02)	H(02)	1.033
B(10)	B(11)	1.777 (11)	B(4)	H(04)	1.140
B(10)	B(9)	1.798 (11)	B(5)	H(05)	1.075
B(11)	C(02)	1.694 (10)	B(6)	H(06)	1.035
B(11)	B(6)	1.759 (12)	B(7)	H(07)	1.116
B(11)	B(12)	1.791 (11)	B(9)	H(09)	1.037
B(11)	B(7)	1.790 (11)	B(10)	H(010)	1.187
B(12)	B(7)	1.775 (11)	B(11)	H(011)	1.075
			B(12)	H(012)	1.089

H), 2.33 (s, 9 H), 2.31 (s, 9 H), −8.59 (dd, 1 H, J_1 = 91.6 Hz, J_2 = 7.32 Hz); $^{11}B\{^1H\}$ NMR (CD_2Cl_2) −23, −15 ppm (7:2); $^{31}P\{^1H\}$ NMR (20% CD_2Cl_2/CH_2Cl_2) 22.4 (s), 2.0 (br q) ppm. Anal. Calcd for $C_{44}H_{53}B_9P_2Ni$: C, 66.06; H, 6.68; B, 12.17; P, 7.74; Ni, 7.34. Found: C, 65.38; H, 6.71; B, 12.25; P, 7.29; Ni, 7.31.

General Procedure for Ligand-Exchange Reactions Using 1a. A 250-mL Schlenk flask was charged with **1a** (1.43 g, 2.00 mmol) and a magnetic stirring bar. The flask was fitted with a rubber septum, vacuum evacuated, and refilled with argon. Dichloromethane (200 mL) was introduced via syringe.

[*closo*-3-CO-3-PPh_3-3,1,2-$NiC_2B_9H_{11}$] (7). Carbon monoxide was introduced into the solution via a syringe needle through the side arm and vented through a needle in the septum cap. The bubbling of carbon monoxide was continued until the reaction was complete (monitored by thin-layer chromatography). Dilution with heptane and solvent removal by vacuum evaporation gave a lavender powder. Two recrystallizations from dichloromethane/heptane afforded the analytically pure red-violet crystalline product (0.84 g, 1.74 mmol, 87%): ^1H NMR (CD_2Cl_2) δ 7.31–7.70 (envelope, 15 H), 2.05 (br s, 2 H); $^{11}B\{^1H\}$ (CD_2Cl_2) −22.62, −13.48, −10.30, −6.32 ppm (3:2:2:2); $^{31}P\{^1H\}$ (20% CD_2Cl_2/CH_2Cl_2) 27.9 (s) ppm. Anal. Calcd for $C_{21}H_{26}B_9PNiO$: C, 52.40; H, 5.44; B, 20.21; P, 6.43; Ni, 12.20. found: C, 52.49; H, 5.37; B, 19.42; P, 6.28; Ni, 12.07.

[*closo*-3-C_5H_5N-3-PPh_3-3,1,2-$NiC_2B_9H_{11}$] (8). Pyridine (10.0 g, 126 mmol) was introduced via syringe, and the solution was stirred overnight. The product precipitates as a green powder upon addition of heptane and volume reduction by rotary evaporation. Two recrystallizations from dichloromethane/heptane gave the analytically pure forest green crystalline product (0.85 g, 1.60 mmol, 80%): ^1H NMR (CD_2Cl_2) δ 8.56 (d, 2 H, J = 4.9 Hz), 7.33–7.78 (envelope, 15 H), 6.9 (t, 3 H, J = 7.3 Hz); $^{11}B\{^1H\}$ NMR (CD_2Cl_2) −20.24, −13.08, −9.50 ppm (3:2:4); $^{31}P\{^1H\}$ NMR (20% CD_2Cl_2/CH_2Cl_2) 36.7 (s) ppm. Anal. Calcd for $C_{25}H_{21}B_9PNiN$: C, 56.38; H, 5.87; B, 18.27; P, 5.82; Ni, 11.03; N, 2.63. Found: C, 56.41; H, 5.92; B, 18.56; P, 5.39; Ni, 10.88; N, 2.90.

General Procedure for the Preparation of [*closo*-3,8-$(PPh_3)_2$-3-H-3,1,2-$NiC_2B_9H_{10}$] (1b) Derivatives. A 250-mL Schlenk flask was charged with complex **1b** (1.43 g, 2.00 mmol) and a magnetic stirring bar and fitted with a reflux condenser. The system was vacuum evacuated and refilled with argon. Freshly distilled benzene (150 mL) was added via syringe.

[*closo*-3-Cl-3,8-PPh_3-3,1,2-$NiC_2B_9H_{10}$] (11). Hydrogen chloride was introduced into the solution via syringe needle through the side arm of the flask. A rapid red to violet color change indicated an immediate reaction. Addition of heptane and removal of solvent by vacuum evaporation gave a purple powder. One recrystallization from dichloromethane/heptane give dark purple crystalline product (1.22 g, 1.62 mmol, 81%): ^1H NMR (CD_2Cl_2) δ 7.24–7.79 (envelope, 30 H), 3.38 (br s, 2 H); $^{11}B\{^1H\}$ NMR (CD_2Cl_2) −19.84, −10.70, −1.95 (d, J = 128 Hz) ppm; $^{31}P\{^1H\}$ NMR (20% CD_2Cl_2/CH_2Cl_2) 18.3 (s), 7.0 (br, q) ppm. Anal. Calcd for $C_{38}H_{40}B_9P_2NiCl$: C, 60.85; H, 5.38; B, 12.97; P, 8.26; Ni, 7.83; Cl, 4.73. Found: C, 62.03; H, 5.45; B, 13.03; P, 7.90; Ni, 7.96; Cl, 5.04.

[*nido*-10-PPh_3-7,8-$C_2B_9H_{11}$] (12). Glacial acetic acid (50 mL) was added via syringe, and the solution was brought to the reflux temperature. The reaction was complete after the red color of the starting material disappeared. Vacuum evaporation of the solution to dryness gave a tan microcrystalline precipitate. Two recrystallizations from dichloromethane/heptane gave a white crystalline product (0.54 g, 1.38 mmol, 69%): ^1H NMR (CD_2Cl_2) δ 6.94–7.62 (envelope, 15 H), 2.56 (br s, 2 H); $^{11}B\{^1H\}$ NMR (CD_2Cl_2) ppm −37.33, −33.35 (d, J = 136 Hz), −20.24, −15.47, −11.09 ppm (1:1:2:3:2); $^{31}P\{^1H\}$ NMR (20% CD_2Cl_2/CH_2Cl_2) 3.5 (br q) ppm. Anal. Calcd for $C_{20}H_{26}B_9P$:

Table IV. Selected Angles (deg) in [*closo*-3-(μ-CO)-8-PPh_3-3,1,2-$NiC_2B_9H_{10}$]$_2$

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
C(01)	B(4)	B(8)	105.61 (53)	C(001)	Ni(3)	C(001)	98.72 (31)
C(01)	B(4)	Ni(3)	67.34 (36)	C(001)	Ni(3)	Ni(3)	50.43 (25)
B(8)	B(4)	Ni(3)	66.26 (35)	C(001)	Ni(3)	C(02)	95.40 (30)
C(02)	B(7)	B(8)	104.98 (52)	C(001)	Ni(3)	B(7)	88.82 (30)
C(02)	B(7)	Ni(3)	66.17 (34)	C(001)	Ni(3)	B(4)	172.30 (32)
B(8)	B(7)	Ni(3)	66.47 (35)	C(001)	Ni(3)	C(01)	130.87 (30)
B(9)	B(8)	P(08)	117.70 (46)	C(001)	Ni(3)	B(8)	125.27 (30)
B(12)	B(8)	P(08)	116.63 (46)	C(001)	Ni(3)	Ni(3)	48.28 (24)
B(7)	B(8)	B(4)	105.34 (52)	C(02)	Ni(3)	B(7)	47.45 (27)
B(7)	B(8)	P(08)	123.91 (48)	C(02)	Ni(3)	B(4)	78.70 (28)
B(7)	B(8)	Ni(3)	64.51 (34)	C(02)	Ni(3)	C(01)	42.99 (24)
B(4)	B(8)	P(08)	125.36 (47)	C(02)	Ni(3)	B(8)	80.49 (26)
B(4)	B(8)	Ni(3)	64.50 (35)	C(02)	Ni(3)	Ni(3)	131.09 (19)
P(08)	B(8)	Ni(3)	114.83 (36)	B(7)	Ni(3)	B(4)	83.54 (30)
O(001)	C(001)	Ni(3)	142.04 (66)	B(7)	Ni(3)	C(01)	78.91 (28)
O(001)	C(001)	Ni(3)	136.60 (63)	B(7)	Ni(3)	B(8)	49.02 (28)
Ni(3)	C(001)	Ni(3)	81.28 (31)	B(7)	Ni(3)	Ni(3)	136.12 (22)
C(02)	C(01)	B(4)	111.83 (55)	B(4)	Ni(3)	C(01)	46.51 (28)
C(02)	C(01)	Ni(3)	67.63 (36)	B(4)	Ni(3)	B(8)	49.24 (29)
B(4)	C(01)	Ni(3)	66.15 (36)	B(4)	Ni(3)	Ni(3)	139.41 (25)
C(01)	C(02)	B(7)	112.03 (53)	C(01)	Ni(3)	B(8)	80.01 (27)
C(01)	C(02)	Ni(3)	69.38 (36)	C(01)	Ni(3)	Ni(3)	133.05 (21)
C(1)	P(08)	C(7)	106.68 (29)	B(8)	Ni(3)	Ni(3)	144.38 (22)
C(1)	P(08)	C(13)	105.75 (29)	B(7)	C(02)	Ni(3)	66.38 (34)
C(1)	P(08)	B(8)	111.02 (30)	C(001)	Ni(3)	B(8)	118.69 (30)
C(7)	P(08)	C(13)	104.96 (29)	C(001)	Ni(3)	C(01)	103.20 (32)
C(7)	P(08)	B(8)	112.40 (31)	C(001)	Ni(3)	B(4)	88.97 (31)
C(13)	P(08)	B(8)	115.39 (31)	C(001)	Ni(3)	B(7)	167.36 (30)
				C(001)	Ni(3)	C(02)	140.63 (31)

C, 60.85; H, 6.64; B, 24.67; P, 7.85. Found: C, 60.60; H, 6.92; B, 24.90; P, 7.93.

[*closo*-(3-(μ-CO)-8-PPh_3-3,1,2-$NiC_2B_9H_{10}$)$_2$] (13). Carbon monoxide was introduced via syringe needle through the side arm of the flask, and the solution was brought to a gentle reflux. The reaction was monitored by thin-layer chromatography and was complete in 6–8 h. The reaction mixture was rotary vacuum evaporated to dryness, and the precipitate was washed with heptane and dried under vacuum to give a red-copper powder (1.41 g, 1.46 mmol, 73%). Two recrystallizations from dichloromethane/heptane gave analytically pure copper-colored crystalline product. The same procedure with complex **7** (0.96 g, 2.00 mmol) afforded complex **13** (0.64 g, 1.34 mmol, 67%): ^1H NMR (CD_2Cl_2) δ 7.32–8.02 (envelope, 15 H), 2.64 (br s, 2 H); $^{11}B\{^1H\}$ NMR (CD_2Cl_2) −19.06, −15.30, −10.66, −7.03 (d, J = 132 Hz) ppm (2:4:2:1); $^{31}P\{^1H\}$ NMR (20% CD_2Cl_2/CH_2Cl_2) 7.7 (br q) ppm. Anal. Calcd for $C_{21}H_{25}B_9PNiO$: C, 52.40; H, 5.44; B, 20.21; P, 6.43; Ni, 12.20. Found: C, 51.99; H, 5.30; B, 19.55; P, 6.54; Ni, 12.26.

Collection and Reduction of X-ray Data. A transparent amber-copper crystal of **13** having approximate dimensions 0.30 × 0.15 × 0.06 mm was used for data collection. Preliminary photographs indicated no symmetry and no systematic absences, indicative of space group $P1$ or $P\bar{1}$. After mounting on an *xyz* goniometer, the crystal was optically centered on a Picker FACS 1 diffractometer equipped with a molybdenum tube ($\lambda_{K\alpha}$ = 0.71069 Å) and a zirconium filter. Preliminary unit cell parameters were determined from a least-squares refinement of the angular settings of 12 accurately centered reflections. The unit cell parameters are given in Table I as part of a summary of data for this study. The density, measured by flotation in distilled water/KI at 21 °C, was 1.265 g/cm^3, in reasonable agreement with the calculated density of 1.29 g/cm^3 for Z = 1. The 4271 reflections, including standards, were measured at 25 °C over a 2θ range of 0–50°, with use of the θ–2θ scan method. Reflections were scanned at a rate of 2°/min over a range of 2.2(1 + 0.692 tan θ)°. Background was measured for 20 s at each end of the scan. Of the reflections measured, 4133 were unique and of these 2233 were considered observed, $I > 3\ \sigma(I)$. Two standard refections were measured after every 100 reflections to monitor tube stability and possible crystal deterioration. There was no observable decay. Intensities were corrected as described previously[18] for Lorentz and polarization effects. An absorption correction was applied with an absorption coefficient (μ) of 8.39 cm^{-1} for Mo Kα radiation.

Scattering factors for neutral nickel, phosphorus, carbon, and boron were taken from ref 19; hydrogen scattering factors were obtained from Stewart, Davidson, and Simpson,[20] and the real and imaginary terms for anomalous scattering of Ni and P were taken from Cromer.[21] The function $\sum w \| F_{obsd} | - | F_{calcd} \|^2$ was minimized in least-squares refinement.

Solution and Refinement of the Structure. The x, y, and z coordinates for the crystallographically unique Ni and P atoms were deduced from the Patterson map. The heavy-atom method allowed successive location of all of the non-hydrogen atoms by iterative least-squares and Fourier calculations (all cage atoms were given boron scattering factors). The positions of the polyhedral carbon atoms were easily recognized by their shorter bond lengths and their smaller temperature factors and were assigned carbon scattering factors. Further least-squares refinement reduced R to 0.068 and R_w to 0.070, and a difference Fourier synthesis indicated the positions of all the hydrogen atoms. Least-squares refinement of the positional parameters of all the atoms and the anisotropic thermal parameters of the heavy atoms and isotropic parameters for other non-hydrogen atoms, with anomalous dispersion terms applied to the scattering of nickel and phosphorus, resulted in convergence at R = 0.057, R_w = 0.061. Hydrogen atoms were assigned isotropic temperature factors of 3.0 Å^2. Isotropic positional and thermal parameters for the [(CO)-$NiC_2B_9H_{10}PPh_3$] unit are listed in Table II. Anisotropic thermal parameters are given in the supplementary material. Atomic labels correspond to those in Figure 5. The most important interatomic distances and angles are listed in Tables III and IV.

The final observed and calculated structure factors are available as supplementary material. The atoms of the polyhedron were labeled according to the nomenclature set forth by IUPAC[22] for boron compounds.

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Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, hydrogen positional parameters, and anisotropic thermal parameters (12 pages). Ordering information is given on any current masthead page.

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Macrotricyclic Hexaamine Cage Complexes of Cobalt(III): Synthesis, Characterization, and Properties

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Syntheses of the sexidentate ligand 1,4,7-tris(2-aminoethyl)-1,4,7-triazacyclononane (taetacn) and chiral [Co(taetacn)]$^{3+}$ are described along with the chiral macrotricyclic cage derivatives [Co(nosartacn)]$^{3+}$ (nosartacn = 9-nitro-1,4,7,11,14,19-hexaazatricyclo[7.7.4.2^{4,14}]docosane), [Co(amsartacn)]$^{3+}$ (amsartacn = 9-amino-1,4,7,11,14,19-hexaazatricyclo[7.7.4.2^{4,14}]docosane), and [Co(azasartacn)]$^{3+}$ (azasartacn = 1,4,7,9,11,14,19-heptaazatricyclo[7.7.4.2^{4,14}]docosane). Their absolute configurations have also been assigned. Electrochemical studies showed reversibility of the Co(III)/Co(II) redox couple for the cage complexes, which are kinetically inert and optically stable in both oxidation states. The visible, rotatory dispersion, and circular dichroism spectra of the Co(III) oxidation states are reported. The kinetics of the electron self-exchange reactions of Co(II)/Co(III)-cage couples were studied to establish if the ready access along the molecular C_3 axis assisted the electron exchange. The rates for the Δ-[Co(amsartacnH)]$^{3+}$/Λ-[Co(amsartacnH)]$^{4+}$ couple (k = 0.04 M^{-1}·s^{-1}, 25 °C, μ = 0.2 M) and the Δ-[Co(amsartacn)]$^{2+}$/Λ-[Co(amsartacn)]$^{3+}$ couple (k = 0.09 M^{-1}·s^{-1}) are not very different from those of related cage systems in which access along the C_3 axis is barred by the ligands.

Introduction

In a recent publication the facile condensation of NH_3 and CH_2O with [Co(en)$_3$]$^{3+}$ to give the [Co(sepulchrate)]$^{3+}$ cage molecule was reported.[2] The synthesis basically involved the construction of a trimethylaminetriyl cap on the trigonal facial arrangement of three primary amine groups of each of the coordinated ethylenediamine ligands in the precursor complex. By inference, this strategy should be generally applicable for building caps on similar facial arrangements of coordinated primary amines in other metal ion complexes, provided their stereochemistry is not prohibitive. This applicability has been demonstrated in one case by the synthesis, from [Co(sen)]$^{3+}$, of the [Co(azamesar)]$^{3+}$ cage complex in which the metal center, as in [Co(sepulchrate)]$^{3+}$, is encapsulated by a macrobicyclic ligand structure.[2] This paper reports the syntheses, by analogous routes, of some novel macrotricyclic (hexaamine)cobalt(III) cage complexes derived from the (1,4,7-tris(2-aminoethyl)-1,4,7-triazacyclononane)cobalt(III) ion (ligand abbreviated "taetacn") (**1**) (Chart I). For practical reasons the cage ligands and their complexes described here have been given shorthand names: [Co(nosartacn)]$^{3+}$ (**2**), [Co(amsartacn)]$^{3+}$ (**3**) (the protonated form of **3** is named [Co(amsartacnH)]$^{4+}$ (**3$^+$**)), [Co(azasartacn)]$^{3+}$ (**4**). The systematic ligand names appear in the abstract.

Experimental Section

Absorption and circular dichroism (CD) spectra were recorded with a Cary 14 spectrophotometer and a Cary 61 CD instrument, respectively. The calibration standard for CD measurements was [(+)$_{589}$-[Co(en)$_3$]Cl$_3$]$_2$·NaCl·6H_2O (0.5 mM, in H_2O, $\epsilon_l - \epsilon_r$ = +1.80 M^{-1}·cm^{-1}/Co in the maximum at 490 nm). All listed values of molar absorptivity (ϵ) and molar CD ($\Delta\epsilon = \epsilon_l - \epsilon_r$) are in units of M^{-1}·cm^{-1}. Optical rotations and rotatory dispersion spectra were measured with a Perkin-Elmer P22 spectropolarimeter (±0.002°) in 1-dm quartz cells. All listed values of specific ([α]$_\lambda$) and molecular ([M]$_\lambda$) rotations are at 25.0 ± 0.1 °C in units of deg·mL·g^{-1}·dm^{-1} and deg·M^{-1}·m^{-1}, respectively. NMR spectra were recorded with JEOL 100-MHz Minimar (^{1}H) and JNM-FX 60-MHz Fourier transform (^{13}C) spectrometers at 30 and 25 °C, respectively, using Me_4Si in $CDCl_3$ as an internal standard for ^{1}H spectra and 1,4-dioxane in D_2O for ^{13}C spectra. Chemical shifts (positive downfield) are given relative to these standards.

Polarograms and cyclic voltammograms were recorded on a PAR electrochemistry system, Model 170, with a conventional three-electrode *iR*-compensated configuration. For studies in water, 0.1 M $NaClO_4$ was used as the supporting electrolyte and a saturated calomel electrode was used as the reference electrode. In acetone and acetonitrile, 0.1 M $(CH_3)_4N(O_3SCF_3)$[3] (TMAT) was used as the supporting electrolyte and Ag/AgCl (0.1 M LiCl in acetone) as the reference electrode. A low-porosity salt bridge of the relevant medium separated the reference electrode from the working compartment. A platinum-wire auxiliary electrode was used on all occasions. The working electrode was a dropping mercury electrode or, for the cyclic voltammograms, a hanging mercury drop electrode. Prior to recording of a polarogram or voltammogram, solutions were thoroughly degassed via a standard purge tube with argon saturated with the solvent used. Results were obtained at ambient temperature, 22 ± 2 °C.

The concentration acid dissociation constant, K_a, was determined by standard procedures[4] in CO_2-free 1.00 M $NaClO_4$ under N_2 at 25.00 ± 0.05 °C with a Radiometer (Copenhagen) PHM 26 pH meter with a G202B glass electrode and a K4112 saturated calomel reference electrode connected via a 1.6 M NH_4NO_3, 0.2 M $NaNO_3$ salt bridge. The instrument was calibrated with hydrogen phthalate (0.05 M, pH 4.00, 25 °C) and borate (0.01 M, pH 9.18, 25 °C) buffers. A standard 1.00 mM HCl (Volucon), 1.00 M $NaClO_4$ solution gave pH 3.00, and pH = −log [H$^+$] was therefore assumed in the region 2.8 < pH < 5.0. All SP-Sephadex C-25 ion-exchange columns used for separations and resolutions were prewashed with the eluant to be used. Complexes were sorbed on the columns by mixing a suspension of the complex in water (10 mL) with an equal volume of resin and carefully placing the resulting suspension evenly at the top of the column before eluting. Dimensions given for Sephadex columns are

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